

THE UNIVERSITY OF CHICAGO

MACROSCALE FABRICATION OF THREE-DIMENSIONAL CARBON ARCHITECTURES  
WITH HIERARCHICAL POROSITY AND TUNABLE MECHANICAL PROPERTIES

A DISSERTATION SUBMITTED TO  
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In gratitude to all who gave me roots and room to grow.

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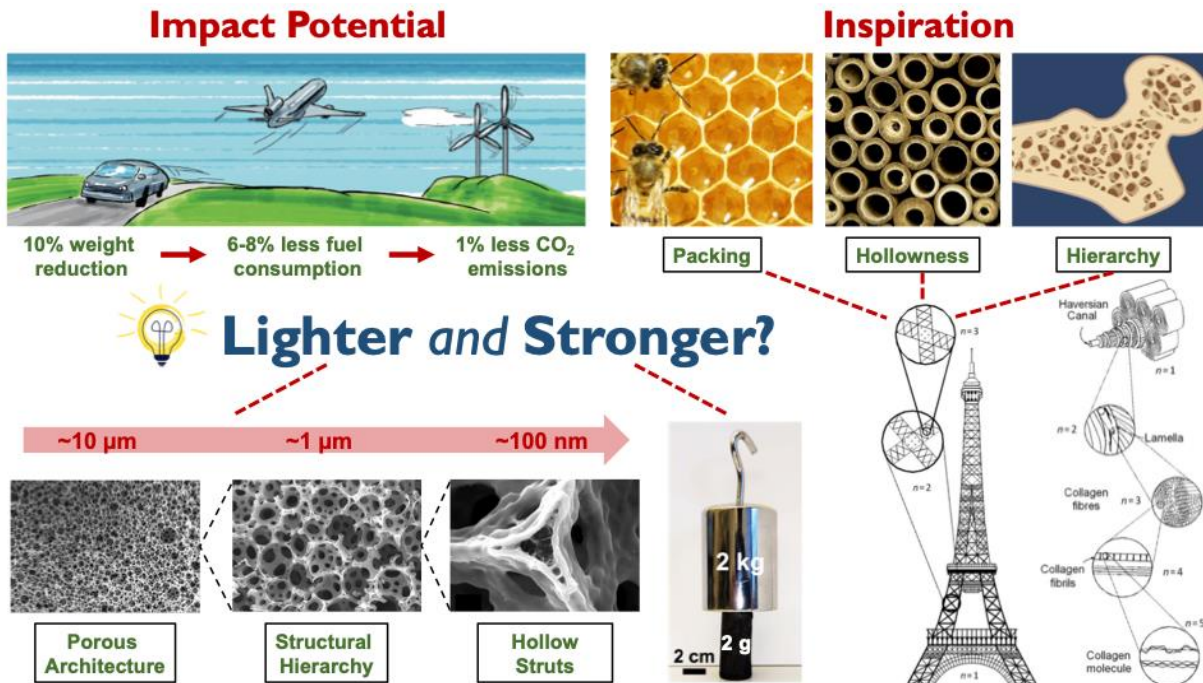
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## ABSTRACT

The strength of a material originates from features across multiple length scales, from atomic bonds to macroscale architecture. While high strength is typically associated with dense materials, such as metals, low-density systems, like foams, often lack mechanical robustness. Natural materials—including bone, wood, and enamel—defy this trade-off through hierarchical architectures that span several orders of magnitude. Inspired by these systems, this thesis explores design strategies for synthetic 3D porous carbon structures that challenge long-standing trade-offs between density, strength, toughness, and dimensional stability. The core innovation is a modular template–coating approach that bridges nanoscale strengthening effects with macroscopic utility. By combining sacrificial porous templates with conformal, high–char-yield coatings, this method enables precise control over shrinkage and mass retention during pyrolysis. Using this strategy, I demonstrate macroscale carbon foams with  $\sim 80\%$  dimensional retention and specific strengths up to  $\sim 0.13 \text{ GPa g}^{-1} \text{ cm}^3$ —among the highest reported for polymer-derived carbons. I further develop a thermally compatible polybenzoxazine system with tunable densities ( $\sim 0.1\text{--}0.7 \text{ g cm}^{-3}$ ) and  $\sim 90\%$  dimensional retention, surpassing conventional approaches in the density–shrinkage landscape. Finally, I demonstrate that partial carbonization of 3D-printed lattices yields hybrid carbon–polymer architectures with specific strengths of  $\sim 128 \text{ MPa g}^{-1} \text{ cm}^3$  and toughnesses of  $\sim 32 \text{ J g}^{-1}$  at only  $\sim 20\%$  shrinkage. Together, these results define a new design space for porous carbon materials—one that combines hierarchical architecture with scalable processing to access combinations of materials properties typically considered mutually exclusive. This work lays the foundation for lightweight, strong, and damage-tolerant carbon materials for next-generation applications in construction, packaging, transportation, and beyond.

# CHAPTER 1

## Lighter *and* Stronger? Rethinking the Design and Fabrication of Three-Dimensional Porous Carbon Architectures

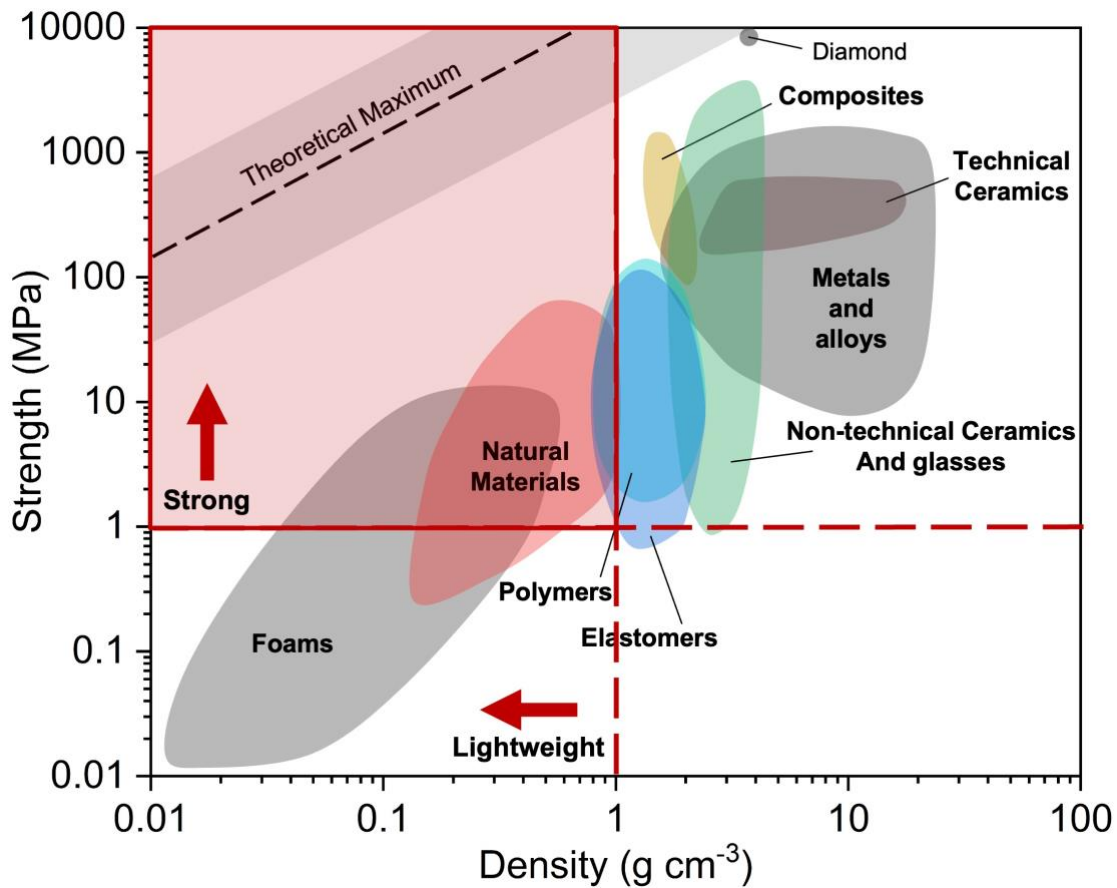


## **1.1 The Density–Strength–Shrinkage Trade-off in Porous Carbons**

Materials that simultaneously achieve low density and high mechanical strength are critically important in modern engineering, with extensive applications across the aerospace, automotive, construction, and energy storage industries<sup>[1]</sup>. A fundamental way to visualize the relationship between these critical material properties is through the Ashby plot—a graphical representation mapping material strength against density (Figure 1). Most synthetic materials occupy distinct regions of this plot: metals and ceramics cluster in areas characterized by high density and strength, while low-density materials, such as foams and aerogels, typically exhibit limited mechanical robustness<sup>[2]</sup>. This inverse relationship between density and strength underscores a longstanding design constraint: combining both attributes in a single material system remains exceptionally challenging. In pyrolytic systems, this trade-off is further complicated by the extreme volumetric shrinkage that accompanies carbonization. While such shrinkage can enable access to nanoscale features where mechanical strengthening effects emerge, it also introduces severe challenges in maintaining structural integrity at larger scales.

Nature provides compelling examples of overcoming this trade-off, often through elegant and efficient use of hierarchical structuring. Take bone, for example—a lightweight material that can support significant mechanical loads. Its architecture consists of a dense cortical shell and a spongy interior filled with trabeculae, providing strength, shock absorption, and damage tolerance<sup>[3]</sup>. Similarly, wood combines a lightweight cellular structure with cellulose fibrils embedded in a lignin matrix, granting both stiffness and resilience<sup>[4,5]</sup>. Nacre (mother-of-pearl) is another remarkable example: it is composed of brittle aragonite platelets arranged in a brick-and-mortar configuration, held together by a thin protein matrix that allows for controlled sliding and crack deflection<sup>[6]</sup>. These materials achieve exceptional specific mechanical properties not solely due to their composition, but also due to their multiscale structural organization—from nanoscale interfaces to macroscale geometry<sup>[7]</sup>. Their architectures exploit mechanisms such as energy dissipation, flaw tolerance, and load redistribution to

achieve high toughness and strength without adding unnecessary mass. Replicating these principles in synthetic materials, particularly in inorganic systems, presents a profound challenge. Inorganic solids lack the self-assembly capabilities and adaptability of biological systems and are typically difficult to shape and structure across scales. Overcoming this requires deliberate design and processing routes that can impose architectural hierarchy while maintaining control over mass, geometry, and mechanical performance.



**Figure 1.** Ashby plot of material strength versus density. A representative strength–density Ashby plot illustrating the fundamental challenge of achieving lightweight and mechanically robust materials. Dense materials (e.g., metals, ceramics) typically exhibit strength, while low-density materials (e.g., foams, aerogels) are typically weak. Natural materials, such as bone, wood, and nacre, challenge this trade-off or mutual exclusivity effectively through the exploitation of structural hierarchy spanning several orders of magnitude in length scale, from the macroscale to the nanoscale, where anomalous strengthening effects emerge.

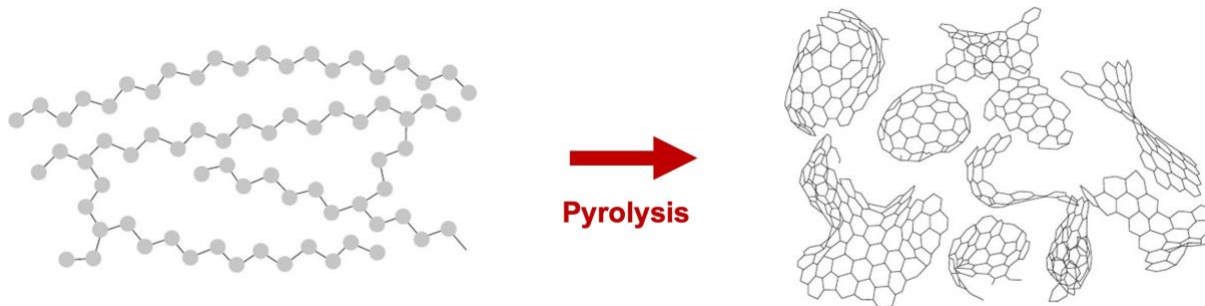
Translating these natural design principles into synthetic inorganic materials requires more than just clever chemistry—it demands processing strategies that can impose precise structural hierarchy across multiple length scales. However, unlike biological systems, most inorganic solids lack the ability to self-organize and are notoriously difficult to shape, especially when both structural hierarchy and mechanical performance must be preserved. As such, controlling the three-dimensional (3D) architecture and density of inorganic solids—such as ceramics, metals, glasses, and carbon—is inherently complex. Unlike polymers, which can be easily shaped through conventional processes, inorganic materials are typically brittle, possess high melting points, and undergo intricate phase transformations, making traditional manufacturing methods inadequate. To overcome these constraints, polymeric precursors are commonly shaped through methods such as mold casting—especially for emulsion-templated foams—or additive manufacturing (AM), which enables greater control over geometric complexity and resolution. Once shaped, these polymers are subsequently transformed into their inorganic form through thermal processing, such as pyrolysis or sintering<sup>[8–12]</sup>. This approach decouples shaping from material transformation, allowing architectural features to span from the macroscale to the nanoscale. It has led to breakthroughs in several intractable material classes<sup>[13–17]</sup>, including ultralight ceramics, optical-grade glasses, and metal–ceramic composites with unprecedented combinations of weight, strength, and toughness, typically mutually exclusive material properties<sup>[18]</sup>.

Among these material systems, carbon stands out for its ability to be derived from a wide range of polymeric precursors via pyrolysis. Pyrolysis refers to the thermal decomposition of organic materials in an inert atmosphere, typically nitrogen or argon, and proceeds through a sequence of overlapping chemical and physical transformations<sup>[19]</sup>. In the early degradation stage (<400 °C), polymer chains break down and release small-molecule volatiles such as water, CO<sub>2</sub>, and methane. This results in significant mass loss and breakdown of the polymer network. At higher temperatures

(>400 °C), the remaining organic material undergoes carbonization, condensing into disordered sp<sup>2</sup>-rich graphitic domains (Figure 2). This stage determines the final microstructure and char yield of the pyrolytic carbon. Importantly, pyrolysis is accompanied by extreme volumetric shrinkage—often exceeding 90%—which drastically influences the mechanical behavior of the final architecture owing to strengthening effects emergent at the nanoscale<sup>[20–22]</sup>.

When pyrolysis is coupled with well-designed polymeric precursor architectures, it enables the formation of geometrically complex, hierarchical, and mechanically robust pyrolytic carbon architectures. These structures vary in size and feature intricate macroscale geometry with nanoscale precision (Figure 4B). The pyrolytic carbon architectures encompass a range of designs, from 3D microarchitected carbon lattices<sup>[23]</sup> that boast a high surface area and an extraordinarily high areal capacitance ( $\sim 5 \text{ F cm}^{-2}$  at  $3 \text{ mA cm}^{-2}$ )<sup>[24]</sup> to nanoarchitected carbon nanolattices with Bayesian-optimized beam shapes and exceptional specific strength ( $\sim 2 \text{ GPa cm}^3 \text{ g}^{-1}$ )<sup>[25]</sup>. These innovations notably overcome the longstanding performance trade-offs between energy density and power density, illustrated by Ragone diagrams, as well as density and strength, represented by Ashby plots<sup>[26]</sup>.

In many cases, carbon microlattices and porous foams fabricated through AM and pyrolysis display size-driven strengthening effects: smaller structural elements contain fewer flaws, experience more uniform stress distributions, and benefit from enhanced load redistribution. These materials



**Figure 2.** Schematic of the pyrolysis process from polymer precursor to pyrolytic carbon. A two-stage transformation pathway: (1) thermal degradation releases volatile byproducts and (2) carbonization condenses residual fragments into disordered sp<sup>2</sup>-rich graphitic domains.

have demonstrated remarkable promise for various structural<sup>[27,28]</sup>, electrochemical<sup>[29–33]</sup>, and biomedical<sup>[34,35]</sup> applications.

Interestingly, the shrinkage that accompanies pyrolysis—long regarded as a drawback due to dimensional instability—can, under the right conditions, enhance mechanical performance<sup>[36–41]</sup>. As structural features shrink, their cross-sectional area decreases, pushing them into size regimes where flaw sensitivity is reduced and strength is increased. This phenomenon explains why pyrolyzed carbon nanolattices can achieve GPa-level strengths at moderate densities. However, as the material is scaled up, these benefits begin to fade. Larger structures become increasingly sensitive to internal defects, residual stresses, and processing inconsistencies—all of which degrade their mechanical performance. Shrinkage that is manageable in small features can lead to distortion, cracking, or catastrophic failure at the macroscale. Yet, if shrinkage is suppressed to avoid these issues, the carbon network may remain underdeveloped, resulting in low density and poor strength. As illustrated in Figure 3, this creates a fundamental trade-off: materials that exploit shrinkage to access nanoscale strengthening effects often cannot be scaled. In contrast, materials with macroscopic dimensions tend to suffer from compromised mechanical properties. Resolving this trade-off is essential for translating architected carbon materials into practical, real-world applications.





## **1.2 Existing Strategies for Shrinkage Suppression and Structural Preservation**

The fabrication of pyrolytic carbon architectures from polymer precursors (Fig. 4A) is complicated by the extreme mass loss and volumetric shrinkage that occur during pyrolysis. As the temperature increases, most organic polymers undergo dehydrogenation, chain scission, and volatilization, resulting in a sharp reduction in char yield, often retaining less than 10–20% of the original mass. This mass loss is accompanied by equally dramatic volume loss, resulting in shrinkage levels that can exceed 90–95% depending on the precursor chemistry and processing conditions (Fig. 4B). Without additional stabilization, this transformation typically leads to pore collapse, shape distortion, and degradation of mechanical performance. To address this, several strategies have been developed to suppress shrinkage and improve dimensional stability, each with varying degrees of success.

One approach involves modular assembly, in which individual microlattices or unit cells are pyrolyzed separately and then joined to form larger structures. While some researchers leverage pyrolytic shrinkage to produce structural colors<sup>[42]</sup> or exploit nanoscale strengthening effects<sup>[43]</sup>, others attempt to compensate for the substantial shrinkage by adjusting the size of polymer precursor<sup>[44–48]</sup> or creating modular assemblies of the carbon product<sup>[49]</sup>. This method involves fabricating small, micro-architected units individually—where shrinkage is more easily controlled<sup>[44]</sup>—and assembling them into larger, macro-scale structures. Though this approach helps preserve the mechanical advantages of nanoscale architectures, it increases fabrication complexity and introduces potential failure points at the interfaces between assembled units.

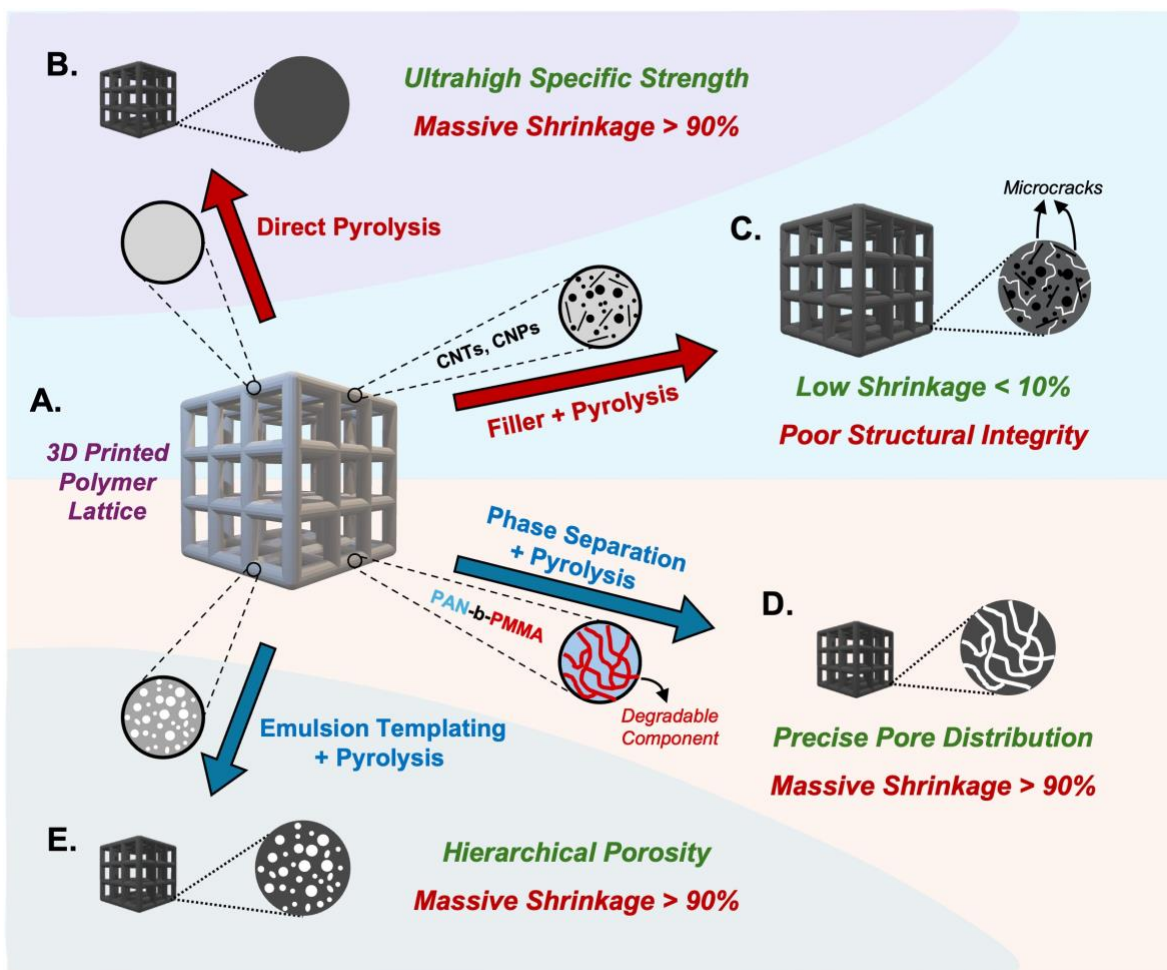
A second class of strategies focuses on stabilizing the polymer precursor itself. For example, efforts to modify polymer precursors, such as pre-oxidation to reduce volatile loss<sup>[50,51]</sup>, crosslinking to increase network rigidity<sup>[52–54]</sup>, and the incorporation of high-char-yield fillers<sup>[55,56]</sup>, such as chopped carbon fibers<sup>[55,57,58]</sup>, carbon nanotubes<sup>[59]</sup> or ceramic MgO particles<sup>[60]</sup>, have helped mitigate shrinkage during pyrolysis, with some systems exhibiting impressively low volumetric shrinkage ( $< 10\%$ ) (Fig.

4C). However, these methods can create new issues, such as filler aggregation and interfacial cracking, which limit control over pore architecture and bulk density. In general, these systems improve dimensional retention at the expense of mechanical resilience.

To address the trade-offs associated with such top-down structural modifications, emerging “bottom-up” templating strategies aim to directly encode hierarchical porosity into the precursor<sup>[61–65]</sup>. For instance, combining 3D printing with polymerization-induced microphase separation (Fig. 4D) and pyrolysis enables simultaneous control over both macro- and nanoscale structures within the printed precursor<sup>[66–69]</sup> and the pyrolytic carbon product<sup>[70–72]</sup>. Likewise, nanostructured carbon pillars fabricated via nanoimprint lithography and bottlebrush block copolymer templates demonstrate remarkable combinations of low density ( $\sim 0.66\text{--}0.82\text{ g cm}^{-3}$ ), ultrahigh strength, and damping capability<sup>[41]</sup>. However, these techniques often rely on complex chemistries or patterning techniques, limiting their scalability and adaptability to macroscale structural features.

Alternatively, emulsion templating offers a scalable and accessible bottom-up route to encode hierarchical porosity with tunable size distribution<sup>[73–76]</sup>. For example, high internal phase emulsions (HIPEs) can be formulated into printable resins and cured through vat photopolymerization, resulting in architected polymer lattices featuring interconnected porosity ranging from tens of nanometers to hundreds of microns (Fig. 4E)<sup>[77–80]</sup>. Upon pyrolysis, these polymer precursors transform into intrinsically porous carbon lattices, characterized by high surface area, tunable porosity, and multiscale structural features<sup>[81,82]</sup>. In contrast to dense-strut systems, these materials comprise built-in voids across multiple length scales; however, their low initial density and thermally delicate network led to significant shrinkage during pyrolysis. Consequently, while emulsion templating facilitates the creation of hierarchical porosity, it intensifies the challenge of maintaining structural and dimensional integrity through pyrolysis.

Despite these efforts, a key challenge remains: most existing strategies address only one aspect of the shrinkage–performance trade-off while compromising another. Modular assembly retains mechanical enhancements but lacks scalability. Crosslinking and filler loading nearly eliminate shrinkage but are mechanically compromised due to structural defects. Emulsion templating and phase separation offer lightweight architectures encoded with strength-imparting properties, but these precursors cannot endure the harsh conditions imposed by pyrolysis. What remains lacking is a unified approach that can simultaneously achieve structural retention, dimensional stability, tunable density, and mechanical robustness, without relying on fragile geometries, additive fillers, or multistep post-processing. This motivates the need for a framework that rethinks the coupling of mass and architecture in pyrolytic carbon systems—an approach explored in the chapters that follow.



**Figure 4.** Pyrolytic conversion strategies and associated trade-offs in the fabrication of 3D porous carbon lattices. **(A)** A 3D-printed polymer lattice with tunable macroscale geometry serves as the common starting point. Arrows indicate distinct pyrolytic conversion strategies, each leading to a different class of carbon architecture shown in panels (B–F). **(B)** Direct pyrolysis yields ultrahigh-strength carbon microlattices but induces extreme shrinkage. **(C)** Incorporating high-char-yield fillers (e.g., CNTs) reduces shrinkage but compromises mechanical homogeneity due to agglomeration and interfacial cracking. **(D)** Pyrolysis of phase-separated porous block copolymers (e.g., PAN-b-PMMA) enables nanoscale porosity; however, it results in substantial shrinkage. **(E)** Pyrolysis of emulsion-templated porous polymers (e.g., polyHIPEs) creates hierarchical porosity but leads to pronounced dimensional loss and deformation.

### **1.3 Scope and Aims**

This thesis explores innovative approaches to addressing a longstanding challenge in materials science: fabricating porous carbon architectures that are simultaneously lightweight, mechanically robust, and dimensionally stable. The chapters that follow develop and apply a modular framework designed to decouple geometric structure from carbon supply, enabling independent control over shrinkage, density, and mechanical performance. At the heart of this work is a new design approach that can overcome multiple trade-offs historically constraining pyrolytic carbon systems, without relying on fragile geometries, chemical fillers, or multistep stabilization processes. Crucially, this framework enables the transfer of strengthening effects typically accessible only at the nanoscale—such as flaw insensitivity and uniform stress distribution—to materials at macroscopic length scales, offering a pathway to achieve strength, toughness, and dimensional retention simultaneously.

- Chapter 2 introduces the template–coating framework and demonstrates its ability to balance shrinkage and structural fidelity in porous carbon foams.
- Chapter 3 builds on this foundation, expanding the accessible design–property space and enabling systematic control over density–shrinkage relationships.
- Chapter 4 explores toughness, utilizing partial carbonization as a strategy to create macroscopic hybrid architectures that are both strong and damage tolerant.
- Chapter 5 examines the broader implications of this strategy, including early applications of electrochemical separations and the design of interpenetrating phase composites.

Together, these studies validate the generality and versatility of the template–coating framework across multiple chemistries and performance goals. By tuning a single design principle, this work demonstrates how to systematically overcome distinct trade-offs—whether between shrinkage and strength, density and shrinkage, or strength and toughness. It offers a scalable platform for designing architected carbon materials that make size effects once confined to the nanoscale accessible at the macroscale.

## **1.4 References**

- [1] M. Bechthold, J. C. Weaver, *Nat. Rev. Mater.* **2017**, 2, 17082.
- [2] M. F. Ashby, *Materials Selection in Mechanical Design*, Butterworth-Heinemann, Amsterdam ; Cambridge, MA, **2017**.
- [3] O. A. Tertuliano, J. R. Greer, *Nat. Mater.* **2016**, 15, 1195.
- [4] U. G. K. Wegst, H. Bai, E. Saiz, A. P. Tomsia, R. O. Ritchie, *Nat. Mater.* **2015**, 14, 23.
- [5] P. Fratzl, R. Weinkamer, *Prog. Mater. Sci.* **2007**, 52, 1263.
- [6] F. Breish, C. Hamm, S. Andresen, *Biomimetics* **2024**, 9, 545.
- [7] R. Lakes, *Nature* **1993**, 361, 511.
- [8] J. U. Surjadi, C. M. Portela, *Nat. Mater.* **2025**, 24, 493.
- [9] G. Lipkowitz, M. A. Saccone, M. A. Panzer, I. A. Coates, K. Hsiao, D. Ilyn, J. M. Kronenfeld, J. R. Tumbleston, E. S. G. Shaqfeh, J. M. DeSimone, *Proc. Natl. Acad. Sci.* **2024**, 121, e2303648121.
- [10] M. A. S. R. Saadi, A. Maguire, N. T. Pottackal, M. S. H. Thakur, M. Md. Ikram, A. J. Hart, P. M. Ajayan, M. M. Rahman, *Adv. Mater.* **2022**, 34, 2108855.
- [11] W. P. Moestopo, A. J. Mateos, R. M. Fuller, J. R. Greer, C. M. Portela, *Adv. Sci.* **2020**, 7, 2001271.
- [12] R. L. Truby, J. A. Lewis, *Nature* **2016**, 540, 371.
- [13] P. R. Onffroy, S. Chiovoloni, H. L. Kuo, M. A. Saccone, J. Q. Lu, J. M. DeSimone, *JACS Au* **2024**, 4, 3706.
- [14] F. Li, S.-F. Liu, W. Liu, Z.-W. Hou, J. Jiang, Z. Fu, S. Wang, Y. Si, S. Lu, H. Zhou, D. Liu, X. Tian, H. Qiu, Y. Yang, Z. Li, X. Li, L. Lin, H.-B. Sun, H. Zhang, J. Li, *Science* **2023**, 381, 1468.
- [15] A. J. D. Shaikeea, H. Cui, M. O'Masta, X. R. Zheng, V. S. Deshpande, *Nat. Mater.* **2022**, 21, 297.

- [16] C. Wang, W. Ping, Q. Bai, H. Cui, R. Hensleigh, R. Wang, A. H. Brozena, Z. Xu, J. Dai, Y. Pei, C. Zheng, G. Pastel, J. Gao, X. Wang, H. Wang, J.-C. Zhao, B. Yang, X. (Rayne) Zheng, J. Luo, Y. Mo, B. Dunn, L. Hu, *Science* **2020**, *368*, 521.
- [17] J. Bauer, L. R. Meza, T. A. Schaedler, R. Schwaiger, X. Zheng, L. Valdevit, *Adv. Mater.* **2017**, *29*, 1701850.
- [18] R. O. Ritchie, *Nat. Mater.* **2011**, *10*, 817.
- [19] G. M. Jenkins, K. Kawamura, *Polymeric Carbons: Carbon Fibre, Glass and Char*, Cambridge University Press, Cambridge, **2011**.
- [20] W. Zhang, Z. Li, R. Dang, T. T. Tran, R. A. Gallivan, H. Gao, J. R. Greer, *Nano Lett.* **2023**, *23*, 8162.
- [21] R. Lontas, J. R. Greer, *Acta Mater.* **2017**, *133*, 393.
- [22] J. R. Greer, W. D. Nix, *Appl. Phys. A* **2005**, *80*, 1625.
- [23] A. Kudo, F. Bosi, *Commun. Mater.* **2020**, *1*, 72.
- [24] Y. Katsuyama, N. Haba, H. Kobayashi, K. Iwase, A. Kudo, I. Honma, R. B. Kaner, *Adv. Funct. Mater.* **2022**, *32*, 2201544.
- [25] P. Serles, J. Yeo, M. Haché, P. G. Demingos, J. Kong, P. Kiefer, S. Dhulipala, B. Kumral, K. Jia, S. Yang, T. Feng, C. Jia, P. M. Ajayan, C. M. Portela, M. Wegener, J. Howe, C. V. Singh, Y. Zou, S. Ryu, T. Filletier, *Adv. Mater.* **2025**, *37*, 2410651.
- [26] L. J. Gibson, M. F. Ashby, *Cellular Solids: Structure and Properties*, Cambridge University Press, **1997**.
- [27] C. M. Portela, B. W. Edwards, D. Veysset, Y. Sun, K. A. Nelson, D. M. Kochmann, J. R. Greer, *Nat. Mater.* **2021**, *20*, 1491.
- [28] X. Zhang, A. Vyatskikh, H. Gao, J. R. Greer, X. Li, *Proc. Natl. Acad. Sci.* **2019**, *116*, 6665.



- [29] H. Li, M. E. Zick, T. Trisukhon, M. Signorile, X. Liu, H. Eastmond, S. Sharma, T. L. Spreng, J. Taylor, J. W. Gittins, C. Farrow, S. A. Lim, V. Crocellà, P. J. Milner, A. C. Forse, *Nature* **2024**, *630*, 654.
- [30] Y. Katsuyama, A. Kudo, H. Kobayashi, J. Han, M. Chen, I. Honma, R. B. Kaner, *Small* **2022**, *18*, 2202277.
- [31] K. Narita, M. A. Citrin, H. Yang, X. Xia, J. R. Greer, *Adv. Energy Mater.* **2021**, *11*, 2002637.
- [32] T. Liu, J. Serrano, J. Elliott, X. Yang, W. Cathcart, Z. Wang, Z. He, G. Liu, *Sci. Adv.* **2020**, *6*, eaaz0906.
- [33] Y. Yao, K. K. Fu, S. Zhu, J. Dai, Y. Wang, G. Pastel, Y. Chen, T. Li, C. Wang, T. Li, L. Hu, *Nano Lett.* **2016**, *16*, 7282.
- [34] M. Taale, B. Schamberger, M. A. Monclus, C. Dolle, F. Taheri, D. Mager, Y. M. Eggeler, J. G. Korvink, J. M. Molina-Aldareguia, C. Selhuber-Unkel, A. D. Lantada, M. Islam, *Adv. Healthc. Mater.* **2024**, *13*, DOI 10.1002/adhm.202303485.
- [35] J. U. Surjadi, Y. Zhou, S. Huang, L. Wang, M. Li, S. Fan, X. Li, J. Zhou, R. H. W. Lam, Z. Wang, Y. Lu, *Matter* **2022**, S2590238522004672.
- [36] X. Zhang, L. Zhong, A. Mateos, A. Kudo, A. Vyatskikh, H. Gao, J. R. Greer, X. Li, *Nat. Nanotechnol.* **2019**, *14*, 762.
- [37] J. Bauer, A. Schroer, R. Schwaiger, O. Kraft, *Nat. Mater.* **2016**, *15*, 438.
- [38] A. Banerjee, D. Bernoulli, H. Zhang, M.-F. Yuen, J. Liu, J. Dong, F. Ding, J. Lu, M. Dao, W. Zhang, Y. Lu, S. Suresh, *Science* **2018**, *360*, 300.
- [39] L. Fan, T. Yang, Y. Zhao, J. Luan, G. Zhou, H. Wang, Z. Jiao, C.-T. Liu, *Nat. Commun.* **2020**, *11*, 6240.
- [40] A. Guell Izard, J. Bauer, C. Crook, V. Turlo, L. Valdevit, *Small* **2019**, *15*, 1903834.

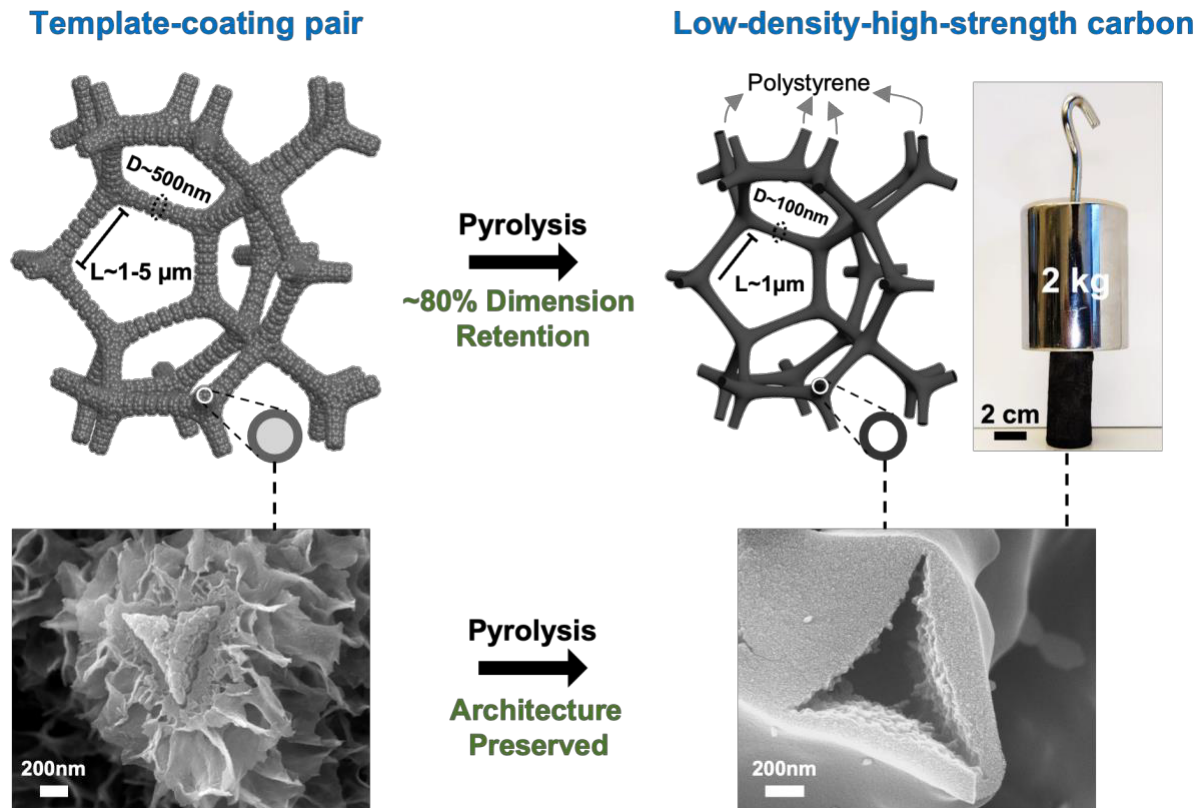
- [41] Z. Li, A. Bhardwaj, J. He, W. Zhang, T. T. Tran, Y. Li, A. McClung, S. Nuguri, J. J. Watkins, S.-W. Lee, *Nat. Commun.* **2024**, *15*, DOI 10.1038/s41467-024-52359-6.
- [42] Y. Liu, H. Wang, J. Ho, R. C. Ng, R. J. H. Ng, V. H. Hall-Chen, E. H. H. Koay, Z. Dong, H. Liu, C.-W. Qiu, J. R. Greer, J. K. W. Yang, *Nat. Commun.* **2019**, *10*, 4340.
- [43] J. R. Greer, W. C. Oliver, W. D. Nix, *Acta Mater.* **2005**, *53*, 1821.
- [44] T. Mori, H. Wang, W. Zhang, C. C. Ser, D. Arora, C.-F. Pan, H. Li, J. Niu, M. A. Rahman, T. Mori, H. Koishi, J. K. W. Yang, *Nat. Commun.* **2023**, *14*, DOI 10.1038/s41467-023-41535-9.
- [45] B. Cardenas-Benitez, C. Eschenbaum, D. Mager, J. G. Korvink, M. J. Madou, U. Lemmer, I. D. Leon, S. O. Martinez-Chapa, *Microsyst. Nanoeng.* **2019**, *5*, 38.
- [46] R. Natu, M. Islam, J. Gilmore, R. Martinez-Duarte, *J. Anal. Appl. Pyrolysis* **2018**, *131*, 17.
- [47] R. G. Denning, C. F. Blanford, H. Urban, H. Bharaj, D. N. Sharp, A. J. Turberfield, *Adv. Funct. Mater.* **2011**, *21*, 1593.
- [48] D. C. Meisel, M. Diem, M. Deubel, F. Pérez-Willard, S. Linden, D. Gerthsen, K. Busch, M. Wegener, *Adv. Mater.* **2006**, *18*, 2964.
- [49] A. Naderi, W. Lin, A. Tarafdar, T. Zhang, Y. Wang, *Commun. Mater.* **2025**, *6*, 13.
- [50] M. Usselman, J. Bansmann, A. J. C. Kuchne, *Adv. Mater.* **2023**, *35*, DOI 10.1002/adma.202208484.
- [51] H. Steldinger, A. Esposito, K. Brunnengräber, J. Gläsel, B. J. M. Etzold, *Adv. Sci.* **2019**, *6*, 1901340.
- [52] Y. Lu, J. Hu, K. W. J. Ng, X. Hu, *Addit. Manuf.* **2024**, *83*, 104053.
- [53] D.-Y. Kang, C. Kim, G. Park, J. H. Moon, *Sci. Rep.* **2015**, *5*, 18185.
- [54] J. W. F. To, Z. Chen, H. Yao, J. He, K. Kim, H.-H. Chou, L. Pan, J. Wilcox, Y. Cui, Z. Bao, *ACS Cent. Sci.* **2015**, *1*, 68.
- [55] S. Park, Z. Cao, D. H. Sung, K. K. Fu, *Adv. Energy Mater.* **2023**, *13*, 2301704.

- [56] M. L. Comroe, K. W. Kolasinski, D. Saha, *Molecules* **2022**, *27*, 5653.
- [57] P. Smith, J. Hu, A. Griffin, M. Robertson, A. Güllen Obando, E. Bounds, C. B. Dunn, C. Ye, L. Liu, Z. Qiang, *Nat. Commun.* **2024**, *15*, 838.
- [58] S. Park, B. Shi, M. M. Islam, J. He, D. H. Sung, C. Zhang, Z. Cao, Y. Shang, L. Liu, K. Fu, *Adv. Funct. Mater.* **2024**, *34*, DOI 10.1002/adfm.202410164.
- [59] C. Zhang, B. Shi, J. He, L. Zhou, S. Park, S. Doshi, Y. Shang, K. Deng, M. Giordano, X. Qi, S. Cui, L. Liu, C. Ni, K. K. Fu, *Adv. Mater.* **2023**, *35*, DOI 10.1002/adma.202208230.
- [60] A. Kudo, K. Kanamaru, J. Han, R. Tang, K. Kisu, T. Yoshii, S. Orimo, H. Nishihara, M. Chen, *Small* **2023**, *19*, DOI 10.1002/sml.202301525.
- [61] S. Wei, C. Wan, X. Li, S. Jia, R. Chen, G. He, Y. Wu, *Adv. Sci.* **2025**, *12*, 2410397.
- [62] N. Kleger, S. Fehlmann, S. S. Lee, C. Dénéréaz, M. Cihova, N. Paunović, Y. Bao, J. Leroux, S. J. Ferguson, K. Masania, A. R. Studart, *Adv. Mater.* **2022**, *34*, 2203878.
- [63] N. Díez, M. Sevilla, A. B. Fuertes, *Carbon* **2021**, *178*, 451.
- [64] M. G. M. Marascio, J. Antons, D. P. Pioletti, P. Bourban, *Adv. Mater. Technol.* **2017**, *2*, 1700145.
- [65] E. C. Lloyd, S. Dhakal, S. Amini, R. Alhasan, P. Fratzl, D. R. Tree, S. Morozova, R. J. Hickey, *Nat. Commun.* **2025**, *16*, 3792.
- [66] V. A. Bobrin, Y. Yao, X. Shi, Y. Xiu, J. Zhang, N. Corrigan, C. Boyer, *Nat. Commun.* **2022**, *13*, 3577.
- [67] Z. Dong, H. Cui, H. Zhang, F. Wang, X. Zhan, F. Mayer, B. Nestler, M. Wegener, P. A. Levkin, *Nat. Commun.* **2021**, *12*, 247.
- [68] B. Deore, K. L. Sampson, T. Lacelle, N. Kredentser, J. Lefebvre, L. S. Young, J. Hyland, R. E. Amaya, J. Tanha, P. R. L. Malenfant, H. W. De Haan, C. Paquet, *Nat. Commun.* **2021**, *12*, 55.
- [69] F. Mayer, D. Ryklin, I. Wacker, R. Curticean, M. Čalkovský, A. Niemeyer, Z. Dong, P. A. Levkin, D. Gerthsen, R. R. Schröder, M. Wegener, *Adv. Mater.* **2020**, *32*, 2002044.

- [70] V. A. Bobrin, H. G. Hackbarth, Y. Yao, D. Kundu, N. M. Bedford, R. P. Kuchel, J. Zhang, N. Corrigan, C. Boyer, *Small Sci.* **2024**, *4*, DOI 10.1002/smssc.202300275.
- [71] M. Robertson, A. Guillen-Obando, A. Barbour, P. Smith, A. Griffin, Z. Qiang, *Nat. Commun.* **2023**, *14*, 639.
- [72] Z. Zhou, T. Liu, A. U. Khan, G. Liu, *Sci. Adv.* **2019**, *5*, eaau6852.
- [73] P. Dhavalikar, J. Sheno, K. Salhadar, M. Chwatko, G. Rodriguez-Rivera, J. Cheshire, R. Foudazi, E. Cosgriff-Hernandez, *Polymers* **2021**, *13*, 1479.
- [74] C. Minas, D. Carnelli, E. Tervoort, A. R. Studart, *Adv. Mater.* **2016**, *28*, 9993.
- [75] S. D. Kimmins, N. R. Cameron, *Adv. Funct. Mater.* **2011**, *21*, 211.
- [76] V. O. Ikem, A. Menner, T. S. Horozov, A. Bismarck, *Adv. Mater.* **2010**, *22*, 3588.
- [77] N. Sengokmen-Ozsoz, F. Claeysens, *Curr. Opin. Colloid Interface Sci.* **2025**, *77*, 101921.
- [78] N. Sengokmen-Ozsoz, M. Aleemardani, M. Palanca, A. Hann, G. C. Reilly, E. Dall'Ara, F. Claeysens, *Biofabrication* **2025**, *17*, 015012.
- [79] D. W. Johnson, C. Sherborne, M. P. Didsbury, C. Pateman, N. R. Cameron, F. Claeysens, *Adv. Mater.* **2013**, *25*, 3178.
- [80] M. Sušec, S. C. Ligon, J. Stampfl, R. Liska, P. Krajnc, *Macromol. Rapid Commun.* **2013**, *34*, 938.
- [81] N. Sengokmen-Ozsoz, R. Boston, J. S. Dean, C. Rodenburg, F. Claeysens, *Carbon* **2025**, *234*, 119933.
- [82] I. Mattich, A. Ofner, A. R. Studart, *Adv. Eng. Mater.* **2025**, *27*, 2401363.

## CHAPTER 2

### Macroscale fabrication of lightweight and strong porous carbon foams through template-coating pair design\*



\*Note: portions of this chapter were taken from a first-authored manuscript published (as of December 2022) to *Advanced Materials* (<https://doi.org/10.1002/adma.202206416>)

## **2.1 Abstract**

Manufacturing of low-density-high-strength carbon foams can benefit the construction, transportation, and packaging industries. One successful route to lightweight and mechanically strong carbon foams involves pyrolysis of polymeric architectures, which is inevitably accompanied by drastic volumetric shrinkage (usually >98%). As such, a challenge of these materials lies in maintaining bulk dimensions of building struts that span orders of magnitude difference in length scale from centimeters to nanometers. This work demonstrates fabrication of macroscale low-density-high-strength carbon foams that feature exceptional dimensional stability through pyrolysis of robust template-coating pairs. The template serves as the architectural blueprint and contains strength-imparting properties (e.g., high node density, small strut dimensions); it is composed of a low char-yielding porous polystyrene backbone with high carbonization-onset temperature. The coating serves to imprint and transcribe the template architecture into pyrolytic carbon; it is composed of a high char-yielding conjugated polymer with a relatively low carbonization-onset temperature. The designed carbonization mismatch enables structural inheritance, while the decomposition mismatch affords hollow struts, minimizing density. The carbons synthesized through this new framework exhibit remarkable dimensional stability ( $\sim 80\%$  dimension retention;  $\sim 50\%$  volume retention) and some of the highest specific strengths ( $\sim 0.13 \text{ GPa g}^{-1} \text{ cm}^3$ ) among reported carbon foams derived from porous polymer templates.

**Keywords:** porous carbon foam, pyrolytic carbon, porous polymer, template-coating pair, macroscale, dimensional stability, specific strength

## **2.2 Introduction**

Macroscale fabrication of low-density, high-strength materials is highly desirable for the production of next-generation, lightweight construction, transportation, and packaging products with increased load-bearing capabilities.<sup>[1,2]</sup> Naturally occurring lightweight porous materials like wood, nacre, and bone demonstrate remarkable fracture resilience and exceptional load-bearing capability under strain.<sup>[3–5]</sup> Such high strength has been ascribed to properties at multiple length scales from the macroscale to the atomic level.<sup>[6–8]</sup> At the molecular level, the bond strength of the constituent atoms dictates the theoretical limit of the bulk materials' strength.<sup>[9]</sup> Beyond intrinsic bond strength, material density largely governs strength: low-density materials tend to be weak, and high-density materials tend to be strong. Hence, it can be surmised that accessing the low-density-high-strength regime via synthetic routes is a grand challenge in materials science as these are frequently mutually exclusive properties.<sup>[10,11]</sup>

To that end, researchers have created a range of mechanically robust and lightweight ( $<1 \text{ g cm}^{-3}$ ) ceramic,<sup>[12–15]</sup> polymeric,<sup>[16,17]</sup> and metallic<sup>[18–21]</sup> architectures.<sup>[22–26]</sup> For high-strength applications specifically, pyrolytic carbon is an attractive material as it can be made porous to minimize density and precisely architected at the micron scale to adopt lattice topologies (microlattices) to maximize strength.<sup>[27–32]</sup> Researchers have primarily looked at the two-step fabrication of pyrolytic carbon microlattices. Step one involves additive manufacturing of polymeric architectures with the desired topology, and step two involves pyrolysis to induce carbonization. The additive manufacturing step is advantageous in producing complex microlattices with hierarchical length scales.<sup>[33–38]</sup> The pyrolysis step prompts linear shrinkage of building struts by  $>80\%$  in each dimension ( $>98\%$  volume shrinkage) which is favorable for the exploitation of size-dependent strengthening effects.<sup>[39–42]</sup>

The mechanical property of porous pyrolytic carbon depends on three characteristic densities: relative density, node density, and strut density (e.g., solid vs. hollow).<sup>[43–46]</sup> By leveraging clever strategies to tune these characteristic densities, pyrolytic carbon architectures that are lightweight and simultaneously strong can be fabricated at a range of densities ( $0.6\text{--}1.4\text{ g cm}^{-3}$ ).<sup>[27–31]</sup> For example, glassy carbon honeycomb microlattices ( $\sim 0.6\text{ g cm}^{-3}$ ) feature record high strengths ( $\sim 1.2\text{ GPa}$ ).<sup>[27]</sup> However, this comes at the cost of dimensional stability ( $<20\%$  dimension retention;  $<1\%$  volume retention). Therefore, accessing such architectures on a macroscopic length scale remains a significant challenge.<sup>[27,47]</sup> This trade-off exists because pyrolytic shrinkage (Fig. 1A) is leveraged to maximize strength in three ways: (1) altering the chemical composition of weak polymeric beams into significantly stronger pyrolytic carbon struts, (2) decreasing strut dimension from  $\sim 1\text{ }\mu\text{m}$  to  $\sim 200\text{ nm}$  and, (3) increasing node density.

Alternatively, pyrolytic carbon architectures with extremely low density ( $<0.03\text{ g cm}^{-3}$ ) can be achieved by maximizing dimensional stability and hence, volume retained through pyrolysis.<sup>[48]</sup> For example, tube-in-tube architected pyrolytic carbon lattices feature densities as low as  $\sim 0.0064\text{ g cm}^{-3}$  by minimizing strut density (hollow beam design) and retaining strut dimensions ( $\sim 1\text{ }\mu\text{m}$  diameter;  $\sim 5\text{ }\mu\text{m}$  pitch size).<sup>[49]</sup> However, high volume retention accompanied by tremendous mass loss causes a considerable reduction in node density which manifests in poor mechanical strength. That is, the combination of low strut cell wall thickness, relatively large strut dimensions, and relatively low node density means that ultra-low-density pyrolytic carbon architectures can be achieved at the cost of low specific strength ( $\sim 0.03\text{ GPa g}^{-1}\text{cm}^3$ ). As such, there is a need for low-density-high-strength pyrolytic carbons that exceed the current mechanical performance of synthetic foams and can also be fabricated in large sizes, that is, on the macroscale.<sup>[50–52]</sup> This later requirement means it is essential to find routes to access high specific strength carbons with improved dimensional stability that do not need to



undergo significant pyrolysis-induced shrinkage to exploit the above-mentioned strengthening effects emergent at the nanoscale.

Presented herein is a platform for the macroscale synthesis of porous pyrolytic carbon foams that optimizes density, strength, and dimensional stability. This platform highlights two key features, resulting in a robust template-coating pair that lends itself exceptionally well to the harsh conditions imposed by pyrolysis. First, the selection of a scalable, porous, open-celled, monolithic architecture with strength-imparting properties—hierarchical porosity, small strut dimensions, and high node density—as the template. Second, the combination of a high-onset carbonization temperature-low char yield polymer template with a relatively low-onset carbonization temperature-high char yield polymer coating. Leveraging these features affords access to macroscale porous carbon foams with (1) deterministic control over density ( $0.04\text{--}0.4\text{ g cm}^{-3}$ ) resulting from tunable coating thickness, (2) hierarchical pore distribution, small strut diameter, and high node density resulting from mismatched template-coating carbonization behavior, and (3) hollow strut architecture resulting from the mismatched template-coating decomposition behavior. Equipped with high dimensional stability ( $\sim 80\%$  dimension retention;  $\sim 50\%$  volume retention) and the above-mentioned strength-imparting properties, the resulting macroscale porous carbon architectures exhibited material strengths of up to  $\sim 44\text{ MPa}$  (at  $\sim 0.41\text{ g cm}^{-3}$ ) and specific strength of up to  $0.13\text{ GPa g}^{-1}\text{cm}^3$ —some of the highest values reported among current synthetic carbonaceous foams.

## **2.3 Results and Discussion**

### **2.3.1 Materials design criteria**

Porous polymer templates are highly tunable materials and can be engineered to exhibit strength imparting properties such as small strut dimension and high node density. The porous polymer templates employed in this study—a subset of emulsion-templated porous polymers known as Polymerized High Internal Phase Emulsion or Poly(HIPE)—are lightweight, low-density, open-celled, architectures spanning the macropore ( $>50\text{nm}$ ), mesopore ( $2\text{--}50\text{nm}$ ) and micropore ( $<2\text{nm}$ ) length scales.<sup>[53]</sup> The poly(HIPE) template was chosen as they intrinsically feature small strut dimensions ( $D\sim 0.1\text{--}1\text{ }\mu\text{m}$ ;  $L\sim 1\text{--}10\text{ }\mu\text{m}$ ) and high node density.<sup>[54]</sup> The strut/cell-size resolution achievable by emulsion-templating (hundreds of nanometers) surpasses those of 3D lithography techniques (ones of microns), albeit with less control over pore distribution.<sup>[49,55]</sup> The volume-average cell size of poly(HIPE)s can be tuned, which is useful to vary the density and, therefore, mechanical properties of resulting porous carbon foams.<sup>[56]</sup> Poly(HIPE)s can also be readily synthesized at scale and as the ability to fabricate macroscale porous carbons is contingent on synthesizing even larger polymeric precursors (on account of shrinkage), it is noteworthy that poly(HIPE)s can be fabricated with macroscopic dimensions ( $>10^{-1}\text{m}$ ) and in industrially relevant quantities.<sup>[57]</sup>

Within the last decade, the fabrication of porous carbons through carbonization of poly(HIPE)s has been explored.<sup>[58,59]</sup> Poly(HIPE) pyrolysis has afforded access to hierarchically porous carbon foams with exceptional properties such as high specific surface area ( $>1000\text{ m}^2\text{ g}^{-1}$ ),<sup>[60,61]</sup> good electrical conductivity,<sup>[62,63]</sup> tunable surface chemistry<sup>[64]</sup> and mechanical stability.<sup>[65]</sup> Typically, during poly(HIPE) pyrolysis, the emulsion-templated polymer that composes the precursor poly(HIPE) (e.g., polystyrene, poly(vinylbenzene chloride), polyacrylonitrile serves as the primary pyrolytic carbon source.<sup>[66]</sup> As such, direct pyrolysis of poly(HIPE) templates results in some combination of low char-

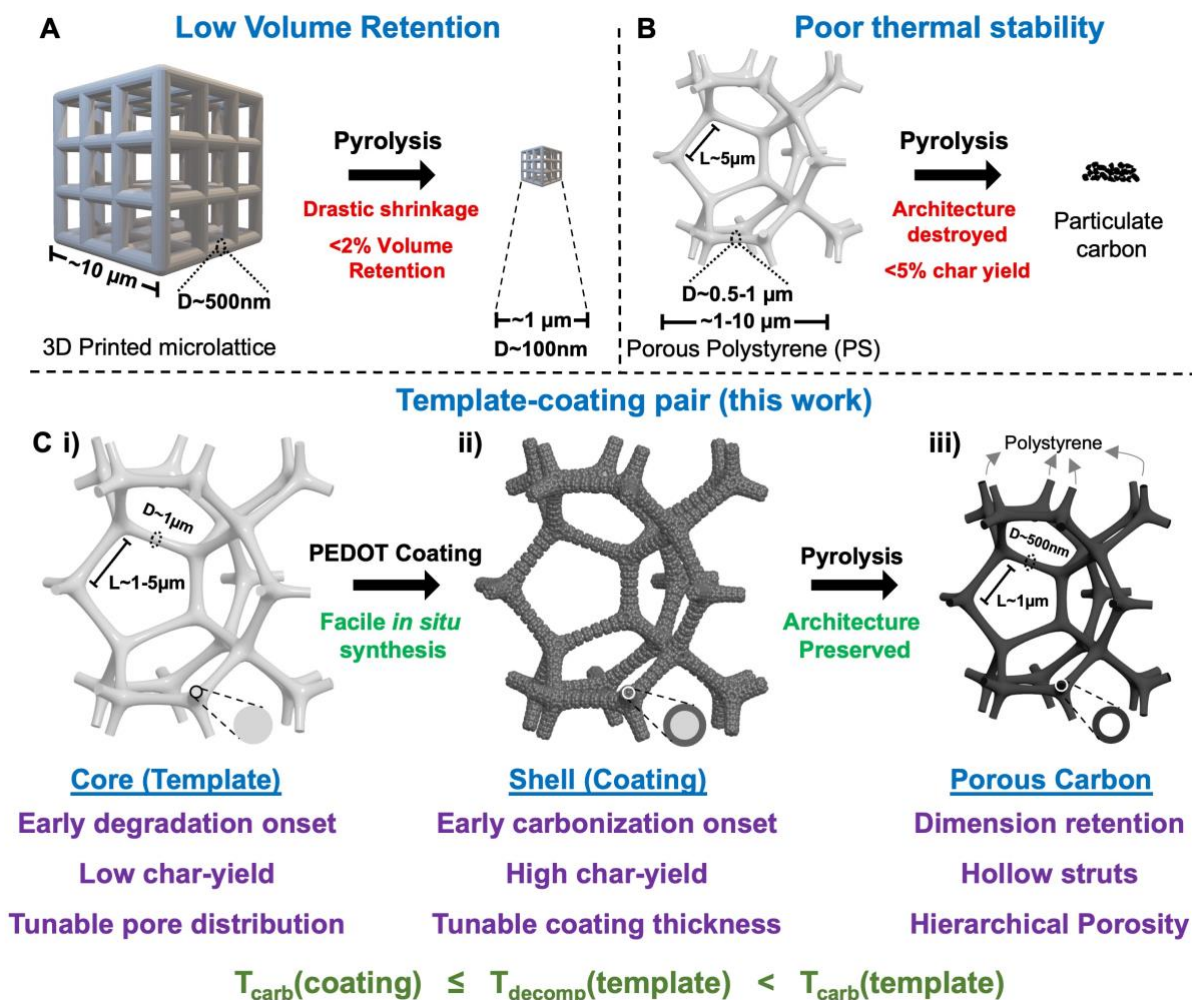
yield (<20 wt%), poor architectural inheritance, and drastic volume shrinkage (>80%). Strategies such as hyper-crosslinking,<sup>[67,68]</sup> sulfonation,<sup>[69]</sup> pickering stabilizer addition,<sup>[70,71]</sup> and porogen incorporation<sup>[72]</sup> have been explored to alleviate some of these issues. The goal of this work was to explore a new strategy to access poly(HIPE)-templated low-density-high-strength porous carbon foams with hollow struts that simultaneously (1) inherit the poly(HIPE)'s unique pore architecture at the microscale and (2) preserve the poly(HIPE)'s bulk dimensions at the macroscale.

The poly(HIPE) employed in this study is composed of crosslinked polystyrene (see SI methods section for detailed synthesis). Polystyrene-based poly(HIPE)s (PS-poly(HIPE)) intrinsically feature a decomposition temperature ( $T_{\text{decomp}}$ ) around 400°C and a much higher carbonization temperature ( $T_{\text{carb}} \sim 700^\circ\text{C}$ ), resulting in low pyrolytic char-yield (<5wt%). Direct pyrolysis of PS-poly(HIPE)s yields particulate carbon (Fig. 1B) as opposed to 3D pyrolytic carbon that mimics the porous template architecture. The low-char yield property of the template can be leveraged to create a hollow strut architecture in the resulting porous carbon providing there exists an alternative pyrolytic carbon source, perhaps in the form of a polymer coating.<sup>[73]</sup> That is, a low char-yield template with a strength-imparting architecture that can be easily evacuated through thermal decomposition when combined with a high char-yield coating conceptually makes for an ideal template-coating pair for the creation of hollow, low-density-high-strength pyrolytic carbon foams. In this template-coating approach, the template serves as the architectural blueprint, and the coating serves as the pyrolytic carbon source that adopts the template architecture. For the template-coating approach to be successful, several criteria—the rationale for which are further elucidated below—need to be satisfied.

First, it is critically important that the coating inherits the template architecture at the microscale (strut dimensions) and macroscale (bulk dimensions). At the microscale, retaining strut dimensions allows for maximizing compressive strength through exploitation of hierarchical length scales, high node density, and small strut dimensions (Fig. 1C-i). At the macroscale, retaining bulk

dimensions and minimizing volume shrinkage provides for a framework that is theoretically capable of producing dimensionally stable porous carbon monoliths—on the order of  $\sim 10 \text{ cm}^3$  and above—with high materials efficiency and without needing to sacrifice mechanical performance. It is proposed that successful architectural inheritance at both length scales will be aided if the polymer coating is converted into a carbon coating prior to decomposition of the template and impending structural collapse, that is,  $T_{\text{carb}}(\text{coating}) \leq T_{\text{decomp}}(\text{template})$  (Fig. 1C-ii). As the primary purpose of the template is to provide architecture, the particulate carbon resulting from template pyrolysis will not play a significant role in imparting strength. Therefore, inconsequential density reduction is achievable by evacuating as much of the template as possible, resulting in a hollow pyrolytic carbon (Fig. 1C-iii). Seeing as template evacuation is contingent on avoiding PS carbonization and promoting degradation as much as possible, it is imperative that  $T_{\text{decomp}}(\text{template}) < T_{\text{carb}}(\text{template})$ . Overall, the strategy to leverage mismatched carbonization and decomposition behavior is summarized as follows:

$$T_{\text{carb}}(\text{coating}) \leq T_{\text{decomp}}(\text{template}) < T_{\text{carb}}(\text{template})$$



**Fig. 1** Schematic illustration of pyrolytic carbon fabrication featuring prior methods, associated challenges and the proposed solution (current work). **(A)** Fabrication of ultra-high strength pyrolytic carbon microlattices via pyrolysis of polymer architectures, highlighting low volume retention  $\sim 1\%$  ( $\sim 80\%$  linear shrinkage) (to scale). **(B)** Pyrolysis of porous polystyrene-based materials resulting in particulate carbon, highlighting poor thermal stability of polymer scaffolds undergoing direct pyrolysis. **(C)** **(i)** Porous architecture of PS-poly(HIPE) featuring strength-imparting properties (interconnected struts, small strut dimensions and high node density) **(ii)** PEDOT coated PS-poly(HIPE) resulting from the coating step with the cross-section featuring a PS core and PEDOT shell and **(iii)** Porous pyrolytic carbon with the poly(HIPE) template architecture preserved and cross section featuring hollow struts;  $\sim 50\%$  volume retention ( $\sim 20\%$  linear shrinkage) to scale.

To satisfy the above-mentioned inequality, a high char-yield coating that serves to imprint and transcribe the template architecture into pyrolytic carbon is required. To that end, the conjugated aromatic backbones of intrinsically conducting polymers, such as polythiophenes, make them highly capable of cyclization, ring fusion, and chain coalescence upon pyrolysis, and as such, they are known to exhibit high char-yields.<sup>[73–75]</sup> In addition, conjugated polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT) can be synthesized *in situ* via chemical oxidative polymerization reactions, which allows for the formation of uniform coatings inside the complex, tortuous architectures of the PS-poly(HIPE). PEDOT has a high char yield (~47 % at 700°C) and relatively early carbonization-onset temperature ( $T_{\text{carb}} \sim 400^\circ\text{C}$ ) making it an ideal coating partner for the PS-poly(HIPE) template in this study on account of the stark differences in their char-yield, thermal decomposition temperature, and carbonization temperature.

To demonstrate that PEDOT-coated PS-poly(HIPE)—herein referred to as PS-PEDOT—is a viable template-coating pair per the aforementioned design criteria, a PS-PEDOT sample ( $[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}] = 1.5\text{M}$ ,  $[\text{EDOT}] = 3.0\text{M}$ ) was synthesized according to the following steps (Fig. 2A–C, see SI methods section for detailed synthesis). The bare PS-poly(HIPE)s were prepared as cylinders with an approximate 2 cm diameter and 3.5 cm height (Fig. 2A, left). The SEM image (Fig. 2A, right) shows the highly porous nature of the PS-poly(HIPE), microscale strength-imparting features such as small struts and high node density. Uniformly cut poly(HIPE) pieces were soaked in a 1.5M solution of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (redox initiator) in tetrahydrofuran (THF) for 24 hours and then dried for 15 minutes under vacuum. The SEM of the partially dried initiator-saturated PS-poly(HIPE) (Fig. 2B) reveals that the  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  crystallized along the interior of the PS-poly(HIPE). The initiator-saturated samples were then immersed in a 3.0M EDOT (monomer) solution at 70°C for 24h, after which they were washed via Soxhlet extraction with methanol and dried under vacuum, resulting in black monoliths consistent with successful PEDOT formation. SEM of the PEDOT coated PS-Poly(HIPE) features

complete coating of the template's internal surface and no qualitative evidence of pore blockage or strut damage (Fig. 2C). The bare PS-poly(HIPE) template, bare PEDOT coating, and PS-PEDOT samples were subject to thermogravimetric analysis (TGA) to quantify  $T_{\text{decomp}}$  and char-yield, variable-temperature scanning electron microscopy (SEM) to confirm architectural inheritance, variable-temperature Raman spectroscopy to quantify  $T_{\text{carb}}$  and ex-situ/in-situ FTIR spectroscopy to unravel the decomposition mechanism of PS-PEDOT.

The TGA data (Fig. 2D) reveal that the PS-PEDOT template-coating pair has a higher char-yield ( $\sim 42.1\%$ ) than bare PS-poly(HIPE) ( $\sim 4.5\%$ ) and suggests that much of the resulting pyrolytic carbon is derived from the PEDOT ( $\sim 46.1\%$ ) rather than the PS. The SEM data shows the destruction of the bare, uncoated PS-poly(HIPE) at around  $400^\circ\text{C}$  (Fig. S1), which is consistent with the decomposition-onset temperature of PS ( $T_{\text{decomp}}(\text{PS}) \sim 400^\circ\text{C}$ ).<sup>[76]</sup> Qualitatively, the SEM images (Fig. 2D, inset) show that the PS-PEDOT retains the template architecture while the bare PS-poly(HIPE) decomposes into particulate carbon (Fig. 1B) upon pyrolysis.

The variable-temperature Raman spectra, wherein  $T_{\text{carb}}$  is defined to be the temperature at which the characteristic G band ( $\sim 1582\text{ cm}^{-1}$ ) and D band ( $\sim 1350\text{ cm}^{-1}$ ) first occur, show that  $T_{\text{carb}}(\text{PS}) \sim 700^\circ\text{C}$  (Fig. 2E) and  $T_{\text{carb}}(\text{PEDOT}) \sim 350\text{-}400^\circ\text{C}$  (Fig. 2F). These data, bolstered by variable-temperature TGA (Fig. S2A-B) and variable-temperature FTIR (Fig. S2C-D), verify that  $T_{\text{carb}}(\text{coating}) \leq T_{\text{decomp}}(\text{template})$ . Satisfaction of this criterion presumably enables architectural inheritance via hardening of the coating prior to template decomposition, thereby preventing imminent collapse of the pyrolyzed coating.

The variable-temperature data also verify that  $T_{\text{decomp}}(\text{template}) < T_{\text{carb}}(\text{template})$ , which should allow the creation of hollow struts. Beyond satisfaction of this temperature criterion, ensuring hollow struts is contingent upon providing enough time for the PS decomposition products to diffuse out through the pores of the highly tortuous architecture. This warrants the inclusion of a hold time  $t_{\text{hold}}$

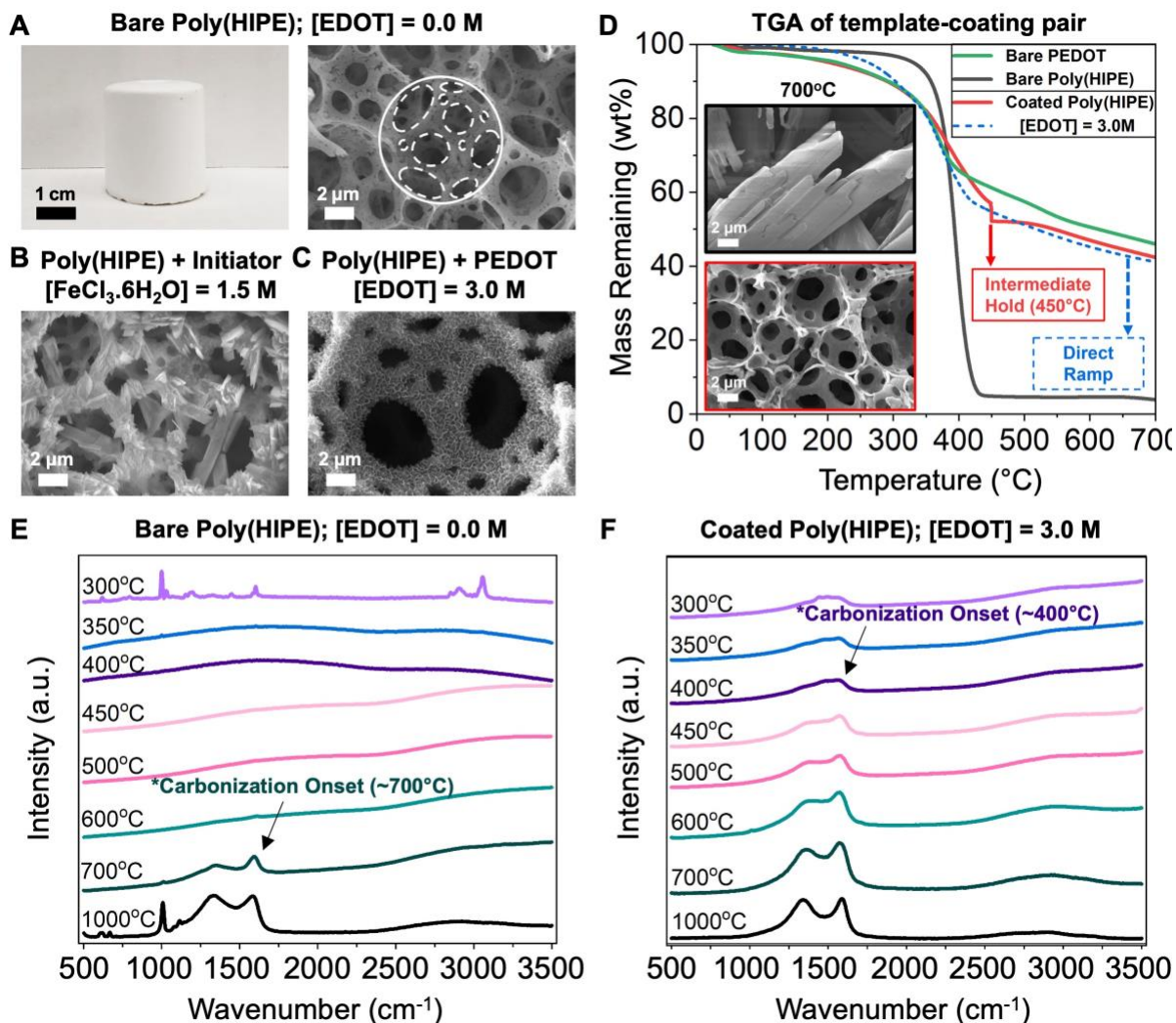
at an intermediate temperature  $T_{\text{isotherm}}$  such that  $T_{\text{decomp}}(\text{template}) < T_{\text{isotherm}} < T_{\text{carb}}(\text{template})$ . Presumably, the placement of this isothermal stage after the onset of template decomposition but before the onset of template carbonization will mitigate the entrapment of (1) re-condensed decomposition products and (2) PS-derived particulate carbon resulting from incomplete pyrolysis of thermally insulated PS pockets.  $T_{\text{isotherm}}$  was set to be 450°C (Fig. S3A), and the hold time ( $t_{\text{hold}}$ ) at  $T_{\text{isotherm}}$  was set to be 1 hour, which proved to be sufficient for complete evacuation of the struts (Fig. S3B-D). The established pyrolysis protocol (10°C min<sup>-1</sup> to 450 °C, 1h hold, 10°C min<sup>-1</sup> to 1000°C, 2h hold) will be referred to herein as the “intermediate hold” protocol. The two-hour long isotherm at 1000°C was included to anneal out any accumulated stresses. Alternative pyrolysis conditions without an intermediate isothermal stage (10°C min<sup>-1</sup> to 1000°C, 2h hold) will be referred to herein as the “direct ramp” protocol. The 10°C min<sup>-1</sup> ramp rate during the carbonization-onset stage (>400°C) was deemed optimal through Raman data which suggests that carbon quality is retained even at this relatively fast heating rate (Fig. S3E).

As a control, bare PS-poly(HIPE) samples were subject to both “direct ramp” and “intermediate hold” pyrolysis at various rapid ramp rates (50°C min<sup>-1</sup>, 75°C min<sup>-1</sup>, and 100°C min<sup>-1</sup>) to confirm the relevance of a coating. SEM shows that bare PS-poly(HIPE) degrades to particulate carbon independent of both ramp rate and pyrolysis protocol (Fig. S4). This confirms that a coating is required, and that rapid pyrolysis of the uncoated PS-poly(HIPE) does not kinetically trap and retain the porous architecture.

This initial set of experiments demonstrates that the PS-PEDOT template-coating pair satisfies the high char-yield and  $T_{\text{carb}}(\text{coating}) \leq T_{\text{decomp}}(\text{template}) < T_{\text{carb}}(\text{template})$  criteria. As a result, the porous pyrolytic carbons feature small strut dimensions (Fig. S5A-B), high node density (Fig. S5C), and hollow struts, all of which are important properties for good mechanical performance.



The conversion of polymeric materials into pyrolytic carbon is mediated by the expulsion of gaseous decomposition products and atomic rearrangement of carbon, resulting in char. To unravel the decomposition pathway of PS-PEDOT, ex-situ variable-temperature TGA/FTIR was used to reveal the chemical transformations undergoing in the char, in-situ TGA-FTIR was used to identify possible gaseous decomposition products, and calculations based on systematic chemical abstraction were used to verify the proposed mechanism. The lost mass mainly comes from  $C_2H_4O_2$ ,  $C_8H_8$ , and S leaving the material as a mixture of hydrocarbon (styrene, toluene, ethylene), oxygenated ( $CO_2$ ,  $H_2O$ ,  $CO$ ), and sulfonated ( $SO_2$ ,  $CS_2$ ) decomposition products (See Fig. S6-S8 and associated discussion for further details).



**Fig. 2** Verification of design criteria through gravimetric, spectroscopic, and microscopic characterization. **(A)** Image of as-prepared PS-poly(HIPE) after washing and drying (left) and SEM image of PS-poly(HIPE) microstructure (right) indicative of open porosity and interconnected struts. The solid circle drawl represents a “void” (1-10  $\mu\text{m}$ ), and the small, dotted circle represents a “pore” (0.1-1  $\mu\text{m}$ ). SEM image of **(B)** PS-poly(HIPE) soaked in a 1.5M  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in THF solution for 24 hours and dried under house vacuum for 15 min. **(C)** PS-poly(HIPE) coated with a layer of PEDOT in a 3.0M EDOT in THF solution after thorough washing and drying under vacuum. **(D)** “Direct ramp” and “Intermediate hold” thermograms of PS-poly(HIPE), PEDOT and PEDOT coated PS-poly(HIPE) ([EDOT]=3.0M) to probe the decomposition-onset temperature and quantify char-yields. The inset on the left contains post-pyrolytic SEM images of bare PS-poly(HIPE)-derived particulate carbon (top; black border) and PEDOT coated PS-poly(HIPE)-derived monolithic carbon (bottom; red border). Variable-temperature Raman spectra ( $2^\circ\text{min}^{-1}$  to  $T^\circ\text{C}$ ) of **(E)** bare PS-poly(HIPE) and **(F)** PEDOT coated PS-Poly(HIPE) ([EDOT]=3.0M) to probe the onset of carbonization.

### 2.3.2 Tuning the properties of porous carbons

To achieve porous carbons with different densities, the effect of varying the reaction monomer concentration ([EDOT]) on the coating (PEDOT) thickness was investigated. PEDOT serves as the primary pyrolytic carbon source, owing to its relatively high-char yield. As such, it is conceivable that the pre-pyrolytic PEDOT coating thickness can be leveraged to gain control over the post-pyrolytic cell wall thickness and density. A series of PEDOT-coated PS-poly(HIPE) samples—herein denoted by PS-PEDOT-x where  $x = [\text{EDOT}] = 0.0$  to  $6.0\text{M}$ —were prepared using the same synthesis and characterizations procedure outlined in the previous section (see SI Methods for detailed synthesis).

SEM images (Fig. 3A-F, left) show that increasing the [EDOT] during the reaction results in an increasingly thick PEDOT shell in the poly(HIPE). Interestingly there appear to be two significant morphological transitions that occur as [EDOT] increases. The first transition occurs between PS-PEDOT-2.0 (Fig. 3A, left), in which the PEDOT forms a particulate and discontinuous layer, and PS-PEDOT-2.5 (Fig. 3B, left), in which the PEDOT forms a continuous and smooth coating layer. Lower [EDOT] implies that fewer EDOT molecules can diffuse into the PS-poly(HIPE) towards the surface-confined initiator crystals (Fig. 2B), resulting in the formation of discrete and discontinuous polymer domains. A second morphological transition occurs between PS-PEDOT-2.5 (Fig. 3B, left) and PS-PEDOT-3.0 (Fig. 3C, left), where the coating appears significantly rougher. Going from PS-PEDOT-2.5 to PS-PEDOT-3.0, the coating appears to form coral-like wrinkle features or "folds". As [EDOT] concentration increases further from  $3.0\text{M}$ , the "folds" seem to get denser and thicker (Fig. 3D-F, left). Several factors can play a role in the resulting morphology of PEDOT coatings, such as choice of redox initiator counter ion,<sup>[77]</sup> solvent medium, and reaction conditions,<sup>[78]</sup> to name a few. Considering that the only reaction variable in this work was monomer concentration [EDOT], it is hypothesized that concentration effects contributed to the morphological differences across PS-PEDOT-x; that is, as the concentration of [EDOT] increased, confinement of the polymer chains in

roughly the same amount of pore space forced the formation of "folds" out-of-plane in the direction perpendicular to the PS surface. Perhaps not surprisingly, TGA data show a strong correlation between [EDOT] concentration—and by virtue, PEDOT coating thickness—and char yield (Fig. S9A-B). To validate that PEDOT is the primary pyrolytic carbon source, the TGA-determined char-yield (wt%) was plotted against the gravimetrically determined PEDOT content (wt%), which was calculated by weighing the PS poly(HIPE) before and after coating, washing, and drying. The linear relationship indicates that coating thickness and char yield are intimately connected (Fig. S9C).

To probe the effects of the PEDOT coating thickness (before pyrolysis) on the strut cell wall thickness (after pyrolysis) and density, pyrolytic carbon samples were prepared from each of the PS-PEDOT-*x* samples in a tube furnace using operating conditions experimentally verified to be nearly identical to those in the TGA (Fig. S9D). The "intermediate hold" protocol (10°C min<sup>-1</sup> to 450°C, 1h hold, 10°C min<sup>-1</sup> to 1000°C, 2h hold) established previously was used in the tube furnace for the fabrication of porous carbons (see SI Methods for detailed procedure), which are herein denoted by "PC-*x*" where "PC" represents "Porous Carbon," and *x* represents the PS-PEDOT-*x* precursor from which the corresponding PC-*x* was synthesized. After pyrolysis under "intermediate hold" conditions, SEM evidence suggests that the PS-poly(HIPE) architectures seem to be preserved in all the PC-*x* materials (Fig. S3). That is, the hierarchical pores, node density, and small strut dimensions appear to be retained. Furthermore, the PS core appears entirely evacuated, resulting in the desirable hollow struts (Fig. 3A-F, right panel). As a control, variable-temperature Raman spectroscopy was conducted for PC-2.0 (Fig. S9E) and PC-5.0 (Fig. S9F) to confirm that the carbonization-onset is independent of coating thickness for [EDOT] ≤ 5.0M and pyrolytic ramp rate ≤ 10°C min<sup>-1</sup>. Additionally, all PC-*x* samples were pyrolyzed under the "direct ramp" protocol, and SEM analysis revealed trapped PS-derived carbon within the strut cell wall, particularly at larger coating thickness ([EDOT] ≥ 3.5) (Fig. S10).

SEM also shows that the thickness of the strut cell wall increases from PC-2.0 to PC-6.0, consistent with the TGA results, which show that the PEDOT, rather than PS, is the primary source of pyrolytic carbon. Furthermore, as is observed among pre-pyrolytic PS-PEDOT-x samples, a morphological transition occurs between PC-2.0 (Fig. 3A, right), where the carbon appears discontinuous and particulate and PC-2.5 (Fig. 3B, right) which appears continuous and smooth. Additionally, as [EDOT] increases, the PEDOT-derived carbon struts appear to contain more defects such as cracks and voids; this is especially evident when comparing the strut cell wall cross-sections of PC-4.0 (Fig. 3E, right) and PC-6.0 (Fig. 3F, right). It is hypothesized that pyrolysis of PC-3.0, PC-3.5, and PC-4.0 result in smooth carbon surfaces because the PEDOT coating undergoes a morphological transition at  $\sim 375^\circ\text{C}$ , as is evidenced by variable-temperature SEM (Fig. S1; right panel), and variable-temperature TGA/FTIR (Fig. S2). This transition could result from the cleavage of the ethylenedioxy moiety and abstraction of sulfur atoms from the PEDOT fraction, which are known to occur in this temperature range (Fig. S7; see SI for detailed discussion). To that end, it is possible that larger and thicker folds like in PC-5.0 and PC-6.0 cause non-uniform heat transfer to occur across the PEDOT shell, resulting in incomplete smoothening of the coating (Fig. S11).

Raman spectroscopy was conducted on PC-x to verify carbon quality, as indicated by the ratio of intensities ( $I_D/I_G$ ) of the characteristic D (disorder band  $\sim 1350\text{ cm}^{-1}$ ) and G (indicative of stretching between two  $\text{sp}^2$  carbons  $\sim 1590\text{ cm}^{-1}$ ) bands respectively (Fig. S12A). The ratio of intensities is approximately 1 for all PC-x indicating the presence of defects and amorphous/disordered domains in the pyrolytic carbons.<sup>[79,80]</sup> An alternative indicator of carbon quality is electrical conductivity, which was measured using a 2-point-probe multimeter setup with the PC-x samples in between copper plates. The electrical conductivity of PC-x monoliths increased from  $19.8 \pm 2.6\text{ S m}^{-1}$  to  $178.3 \pm 19.9\text{ S m}^{-1}$  from PC-2.0 to PC-6.0 respectively (Fig. S12B), which is consistent with that of porous vitreous carbon foams of comparable relative density.<sup>[37,62,81]</sup> However, the electrical conductivity is presumably

an underestimate, seeing as relative density indicative of void fraction) is not considered; rather, the PC-x samples are treated as solid blocks (Fig. 3G).

X-ray photoelectron spectroscopy (XPS) was conducted on PC-x to investigate the surface chemical composition of PC-x (Fig. S12C). The survey spectra confirm the presence of three prominent peaks corresponding to S2p ( $\sim 165$  eV), C1s ( $\sim 285$  eV), and O1s ( $\sim 533$  eV). The C1s peak can be deconvoluted into four peaks assigned to be C=C ( $sp^2$ ; 284.8 eV), C-C ( $sp^3$ ; 285.1 eV), C-O (287.2 eV), and C=O (290.6 eV), which is in agreement with the functional groups typically found in polymer-derived pyrolytic carbon (Fig. S12D).<sup>[82]</sup> Consistent with the Raman data (Fig. S12A), the  $sp^2$  and  $sp^3$  carbon peaks indicate graphitic and amorphous carbon domains, respectively. Consistent with the high binding energy peaks in the C1s spectrum, the O1s peak can be deconvoluted into two peaks assigned to be C=O (532.7 eV) and C-O (534.3 eV), indicative of oxygen functionalized carbon (Fig. S12E). The pair of deconvoluted S2p peaks at 164.1 eV and 165.3 eV are assigned to the C-S-C  $2p_{3/2}$  and C-S-C  $2p_{1/2}$ —due to spin-orbit coupling—respectively (Fig. S12F). This is indicative of doped sulfur atoms in the pyrolytic carbon framework. The second pair of peaks are assigned to the C-SO<sub>x</sub>  $2p_{3/2}$  ( $\sim 166.1$  eV) and  $2p_{1/2}$  ( $\sim 168.7$  eV), which could be indicative of oxidized S species.<sup>[83]</sup> As expected, the X-ray diffraction (XRD) pattern of PC-x shows two broad peaks centered at  $22^\circ$  and  $44^\circ$ , representative of the (002) and (100) diffraction modes of pyrolytic carbon, respectively (Fig. S13). This suggests the formation of aromatic ribbon structures that are stacked and tangled resulting in a strained disordered carbon network.<sup>[80,84,85]</sup>

The porous carbon samples were subjected to transmission electron microscopy (TEM) and Brunauer–Emmett–Teller (BET) analysis to verify hierarchical structures. The TEM images (Fig. S14 A-D) are provided alongside SEM images (Fig. S14 E-F) for comparison. The images reveal a highly interconnected network structure within the struts with characteristic dimensions on the order of  $\sim 10$ -50 nm. There is also evidence of small pore dimensions on the order of tens of nanometers. This type

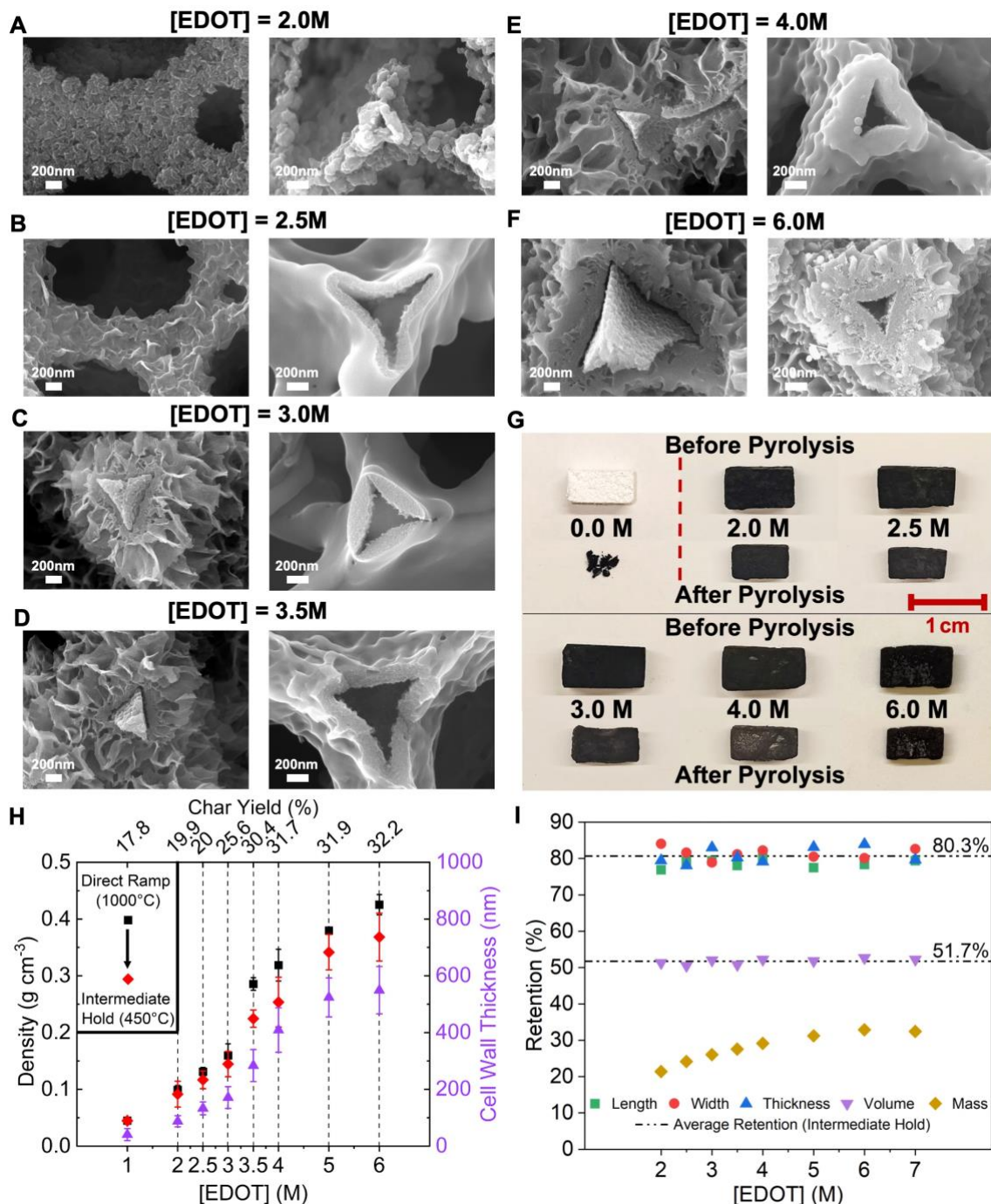
of interconnected network structure composed of small structural features is known to contribute to the exceptional mechanical properties demonstrated by natural (e.g., bone) and synthetic (e.g., steel) materials.<sup>[4,86]</sup> BET analysis suggests the presence of a high density of micropores (<2nm) in all PC-x, resulting in high specific surface areas ranging from ~500-800 m<sup>2</sup>g<sup>-1</sup> (Fig. S15). Taken together, electron microscopy and surface area analysis techniques suggest that the PC-x samples are hierarchically porous; the SEM images show interconnected macropores (>50 nm), TEM suggests mesoporosity (2-50 nm), and BET provides evidence of microporosity (<2nm).

The densities of PC-x samples were calculated and tracked by measuring the mass and bulk volume before (Fig. S16) and after pyrolysis (Fig 3H). The density (left y-axis) and cell wall thickness (right y-axis) are reported as a function of [EDOT] used in the synthesis of the precursors PS-PEDOT-x. It can be seen that the density and cell wall thickness (quantified using ImageJ analysis software; Fig. S17) increases as a function of [EDOT] (2.0M – 6.0M). As expected, the carbon with the smallest cell wall thickness (PC-2.0; 87.4 ± 19.9 nm) had the lowest density (~0.09 g cm<sup>-3</sup>), and the carbon with the highest strut-wall thickness (PC-6.0; 550.0 ± 83.4 nm) had the highest density (~0.37 g cm<sup>-3</sup>).

The density profile for the samples resulting from the “direct ramp” (black square) protocol features a large discontinuity in going from PC-3.0 to PC-3.5; there is an abrupt increase in density but not in cell wall thickness. Furthermore, SEM characterization (Fig. S10) suggests that when the strut size gets thick enough (>200 nm; PC-3.0 through PC-6.0), a greater amount of carbon is trapped inside the struts. Taken together, the data suggest that the entrapment of PS-derived carbon within thicker-walled struts during “direct ramp” pyrolysis contributes to the abrupt increase in char yield and density but not in cell wall thickness (Fig. 3H). As expected, the densities of the PC-x samples when pyrolyzed under the “intermediate hold” conditions are consistently lower by ~15% on average compared to the “direct ramp” control samples. That being said, the discontinuity in density when

going from PC-3.0 to PC-3.5, while certainly reduced, still exists. This could be attributed to morphological changes such as increased surface roughness among samples with higher cell wall thickness (Fig. 2D-F; right panel).



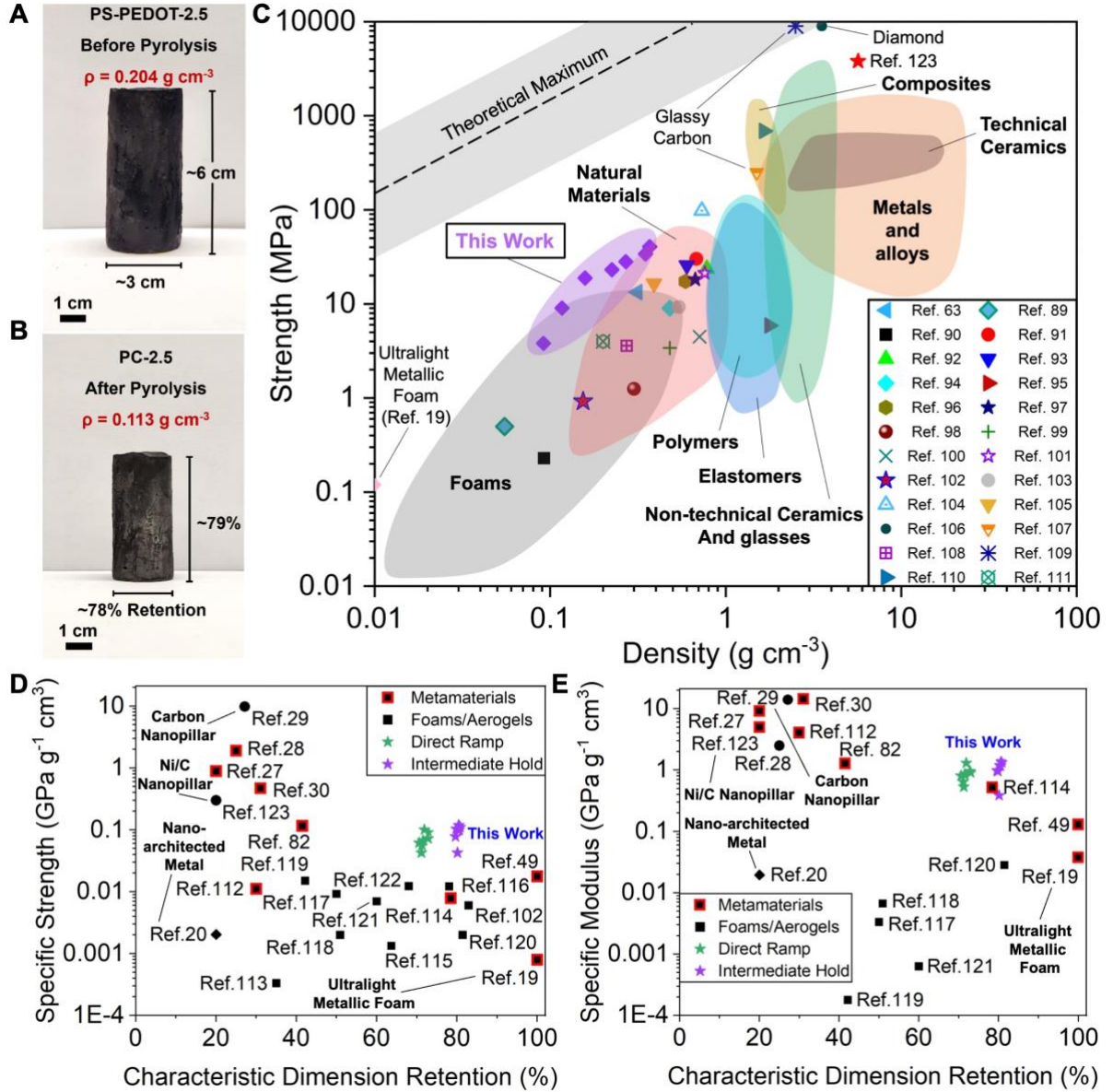


**Fig. 3** Tuning the properties of pyrolytic carbons PC-x by tuning PEDOT coating thickness via [EDOT] concentration used in the synthesis of the pyrolytic precursors PS-PEDOT-x. **(A-F)** SEM images of PS-PEDOT-x (left), PC-x (right) pyrolyzed under “Intermediate hold” conditions ( $10^{\circ}\text{C min}^{-1}$  to  $450^{\circ}\text{C}$ , 1h hold,  $10^{\circ}\text{C min}^{-1}$  to  $1000^{\circ}\text{C}$ , 2h hold). **(G)** Images of bulk PC-x monoliths before and after pyrolysis (scale bar applicable to all samples). **(H)** [EDOT] (M) versus density ( $\text{g cm}^{-3}$ ), cell wall thickness (nm) and direct ramp char yield ( $1000^{\circ}\text{C}$ ; dotted lines) of porous carbons pyrolyzed under “Direct ramp” (black squares) conditions and “Intermediate hold” (red diamonds). **(I)** Property retention of macroscale PC-x (mass, length, width, thickness, volume) pyrolyzed under the “Intermediate hold” conditions.

The volume retention of PC-x was calculated by tracking each sample's dimensions (length, width, and thickness) before and after pyrolysis (Fig. 3G). Regardless of the PC-x examined, the dimensional retention was  $\sim 80.3\%$  ( $50.1\%$  volume retention), which means that the PC-x samples only shrank by  $\sim 50\%$  as opposed to  $>98\%$  shrinkage observed in other approaches (Fig. 3I).<sup>[27–32]</sup> Any geometric imperfections observed in PC-x could be attributed to local variations in coating thickness and morphology in PS-PEDOT-x, especially at higher [EDOT] concentrations. Interestingly, the dimension retention under “direct ramp” conditions was measured to be lower at  $\sim 71.2\%$  ( $\sim 36.7\%$  volume retention; Fig. S18). Studies have shown that carbonization temperature, more so than ramp rate or dwell time, plays a significant role in determining the shrinkage of polymeric precursors undergoing pyrolysis.<sup>[87,88]</sup> To that end, it is hypothesized the hour-long isothermal stage at  $450^\circ\text{C}$ —such that  $T_{\text{isotherm}} > T_{\text{carb}}(\text{coating})$  (Fig. 2F)—alleviates shrinkage stress by providing more time for complete carbonization of the PEDOT-derived carbon shell. Presumably, the hardening of the shell sets the bulk dimensions of the porous carbon monolith, effectively limiting further shrinkage during the second pyrolysis stage ( $450^\circ\text{C}$  to  $1000^\circ\text{C}$ , 2h hold). Even though “direct ramp” and “intermediate hold” pyrolysis result in similar char yields (Fig. S3A), the alleviated volume retention among “intermediate hold” PC-x samples contributes to the overall density reduction (Fig. 3H; black arrow in legend represents density reduction).

Dimensional stability—and therefore volume retention—is a key consideration when fabricating low-density-high-strength porous carbons that are macroscopic in size. This is because the volume retained by the pyrolytic product dictates the required size of the pyrolytic precursor. That is, the polymeric precursors need not be unreasonably large to obtain a final pyrolytic carbon product of desired macroscopic size. To highlight this, a relatively large cylindrical sample of PS-PEDOT-2.5 (Fig. 4A; diameter  $\sim 3$  cm and height  $\sim 6$  cm;  $V \sim 42 \text{ cm}^3$ ;  $\rho \sim 0.204 \text{ g cm}^{-3}$ ) was pyrolyzed in a ceramic tube furnace to yield a macroscale ( $>10^{-1}$  m length scale) porous carbon (Fig. 4B;  $V \sim 20 \text{ cm}^3$ ;  $\rho \sim 0.113$

g cm<sup>-3</sup>) with the expected density ( $\sim 0.113$  g cm<sup>-3</sup>), dimension retention ( $\sim 78\%$  in diameter,  $\sim 79\%$  in length,  $\sim 48\%$  in volume) and cell wall morphology (Fig. S19). To access a porous carbon of this size using prior pyrolysis techniques that commonly result in significantly more shrinkage<sup>[27–32]</sup>, the volume of the polymeric precursor would need to be  $\sim 1000$  cm<sup>3</sup> ( $\sim 25$  times larger).



**Fig. 4** Macroscale fabrication of PC-x **(A)** before pyrolysis (PS-PEDOT-2.5) and **(B)** after pyrolysis (PC-2.5) with corresponding density and dimension retention. **(C)** Ashby chart comparing the mechanical performance of PC-x (this work) against other synthetic, natural, and technical materials. Beyond specified references<sup>[19, 63, 89–111, 123]</sup> as seen in the legend, materials property data used to create the Ashby chart were obtained from CES EduPack 2019, ANSYS Granta © 2020 Granta Design. Plots of characteristic dimension retention versus **(D)** specific strength and **(E)** specific modulus as a way to showcase optimized dimensional stability and specific properties as compared to other pyrolytic carbon architectures (unless otherwise labelled)<sup>[19, 20, 27–30, 49, 82, 102, 112–123]</sup>.

### 2.3.3 Mechanical Properties of porous carbons

The compressive strengths of the porous carbon monoliths PC-x were explored by plotting strength as a function of density in the form of an Ashby chart, which captures the density-mechanical property (e.g., strength, modulus, fracture toughness) relationships observed in natural and synthetic materials alike (Fig. S20). Referencing Ashby charts, it can be surmised that high-density materials tend to be stronger and stiffer and low-density materials tend to be weaker and more flexible. Perhaps not surprisingly, among these porous carbons, there is a positive correlation between density, which varies from  $0.07 \text{ g cm}^{-3}$  (PC-2.0) to  $0.41 \text{ g cm}^{-3}$  (PC-6.0), and strength, which varies from 3.2 to 44.1 MPa respectively (Fig. 4C). Compared to materials that fall within a similar range of densities—synthetic foams and a small sector of natural materials—the materials featured in this work are stronger (Fig.S21-S23; Table S2-S3 in SI materials and methods section). To the best of our knowledge, these lightweight porous carbon foams exceed the mechanical strength exhibited by current synthetic carbonaceous foams,<sup>[19, 63, 89–111, 123]</sup> whose mechanical performances are plotted in Fig. 4C for comparison. The presence of hierarchical length scales and structural features with small characteristic dimensions (Fig. S14-S15) supports the hypothesis that size-based strengthening effects could indeed play a role in compressive strength enhancement among the PC-x porous carbon architectures.<sup>[27,42]</sup>

Looking more closely at the density-strength relationship exhibited by PC-x, the strength increases linearly with density up until PC-3.0. At this point, there appears to be a discontinuity in strength. When going from PC-3.0 to 3.5, the density increases from  $0.16$  to  $0.22 \text{ g cm}^{-3}$  while there is only a marginal gain in strength of  $\sim 5$  MPa. This discontinuity coincides with the minor density discontinuity observed in Fig. 3H, which could be attributed to non-quantifiable morphological effects that alter the skeletal density.

To verify that cell wall morphology indeed plays a role in altering strength, PC-x samples with cell wall thicknesses comparable to those seen in PC-5.0 ( $\sim 524 \text{ nm}$ ) and PC-6.0 ( $\sim 550 \text{ nm}$ ) (Fig. 3F,

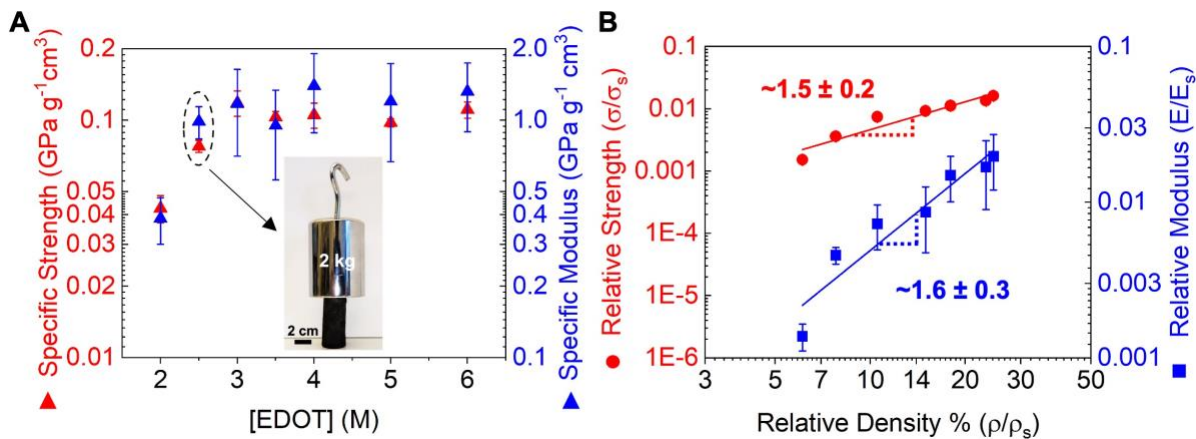
right) but without defects were fabricated via a sequential coating/pyrolysis procedure outlined in Fig. S24. The rationale is that two thinner coatings, as opposed to one thick coating, could result in a similarly thick but defect-free carbon cell wall. In brief, PC-2.5 samples with smooth cell wall cross-sections (Fig. 3B, right; Fig. S24A) were re-coated with a layer of PEDOT ([EDOT]=2.5M) (Fig. S24B) and then re-pyrolyzed with the hopes that the cell wall thickness would increase but remain free of defects, as was the case (Fig. S24C). The same procedure was repeated with PC-3.0 and PC-4.0 (Fig. S24D). The sequential coating/pyrolysis expectedly resulted in increased cell wall thickness (Fig. S24E) and density (Fig. S24F) compared to the PC-x starting materials. The mechanical strength data of the twice coated/pyrolyzed samples (Fig. S24G) revealed that among materials of similar densities, the porous carbon with a smoother cell wall morphology resulting from the sequential coating strategy featured comparable, if not greater, strengths than their once-coated counterparts (Fig. S24G, SEM images).

Towards contextualizing the benefits of dimensional stability towards macroscale fabrication of low-density-high strength PC-x systems, their specific strength (Fig. 4D) and specific modulus (Fig. 4E) are plotted as a function of characteristic dimension retention (%): An indicator of dimensional stability assuming linear isotropic shrinkage of pyrolytic precursors. On the top left of these charts (low retention–high strength region), intricate pyrolytic carbon architectures formed via pyrolysis-induced shrinkage of polymeric precursors are extremely strong but at the cost of low dimensional stability (< 25% dimension retention, <2% volume retention).<sup>[27–30,123]</sup> On the bottom right (high-retention-low-strength region), materials that feature excellent dimensional retention at the cost of low specific mechanical strength can be found.<sup>[19,20,49,52,102,112–122]</sup> Our materials, which appear in the top right region (high retention–high strength), demonstrate optimized performance between dimensional retention and specific strength.

The marginal gain in strength as a function of density is best captured by plotting specific strength ( $\text{GPa g}^{-1}\text{cm}^3$ ) as a function of [EDOT] used in the synthesis of the PS-PEDOT-x precursor (Fig. 5A; Table S3 in SI materials and methods section). From PC-2.0 to PC-3.0 the specific strength increases from 0.04 to 0.13  $\text{GPa g}^{-1}\text{cm}^3$ . The increase in specific strength in going from PC-2.0 to PC-2.5 could be explained by the stark morphological change when comparing the two samples (Fig. 3A-B). The carbon that composes PC-2.0 is particulate in nature compared to PC-2.5 and PC-3.0, which exhibit smooth carbon morphologies. PC-3.0 exhibits the maximum specific strength at 0.13  $\text{GPa g}^{-1}\text{cm}^3$ , after which the specific strength appears to plateau at  $\sim 0.1 \text{ GPa g}^{-1}\text{cm}^3$ . Importantly and in accordance with previous data, the larger scale PC-2.5 sample (Fig. 4A-B; Fig. 5A, inset) featured compressive and specific strengths of  $\sim 7.78 \text{ MPa}$  and  $\sim 68.85 \text{ MPa g}^{-1}\text{cm}^3$  ( $\rho = 0.113 \text{ g cm}^{-3}$ ) respectively (Fig. S25). Any deviations from the expected mechanical properties of PC-2.5 (Fig. 4C) could be explained by the presence of small but visible cracks on the PC-2.5 sample surface (Fig. S25; inset images).

Figure 5B shows the relationship between relative density (6 - 25%) and relative strength (left y-axis)/relative modulus (right y-axis) (Table S3 in SI materials and methods section). The mechanical properties of cellular solids such as foams with stochastic architectures—as exhibited by PC-x—decrease with decreasing relative density (relative to bulk pyrolytic carbon) and the scaling exponents— $m$  for compressive modulus and  $n$  for compressive strength—capture the rate at which said mechanical property reduction occurs. The scaling exponents—extracted from the slope of the linear fit on log-log plots—are indicative of deviation from ideal behavior (unity).<sup>[10,124,125]</sup> For rigid, open-celled, random foams with hollow strut architecture,  $m$  tends to 2 (for compressive modulus  $E$ ), and  $n$  tends to 1.5 (for compressive strength  $\sigma$ ).<sup>[43,44,125,126]</sup> For the materials featured in this work, the scaling exponents were calculated to be  $m = 1.6 \pm 0.3$  and  $n = 1.5 \pm 0.2$ . For materials with  $n=1.5$ , which appears to be the case here, it is hypothesized that fracture-dominated behavior—as opposed

to buckling-dominated behavior seen with elastomeric foams—is the dominant failure mechanism under compressive strain. Post-mortem SEM characterization of crushed samples supports this hypothesis (Fig S26).



**Fig. 5** Specific mechanical properties of PC-x. **(A)** specific strength/modulus ( $\text{GPa g}^{-1}\text{cm}^3$ ) as a function of [EDOT](M) used in the synthesis of pyrolytic carbons PC-x where  $x = [\text{EDOT}] \text{ M}$  and **(B)** Relative strength/modulus (nondim) as a function of relative density (nondim) supplemented with linear fit models and corresponding strength/stiffness scaling exponents.



## **2.4 Conclusion**

There is a need for low-density-high-strength carbon foams that exceed the current mechanical performance of synthetic foams and can also be fabricated on a macroscopic length scale. Previous approaches start with 3D-printed polymeric lattices that are pyrolytically shrunk down by >98% in volume to exploit strengthening effects emergent at the nanoscale. Complementary to previous approaches, this approach starts with a scalable polymer template that features desirable strength-imparting properties—hierarchical pore distribution, small strut diameter, and high node density—to circumvent the need for pyrolytic shrinkage to exploit size-based strengthening effects. This work demonstrates macroscale synthesis of low-density-high-strength porous carbon foams through the pyrolysis of a relatively high carbonization-onset temperature, low char-yielding porous polymer template coated with a relatively low carbonization-onset temperature, high char-yielding polymer coating. By leveraging differences in thermal behavior between the template and coating, it is possible to access low-density-high-strength porous carbons with (1) deterministic control over density (0.04-0.4 g cm<sup>-3</sup>), (2) hierarchical structures, small strut diameter, and high node density, resulting from mismatched carbonization properties, and (3) hollow strut architecture resulting from mismatched decomposition properties. The carbons synthesized through this new framework exhibit remarkably high dimensional stability (~80% dimensional retention; ~50% volume retention) and some of the highest specific strengths (up to ~0.13 GPa g<sup>-1</sup>cm<sup>3</sup>) relative to reported pyrolytic carbon foams derived from stochastic polymer templates.

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## **2.6 References**

- [1] K. Narita, M. A. Citrin, H. Yang, X. Xia, J. R. Greer, *Adv. Energy Mater.* **2021**, *11*, 2002637.
- [2] L. E. Asp, K. Bouton, D. Carlstedt, S. Duan, R. Harnden, W. Johannisson, M. Johansen, M. K. G. Johansson, G. Lindbergh, F. Liu, K. Peuvot, L. M. Schneider, J. Xu, D. Zenkert, *Adv Energy Sustain Res* **2021**, *2*, 2000093.
- [3] P. Fratzl, R. Weinkamer, *Progress in Materials Science* **2007**, *52*, 1263.
- [4] O. A. Tertuliano, J. R. Greer, *Nature Mater* **2016**, *15*, 1195.
- [5] S. Xiao, C. Chen, Q. Xia, Y. Liu, Y. Yao, Q. Chen, M. Hartsfield, A. Brozena, K. Tu, S. J. Eichhorn, Y. Yao, J. Li, W. Gan, S. Q. Shi, V. W. Yang, M. Lo Ricco, J. Y. Zhu, I. Burgert, A. Luo, T. Li, L. Hu, *Science* **2021**, *374*, 465.
- [6] R. Lakes, *Nature* **1993**, *361*, 511.
- [7] H. Gao, B. Ji, I. L. Jager, E. Arzt, P. Fratzl, *Proceedings of the National Academy of Sciences* **2003**, *100*, 5597.
- [8] J. Aizenberg, J. C. Weaver, M. S. Thanawala, V. C. Sundar, D. E. Morse, P. Fratzl, *Science* **2005**, *309*, 275.
- [9] F. P. Beer, *Mechanics of Materials*, McGraw-Hill Education, New York, NY, **2020**.
- [10] N. A. Fleck, V. S. Deshpande, M. F. Ashby, *Proc. R. Soc. A.* **2010**, *466*, 2495.
- [11] M. F. Ashby, *Materials Selection in Mechanical Design*, Butterworth-Heinemann, Amsterdam ; Cambridge, MA, **2017**.
- [12] D. Jang, L. R. Meza, F. Greer, J. R. Greer, *Nature Mater* **2013**, *12*, 893.
- [13] L. R. Meza, S. Das, J. R. Greer, *Science* **2014**, *345*, 1322.
- [14] Z. C. Eckel, C. Zhou, J. H. Martin, A. J. Jacobsen, W. B. Carter, T. A. Schaedler, *Science* **2016**, *351*, 58.

- [15] J. Bauer, C. Crook, A. Guell Izard, Z. C. Eckel, N. Ruvalcaba, T. A. Schaedler, L. Valdevit, *Matter* **2019**, *1*, 1547.
- [16] J. Bauer, S. Hengsbach, I. Tesari, R. Schwaiger, O. Kraft, *Proceedings of the National Academy of Sciences* **2014**, *111*, 2453.
- [17] W. P. Moestopo, A. J. Mateos, R. M. Fuller, J. R. Greer, C. M. Portela, *Adv. Sci.* **2020**, *7*, 2001271.
- [18] C. A. Volkert, E. T. Lilleodden, D. Kramer, J. Weissmüller, *Appl. Phys. Lett.* **2006**, *89*, 061920.
- [19] T. A. Schaedler, A. J. Jacobsen, A. Torrents, A. E. Sorensen, J. Lian, J. R. Greer, L. Valdevit, W. B. Carter, *Science* **2011**, *334*, 962.
- [20] A. Vyatskikh, S. Delalande, A. Kudo, X. Zhang, C. M. Portela, J. R. Greer, *Nat Commun* **2018**, *9*, 593.
- [21] Z. Jiang, J. H. Pikul, *Nat. Mater.* **2021**, *20*, 1512.
- [22] X. Li, H. Gao, *Nature Mater* **2016**, *15*, 373.
- [23] J. Bauer, L. R. Meza, T. A. Schaedler, R. Schwaiger, X. Zheng, L. Valdevit, *Adv. Mater.* **2017**, *29*, 1701850.
- [24] J. R. Greer, J. Park, *Nano Lett.* **2018**, *18*, 2187.
- [25] R. Schwaiger, L. R. Meza, X. Li, *MRS Bull.* **2019**, *44*, 758.
- [26] X. Zhang, Y. Wang, B. Ding, X. Li, *Small* **2020**, *16*, 1902842.
- [27] J. Bauer, A. Schroer, R. Schwaiger, O. Kraft, *Nature Mater* **2016**, *15*, 438.
- [28] X. Zhang, A. Vyatskikh, H. Gao, J. R. Greer, X. Li, *Proc Natl Acad Sci USA* **2019**, *116*, 6665.
- [29] X. Zhang, L. Zhong, A. Mateos, A. Kudo, A. Vyatskikh, H. Gao, J. R. Greer, X. Li, *Nat. Nanotechnol.* **2019**, *14*, 762.
- [30] A. Kudo, F. Bosi, *Commun Mater* **2020**, *1*, 72.

- [31] C. M. Portela, B. W. Edwards, D. Veyssset, Y. Sun, K. A. Nelson, D. M. Kochmann, J. R. Greer, *Nat. Mater.* **2021**, *20*, 1491.
- [32] C. Crook, J. Bauer, A. Guell Izard, C. Santos de Oliveira, J. Martins de Souza e Silva, J. B. Berger, L. Valdevit, *Nat Commun* **2020**, *11*, 1579.
- [33] M. Hegde, V. Meenakshisundaram, N. Chartrain, S. Sekhar, D. Tafti, C. B. Williams, T. E. Long, *Adv. Mater.* **2017**, *29*, 1701240.
- [34] U. G. K. Wegst, H. Bai, E. Saiz, A. P. Tomsia, R. O. Ritchie, *Nature Mater* **2015**, *14*, 23.
- [35] D. W. Yee, M. L. Lifson, B. W. Edwards, J. R. Greer, *Adv. Mater.* **2019**, *31*, 1901345.
- [36] Q. Geng, D. Wang, P. Chen, S.-C. Chen, *Nat Commun* **2019**, *10*, 2179.
- [37] K. Nakanishi, S. Hofmann, *APL Materials* **2020**, *8*, 021106.
- [38] Q. Li, J. Kulikowski, D. Doan, O. A. Tertuliano, C. J. Zeman, M. M. Wang, G. C. Schatz, X. W. Gu, *Science* **2022**, *378*, 768.
- [39] J. R. Greer, W. C. Oliver, W. D. Nix, *Acta Materialia* **2005**, *53*, 1821.
- [40] J.-Y. Kim, J. R. Greer, *Acta Materialia* **2009**, *57*, 5245.
- [41] Z. W. Shan, R. K. Mishra, S. A. Syed Asif, O. L. Warren, A. M. Minor, *Nature Mater* **2008**, *7*, 115.
- [42] J. R. Greer, W. D. Nix, *Appl. Phys. A* **2005**, *80*, 1625.
- [43] L. J. Gibson, M. F. Ashby, *Proc. R. Soc. Lond. A.* **1982**, *382*, 20.
- [44] M. F. Ashby, *Phil. Trans. R. Soc. A.* **2006**, *364*, 15.
- [45] D. Rayneau-Kirkhope, Y. Mao, R. Farr, *Phys. Rev. Lett.* **2012**, *109*, 204301.
- [46] T. Woignier, J. Reynes, A. Hafidi Alaoui, I. Beurroies, J. Phalippou, *Journal of Non-Crystalline Solids* **1998**, *241*, 45.

- [47] B. Cardenas-Benitez, C. Eschenbaum, D. Mager, J. G. Korvink, M. J. Madou, U. Lemmer, I. D. Leon, S. O. Martinez-Chapa, *Microsyst Nanoeng* **2019**, *5*, 38.
- [48] R. W. Pekala, R. W. Hopper, *J Mater Sci* **1987**, *22*, 1840.
- [49] J. Ye, L. Liu, J. Oakdale, J. Lefebvre, S. Bhowmick, T. Voisin, J. D. Roehling, W. L. Smith, M. R. Cerón, J. van Ham, L. B. Bayu Aji, M. M. Biener, Y. M. Wang, P. R. Onck, J. Biener, *Nat. Mater.* **2021**, *20*, 1498.
- [50] S. Park, B. Shi, Y. Shang, K. Deng, K. Fu, *Nano Lett.* **2022**, *22*, 9462.
- [51] X. Zheng, W. Smith, J. Jackson, B. Moran, H. Cui, D. Chen, J. Ye, N. Fang, N. Rodriguez, T. Weisgraber, C. M. Spadaccini, *Nature Mater* **2016**, *15*, 1100.
- [52] C. B. Arrington, D. A. Rau, J. A. Vandenbrande, M. Hegde, C. B. Williams, T. E. Long, *ACS Macro Lett.* **2021**, *10*, 412.
- [53] N. R. Cameron, *Polymer* **2005**, *46*, 1439.
- [54] M. S. Silverstein, H. Tai, A. Sergienko, Y. Lumelsky, S. Pavlovsky, *Polymer* **2005**, *46*, 6682.
- [55] L. Bourdon, J.-C. Maurin, K. Gritsch, A. Brioude, V. Salles, *ACS Biomater. Sci. Eng.* **2018**, *4*, 3927.
- [56] J. H. Aubert, A. P. Sylwester, *J Mater Sci* **1991**, *26*, 5741.
- [57] M. S. Silverstein, *Progress in Polymer Science* **2014**, *39*, 199.
- [58] T. Zhang, R. A. Sanguramath, S. Israel, M. S. Silverstein, *Macromolecules* **2019**, *52*, 5445.
- [59] M. S. Silverstein, *Polymer* **2017**, *126*, 261.
- [60] A. Horowitz, G. Shaul, M. S. Silverstein, *Polym Int* **2021**, *70*, 1404.
- [61] R. T. Woodward, F. Markoulidis, F. De Luca, D. B. Anthony, D. Malko, T. O. McDonald, M. S. P. Shaffer, A. Bismarck, *J. Mater. Chem. A* **2018**, *6*, 1840.
- [62] W. Hu, F. Xie, Y. Li, Z. Wu, K. Tian, M. Wang, L. Pan, L. Li, *Langmuir* **2017**, *33*, 13364.

- [63] S. Kovačič, B. Schafzahl, N. B. Matsko, K. Gruber, M. Schmuck, S. Koller, S. A. Freunberger, C. Slugovc, *ACS Appl. Energy Mater.* **2022**, acsaem.2c02787.
- [64] Y. Zhao, A. Wang, L. Shen, Z. Zhao, L. Xiao, L. Hou, *J of Applied Polymer Sci* **2022**, 139, DOI 10.1002/app.52417.
- [65] K. Kapilov-Buchman, L. Portal, Y. Zhang, N. Fechler, M. Antonietti, M. S. Silverstein, *J. Mater. Chem. A* **2017**, 5, 16376.
- [66] N. Cohen, M. S. Silverstein, *Polymer* **2011**, 52, 282.
- [67] S. Israel, I. Gurevitch, M. S. Silverstein, *Polymer* **2015**, 72, 453.
- [68] R. T. Woodward, A. Jobbe-Duval, S. Marchesini, D. B. Anthony, C. Petit, A. Bismarck, *Polymer* **2017**, 115, 146.
- [69] U. M. Patil, R. V. Ghorpade, M. S. Nam, A. C. Nalawade, S. Lee, H. Han, S. C. Jun, *Sci Rep* **2016**, 6, 35490.
- [70] R. T. Woodward, D. W. H. Fam, D. B. Anthony, J. Hong, T. O. McDonald, C. Petit, M. S. P. Shaffer, A. Bismarck, *Carbon* **2016**, 101, 253.
- [71] R. Woodward, F. De Luca, A. Roberts, A. Bismarck, *Materials* **2016**, 9, 776.
- [72] S. Israel, M. Levin, S. Oriel, D. Mayer, I. Lerner, M. S. Silverstein, *Macromolecules* **2022**, 55, 1992.
- [73] F. Xu, D. Wu, R. Fu, B. Wei, *Materials Today* **2017**, 20, 629.
- [74] G. M. Jenkins, K. Kawamura, *Polymeric Carbons: Carbon Fibre, Glass and Char*, Cambridge University Press, Cambridge, **2011**.
- [75] G. E. Zaikov, R. M. Aseeva, *Makromolekulare Chemie. Macromolecular Symposia* **1993**, 74, 21.
- [76] X. Yang, L. Tan, L. Xia, C. D. Wood, B. Tan, *Macromol. Rapid Commun.* **2015**, 6.
- [77] W. Shi, Q. Yao, S. Qu, H. Chen, T. Zhang, L. Chen, *NPG Asia Mater* **2017**, 9, e405.
- [78] Z. A. King, C. M. Shaw, S. A. Spanninga, D. C. Martin, *Polymer* **2011**, 52, 1302.

- [79] J. Hodkiewicz, T. F. Scientific, *Thermo Scientific Application Note 51946* **2010**, 5.
- [80] G. M. Jenkins, K. Kawamura, *Nature* **1971**, 231, 175.
- [81] L. Qiu, J. Z. Liu, S. L. Y. Chang, Y. Wu, D. Li, *Nat Commun* **2012**, 3, 1241.
- [82] J. U. Surjadi, Y. Zhou, S. Huang, L. Wang, M. Li, S. Fan, X. Li, J. Zhou, R. H. W. Lam, Z. Wang, Y. Lu, *Matter* **2022**, S2590238522004672.
- [83] S. Yang, L. Zhi, K. Tang, X. Feng, J. Maier, K. Müllen, *Adv. Funct. Mater.* **2012**, 22, 3634.
- [84] T. Noda, M. Inagaki, *BCSJ* **1964**, 37, 1534.
- [85] Z. Q. Li, C. J. Lu, Z. P. Xia, Y. Zhou, Z. Luo, *Carbon* **2007**, 45, 1686.
- [86] M. Koyama, Z. Zhang, M. Wang, D. Ponge, D. Raabe, K. Tsuzaki, H. Noguchi, C. C. Tasan, *Science* **2017**, 355, 1055.
- [87] M. A. T. Jaya, W. M. H. F. W. Harun, M. A. Ahmad, *J. of Applied Sciences* **2014**, 14, 1359.
- [88] R. Natu, M. Islam, J. Gilmore, R. Martinez-Duarte, *Journal of Analytical and Applied Pyrolysis* **2018**, 131, 17.
- [89] D. Liu, C. Chen, Y. Zhou, Y. Bao, R. Wang, Y. Liu, S. He, H. Huang, C. Zhang, B. Foster, T. Li, L. Hu, *Small Methods* **2021**, 5, 2001188.
- [90] S. M. Manocha, K. Patel, L. M. Manocha, *INDIAN J. ENG. MATER. SCI.* **2010**, 5.
- [91] Q. Yan, R. Arango, J. Li, Z. Cai, *Materials & Design* **2021**, 201, 109460.
- [92] S. Li, Y. Song, Y. Song, J. Shi, L. Liu, X. Wei, Q. Guo, *Carbon* **2007**, 45, 2092.
- [93] S. Zhang, M. Liu, L. Gan, F. Wu, Z. Xu, Z. Hao, L. Chen, **n.d.**, 1.
- [94] R. Fu, B. Zheng, J. Liu, S. Weiss, J. Y. Ying, M. S. Dresselhaus, G. Dresselhaus, J. H. Satcher, T. F. Baumann, *J. Mater. Res.* **2003**, 18, 2765.
- [95] K. Jurkiewicz, M. Pawlyta, D. Zygadlo, D. Chrobak, S. Duber, R. Wrzalik, A. Ratuszna, A. Burian, *J Mater Sci* **2018**, 53, 3509.



- [96] B. Tsyntsarski, B. Petrova, T. Budinova, N. Petrov, M. Krzesinska, S. Pusz, J. Majewska, P. Tzvetkov, *Carbon* **2010**, *48*, 3523.
- [97] C. Chen, E. B. Kennel, A. H. Stiller, P. G. Stansberry, J. W. Zondlo, *Carbon* **2006**, *44*, 1535.
- [98] M. Karthik, A. Faik, S. Doppiu, V. Roddatis, B. D'Aguanno, *Carbon* **2015**, *87*, 434.
- [99] N. Amini, K.-F. Aguey-Zinsou, Z.-X. Guo, *Carbon* **2011**, *49*, 3857.
- [100] P. Jana, V. Fierro, A. Celzard, *Industrial Crops and Products* **2016**, *89*, 498.
- [101] H. Liu, T. Li, X. Wang, W. Zhang, T. Zhao, *Journal of Analytical and Applied Pyrolysis* **2014**, *110*, 442.
- [102] L. Zhang, M. Liu, S. Roy, E. K. Chu, K. Y. See, X. Hu, *ACS Appl. Mater. Interfaces* **2016**, *8*, 7422.
- [103] R. Kumar, S. R. Dhakate, T. Gupta, P. Saini, B. P. Singh, R. B. Mathur, *J. Mater. Chem. A* **2013**, *1*, 5727.
- [104] S. Lei, Q. Guo, J. Shi, L. Liu, *Carbon* **2010**, *48*, 2644.
- [105] C. R. Thomas, *Materials Science and Engineering* **1973**, *12*, 219.
- [106] A. Banerjee, D. Bernoulli, H. Zhang, M.-F. Yuen, J. Liu, J. Dong, F. Ding, J. Lu, M. Dao, W. Zhang, Y. Lu, S. Suresh, *Science* **2018**, *360*, 300.
- [107] R. E. Bullock, J. L. Kaae, *J Mater Sci* **1979**, *14*, 920.
- [108] Y. Yuan, Y. Ding, C. Wang, F. Xu, Z. Lin, Y. Qin, Y. Li, M. Yang, X. He, Q. Peng, Y. Li, *ACS Appl. Mater. Interfaces* **2016**, *8*, 16852.
- [109] M. Hu, J. He, Z. Zhao, T. A. Strobel, W. Hu, D. Yu, H. Sun, L. Liu, Z. Li, M. Ma, Y. Kono, J. Shu, H. Mao, Y. Fei, G. Shen, Y. Wang, S. J. Juhl, J. Y. Huang, Z. Liu, B. Xu, Y. Tian, *Sci. Adv.* **2017**, *3*, e1603213.
- [110] J. Wang, *Electrochimica Acta* **1981**, *26*, 1721.
- [111] A. Szczurek, V. Fierro, A. Pizzi, A. Celzard, *Carbon* **2014**, *74*, 352.

- [112] X. Zheng, H. Lee, T. H. Weisgraber, M. Shusteff, J. DeOtte, E. B. Duoss, J. D. Kuntz, M. M. Biener, Q. Ge, J. A. Jackson, S. O. Kucheyev, N. X. Fang, C. M. Spadaccini, *Science* **2014**, *344*, 1373.
- [113] H. Steldinger, A. Esposito, K. Brunnengräber, J. Gläsel, B. J. M. Etzold, *Adv. Sci.* **2019**, *6*, 1901340.
- [114] X. Chen, G. Zhao, Y. Wu, Y. Huang, Y. Liu, J. He, L. Wang, Q. Lian, D. Li, *Carbon* **2017**, *123*, 34.
- [115] J. Du, W.-C. Li, Z.-X. Ren, L.-P. Guo, A.-H. Lu, *Journal of Energy Chemistry* **2020**, *42*, 56.
- [116] X. Jia, B. Dai, Z. Zhu, J. Wang, W. Qiao, D. Long, L. Ling, *Carbon* **2016**, *108*, 551.
- [117] X. Ye, Z. Chen, S. Ai, B. Hou, J. Zhang, Q. Zhou, H. Liu, S. Cui, *Journal of Analytical and Applied Pyrolysis* **2019**, *142*, 104619.
- [118] X. Zhang, J. Zhao, X. He, Q. Li, C. Ao, T. Xia, W. Zhang, C. Lu, Y. Deng, *Carbon* **2018**, *127*, 236.
- [119] Q. Lin, S. Dong, L. Qu, C. Fang, K. Luo, *Journal of Analytical and Applied Pyrolysis* **2014**, *106*, 164.
- [120] J. Li, Y. Ding, N. Yu, Q. Gao, X. Fan, X. Wei, G. Zhang, Z. Ma, X. He, *Carbon* **2020**, *158*, 45.
- [121] X. Ye, Z. Chen, S. Ai, B. Hou, J. Zhang, Q. Zhou, H. Liu, S. Cui, *Mater. Res. Express* **2019**, *6*, 075601.
- [122] M. Letellier, C. Delgado-Sanchez, M. Khelifa, V. Fierro, A. Celzard, *Carbon* **2017**, *116*, 562.
- [123] J. Bauer, M. Sala-Casanovas, M. Amiri, L. Valdevit, *Sci. Adv.* **2022**, *8*, eabo3080.
- [124] M. Ashby, *Materials Selection In Mechanical Design*, Butterworth-Heinemann, Oxford, UK, **2016**.
- [125] R. J. Mora, A. M. Waas, *Proc. R. Soc. Lond. A* **2002**, *458*, 1695.
- [126] R. Brezny, D. J. Green, *J American Ceramic Society* **1993**, *76*, 2185.
- [127] T. C. Triantafillou, L. J. Gibson, *International Journal of Mechanical Sciences* **1990**, *32*, 479.

## **CHAPTER 2 – SUPPORTING INFORMATION**

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## Experimental Materials and Methods Section

Materials

Instrumentation

Methods

Synthesis of PS-Poly(HIPE)s

Figure S27 – Reaction Scheme for PS-poly(HIPE) synthesis

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Synthesis of PEDOT-coated poly(HIPE)s (PS-PEDOT-x)

Figure S28– PS-PEDOT-x reaction scheme

Synthesis of porous carbons (PC-x)

Measurement of density and dimensional stability/volume retention

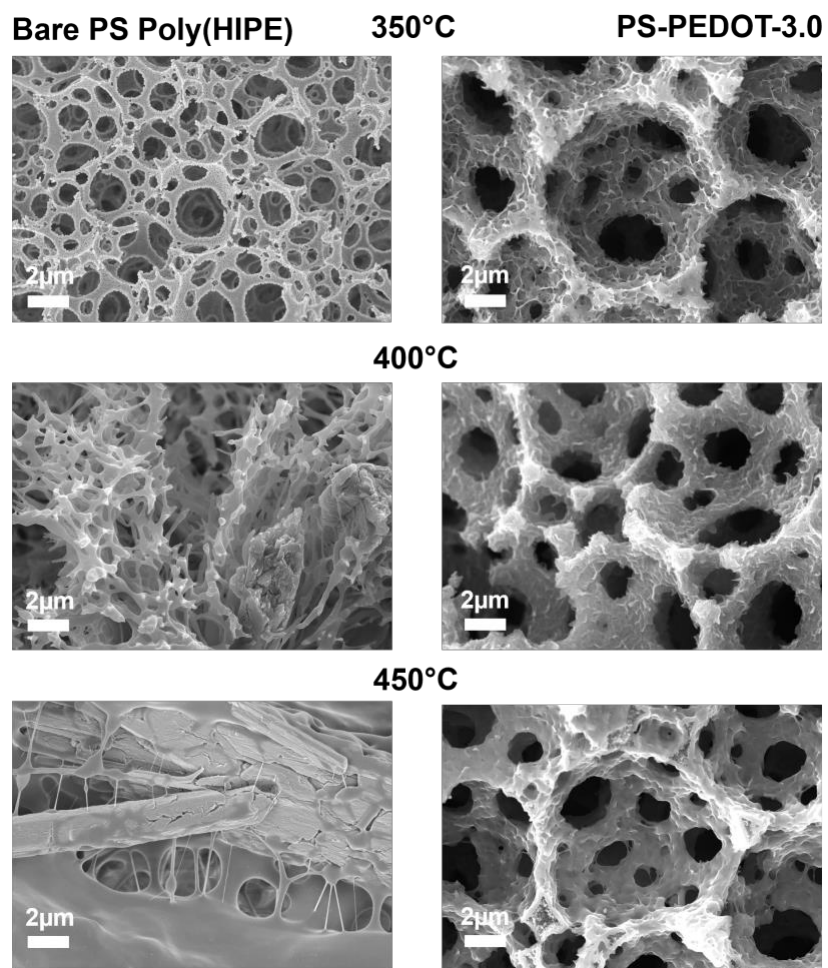
Measurement of mechanical properties

Table S2 – Mechanical property data tables

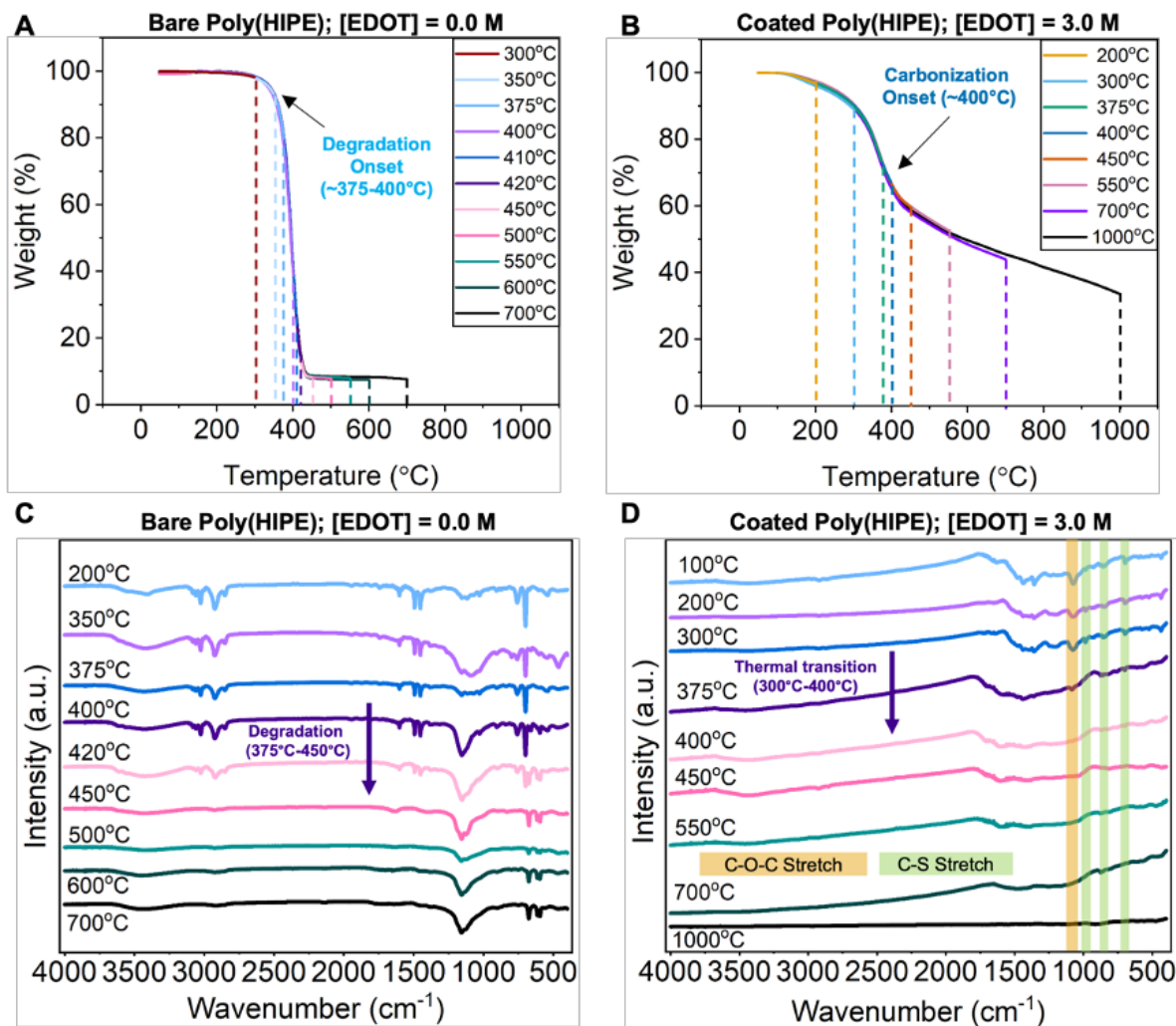
Table S3 – Specific/Relative mechanical properties

Predicted residual mass and char yield calculations

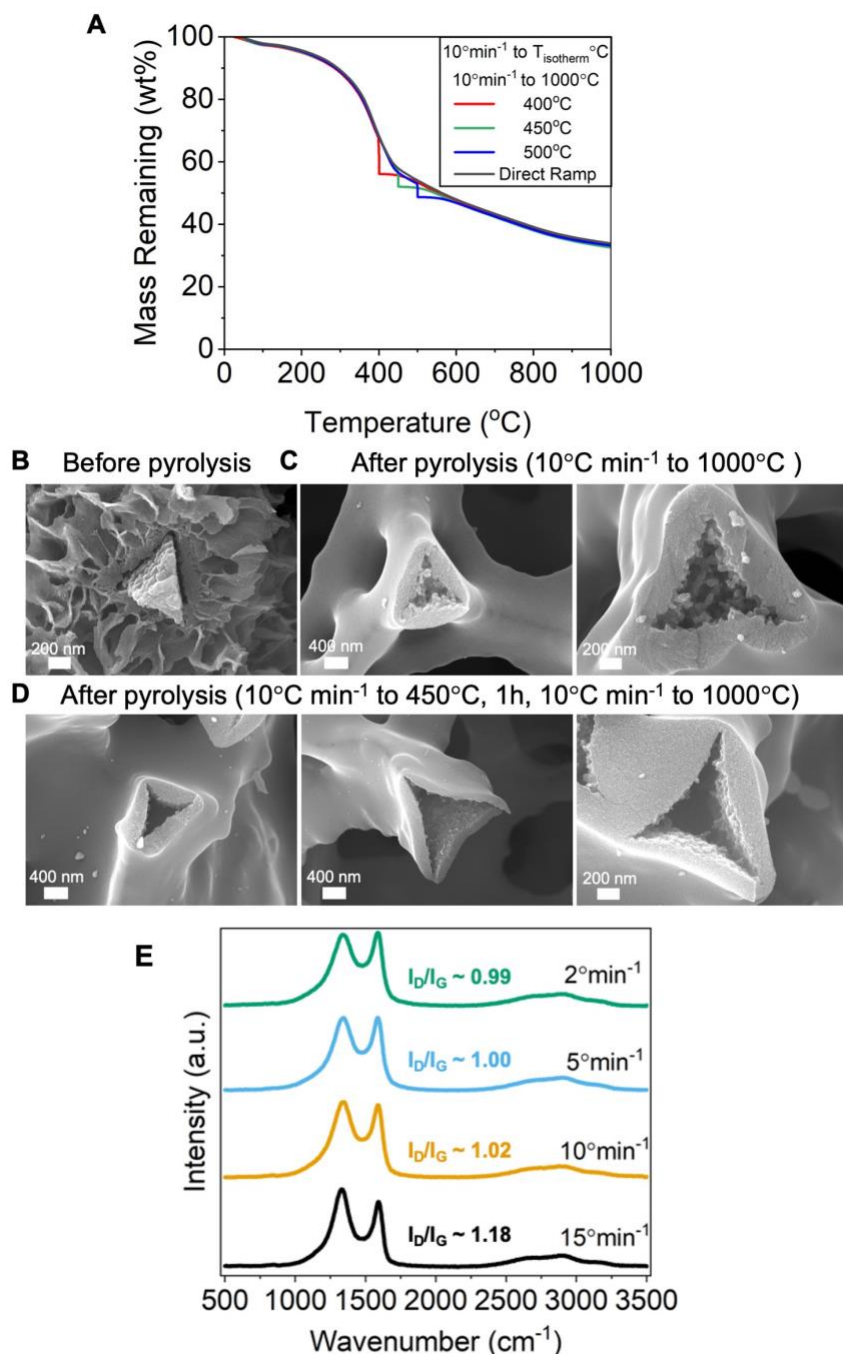
References (SI)



**Fig. S1** SEM images of bare poly(HIPE) (no coating; [EDOT]=0.0M) (left) and PEDOT coated PS-poly(HIPE) ([EDOT]=3.0M) (right) pyrolyzed at 350°C, 400°C and 450°C.

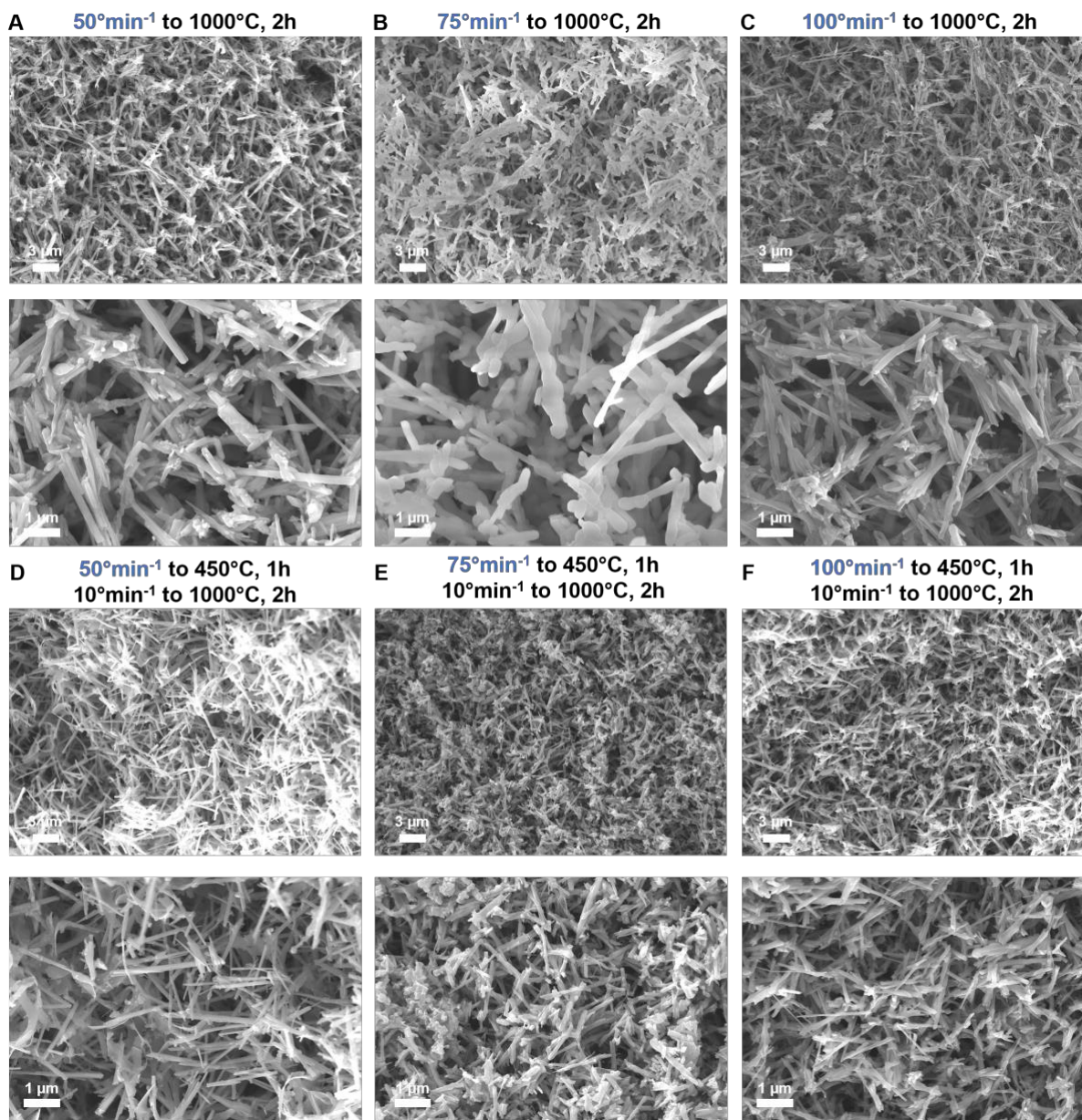


**Fig. S2** *Ex-situ* variable-temperature TGA of **(A)** bare poly(HIPE) (no coating; [EDOT]=0.0M) and **(B)** PEDOT coated poly(HIPE) ([EDOT]=3.0M) indicating decomposition onset and char-yield. Variable-temperature FTIR of **(C)** bare poly(HIPE) (no coating; [EDOT]=0.0M) and **(D)** PEDOT coated poly(HIPE) ([EDOT]=3.0M). Panel **(D)** shows the disappearance of C-O-C (~1075 cm<sup>-1</sup>) and C-S (~985, ~850 and ~698 cm<sup>-1</sup>) stretching peaks. This is in accordance with prior variable-temperature SEM data (Fig. S1) showing a morphological transition in the 300-400°C range. A ramp rate of 2°min<sup>-1</sup> was used for the above variable-temperature experiments.



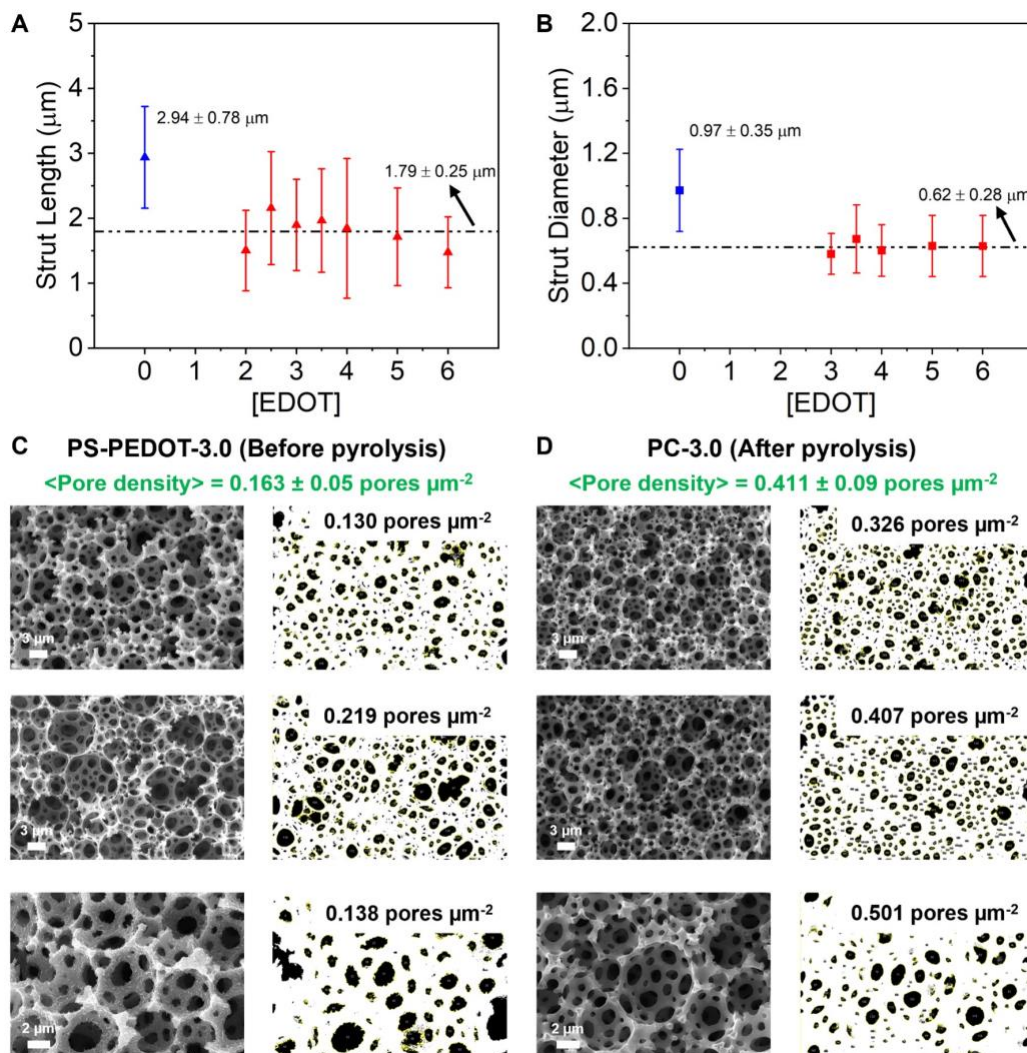
**Fig. S3** (A) TGA of PS-PEDOT ([EDOT]=3.0M; 10°C min<sup>-1</sup> to T<sub>isotherm</sub> °C, 1h hold, 10°C min<sup>-1</sup> to 1000°C) with an hour-long isothermal stage at implemented at three trial temperatures (T<sub>isotherm</sub> = 400°C, 450°C, 500°C). Control thermogram without the isothermal stage shown alongside for comparison. SEM images of (B) PS-PEDOT-3.0 before pyrolysis, (C) PC-3.0 resulting from direct ramp pyrolysis at 10°C min<sup>-1</sup> to 1000°C showing entrapped particulate carbon within struts and (D) PC-x resulting from intermediate hold pyrolysis at 10°C min<sup>-1</sup> to 450°C, 1h hold, 10°C min<sup>-1</sup> to 1000°C showing hollow struts. (E) Raman spectra of PC-3.0 pyrolyzed at different ramp rates (2-15°C min<sup>-1</sup> to 1000°C) suggesting that carbon quality appears independent of ramp rates below 10°C min<sup>-1</sup>.





**Fig. S4** SEM images of bare PS poly(HIPE) derived carbon pyrolyzed under the following conditions: “Direct Ramp” – **(A)**  $50^{\circ}\text{min}^{-1}$  to  $1000^{\circ}\text{C}$ , 2h hold and **(B)**  $75^{\circ}\text{min}^{-1}$  to  $1000^{\circ}\text{C}$ , 2h hold and **(C)**  $100^{\circ}\text{min}^{-1}$  to  $1000^{\circ}\text{C}$ , 2h hold and “Intermediate Hold” – **(D)**  $50^{\circ}\text{min}^{-1}$  to  $450^{\circ}\text{C}$ , 1h hold,  $10^{\circ}\text{min}^{-1}$  to  $1000^{\circ}\text{C}$ , 2h hold, **(E)**  $75^{\circ}\text{min}^{-1}$  to  $450^{\circ}\text{C}$ , 1h hold,  $10^{\circ}\text{min}^{-1}$  to  $1000^{\circ}\text{C}$ , 2h hold and **(F)**  $100^{\circ}\text{min}^{-1}$  to  $450^{\circ}\text{C}$ , 1h hold,  $10^{\circ}\text{min}^{-1}$  to  $1000^{\circ}\text{C}$ , 2h hold.



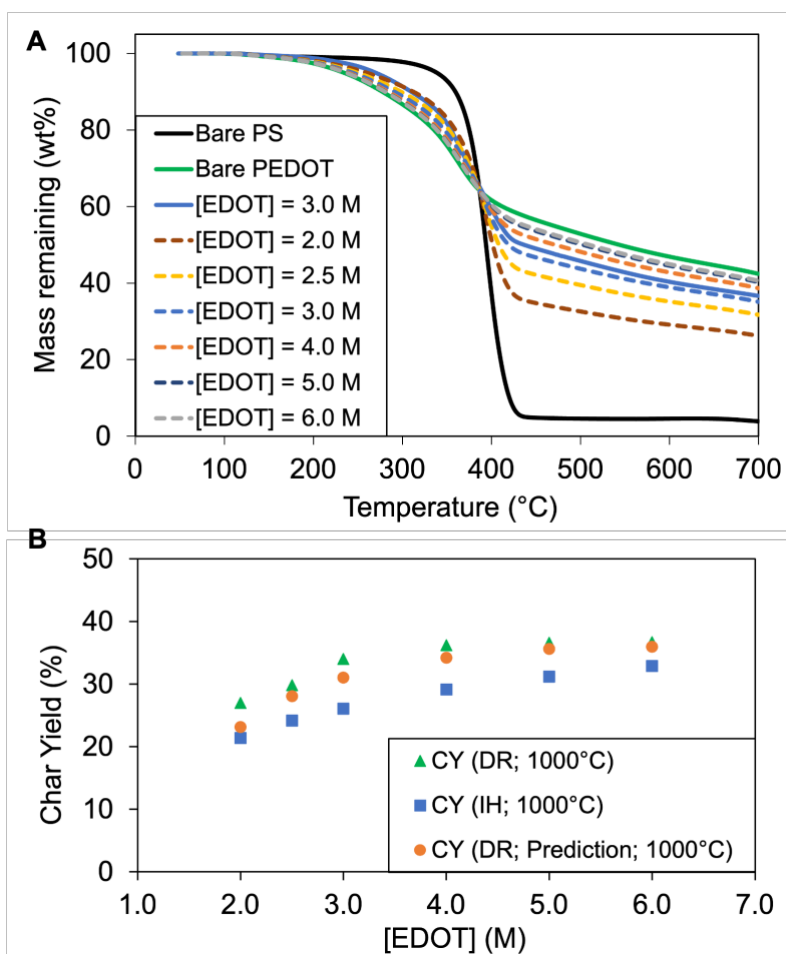


**Fig. S5** (A) Average strut length and (B) average strut diameter of PS-PEDOT- $x$ . Note that strut dimensions decrease upon pyrolysis which is expected due to shrinkage. (C) SEM images of PS-PEDOT-3.0 ([EDOT]=3.0M) (left) and corresponding ImageJ processed images (right). (D) SEM images of PC-3.0 after pyrolysis under intermediate hold conditions (left) and corresponding ImageJ processed images (right).

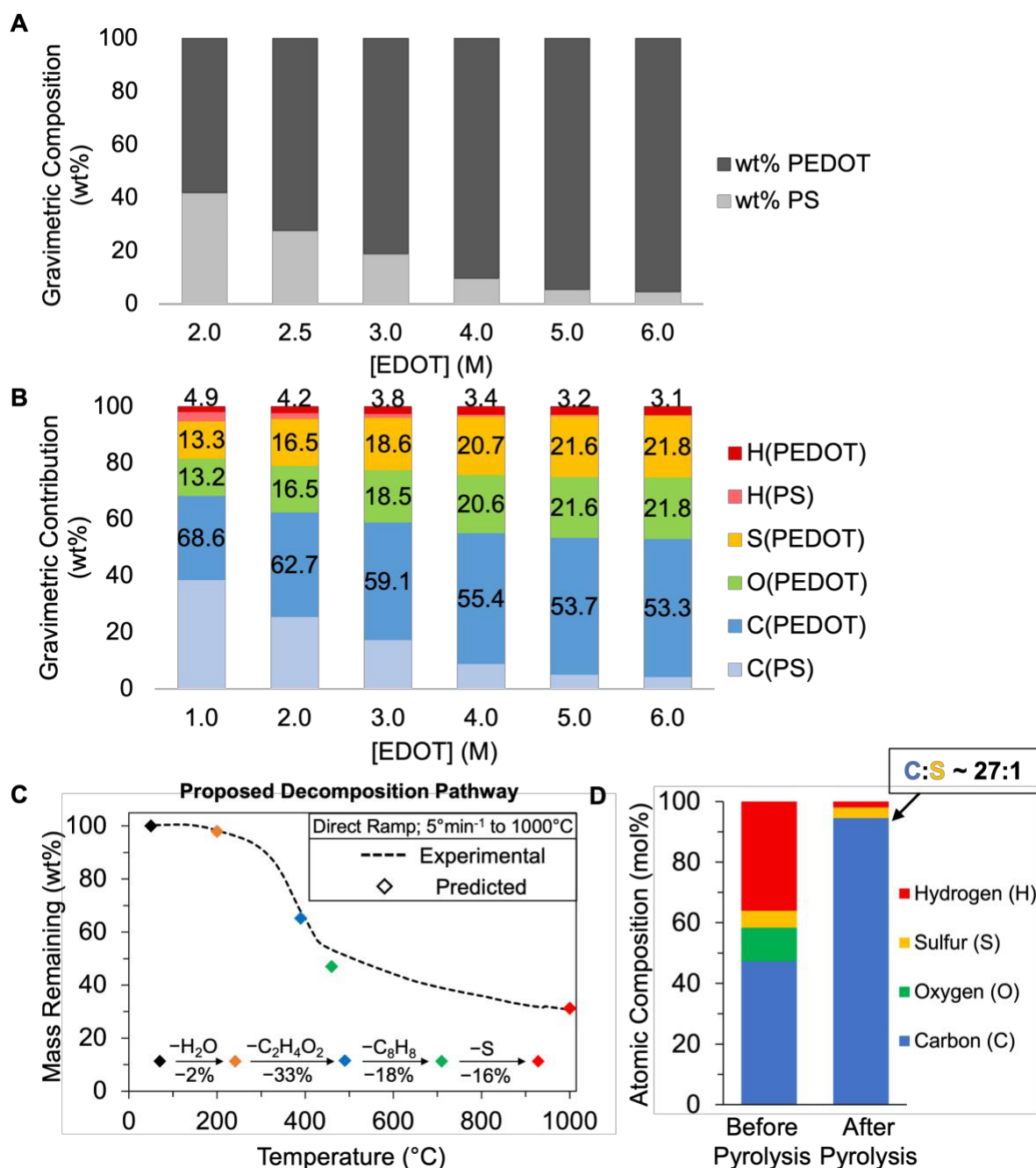
The mechanical properties of cellular solids, such as the porous carbon foams under investigation, are strongly dependent on (1) the number of struts that meet at a node (nodal connectivity) as well as (2) the number of nodes per unit volume (node density).<sup>[1–3]</sup> In the case of poly(HIPE)s, the void dimensions dictate the node density. Smaller droplets in the HIPE—controlled by surfactant type and weight fraction<sup>[4]</sup>—lead to more voids per unit volume in the poly(HIPE), which also means more nodes per unit volume.<sup>[5]</sup> The nodal connectivity is determined by the degree of interconnectedness

related to pore formation (within voids) during the drying stage. The PS poly(HIPE)s used in this work have small void/pore dimensions and high pore density, leading to high nodal connectivity and node density. We provide the values of strut length, strut diameter, and pore density (calculated through image analysis) to quantify node density as these are proportional (Fig. S5).

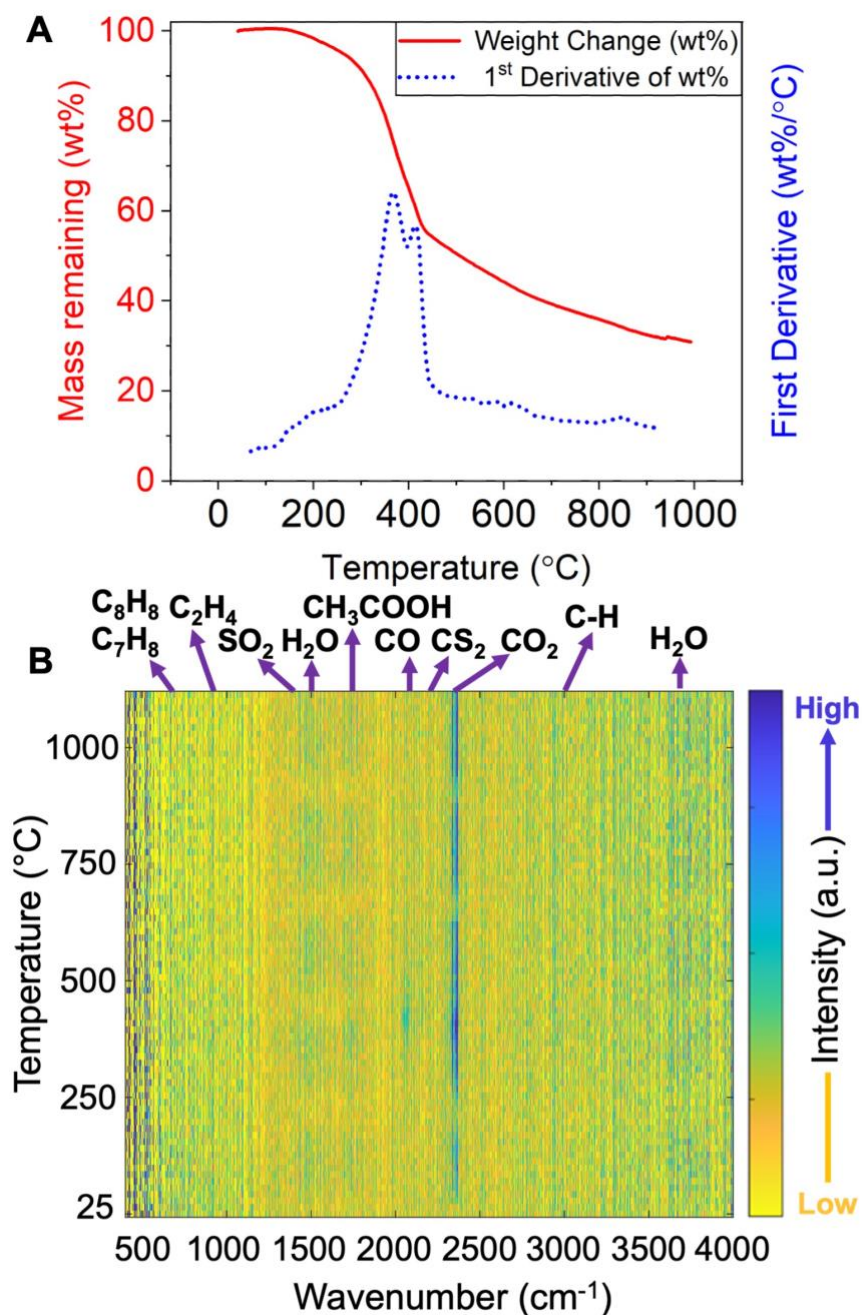
The pore density of the PS-PEDOT-3.0 is  $\sim 0.16 \pm 0.05$  pores per  $\mu\text{m}^2$  (Fig. S5C). Upon pyrolysis, there is an expected increase in pore density owing to shrinkage. The pore density of PC-3.0 is  $\sim 0.41 \pm 0.09$  pores per  $\mu\text{m}^2$  representing a 2.5-fold increase in pore density compared to the pyrolytic precursor (Fig. S5D). The pyrolysis stage not only prompts the conversion of soft polymeric struts to hard pyrolytic carbon but also increases pore density through shrinkage, enabling high compressive strength demonstrated by PC-x.



**Fig. S6 (A)** Comparison of experimental and predicted thermograms of PS-PEDOT-x samples. Predicted thermograms are derived by taking averages of the bare template and bare coating thermograms (black and green solid lines respectively) weighted by the gravimetric composition of PS and PEDOT in PS-PEDOT-x where  $x = [\text{EDOT}] \text{ M}$ . **(B)** Comparison of experimental (direct ramp/intermediate hold) and predicted char yields of PS-PEDOT-x.



**Fig. S7 (A)** Gravimetric composition of PS-PEDOT as a function of [EDOT] (M). **(B)** Elemental contribution (C, O, S, H) from PS and PEDOT. Numbers in the bars represent total elemental composition. **(C)** Experimental thermogram (dotted line) and predicted residual mass values (data points). Labeled arrows represent the abstracted moiety and the resulting mass loss (wt%). See SI methods section titled “Predicted residual mass and char yield calculations” for calculation details and data tables. **(D)** Atomic composition of PS-PEDOT ([EDOT]=3.0M; before pyrolysis) and PC-3.0 (after pyrolysis; 5°min<sup>-1</sup> to 1000°C) based on chemical abstraction calculation method.



**Fig. S8** In-Situ TGA-FTIR experiment. **(A)** The Thermogram of PS-PEDOT-3.0 ([EDOT] = 3.0M; 5°min<sup>-1</sup> to 1000°C) with first-order derivative indicates decomposition rates. **(B)** Waterfall plot of *in-situ* FTIR spectra collected from 25°C to T<sub>f</sub> = 1000°C. The color bar indicates peak intensity, and the peak position indicates the gaseous species detected and the corresponding evolution temperature. The color change (yellow to blue) along the intensity axis indicates the amount of gas detected.

## Decomposition mechanisms underlying pyrolysis of PS-PEDOT

The conversion of polymeric materials into pyrolytic carbon is mediated by the expulsion of decomposition products and simultaneous atomic rearrangement of carbon. To unravel the decomposition pathway, we combine insights from *ex-situ* variable-temperature TGA/FTIR (Fig. S2), predictive char yield/residual mass calculations (Fig. S6-S7), and *in-situ* TGA-FTIR (Fig. R8). Each technique and related findings are discussed below:

- ***Ex-situ* variable-temperature TGA/FTIR (Fig. S2):**

*Ex-situ* techniques such as variable-temperature TGA and subsequent FTIR analysis of the char are leveraged to understand the chemical transformations undergoing during pyrolysis (Fig. S2). TGA provides critical information about decomposition-onset temperatures and rates of mass loss, and FTIR provides valuable spectral information regarding chemical transformations undergoing in the char.

The variable-temperature TGA data of bare PS features a single decomposition event in the range of 375-450°C and a final char yield of ~3.27 wt% (Fig. S2A). The *ex-situ* FTIR analysis of bare PS-derived char suggests that PS decomposition occurs in the ~375-450°C range, evidenced by the disappearance of several—aromatic C-H stretching (~3000-3100 cm<sup>-1</sup>), CH<sub>2</sub> symmetric and symmetric stretching (2800-3000 cm<sup>-1</sup>), C=C bending (~1650-2000 cm<sup>-1</sup>), aromatic C=C ring modes (~1400-1650 cm<sup>-1</sup>) and aromatic C-H bending (~750 cm<sup>-1</sup>)—peaks in the 350-450°C range (Fig. S2C). The TGA data of PS-PEDOT ([EDOT]=3.0 M; ~31.1 wt% char yield at 1000°C) features three apparent mass loss events in the ~200-350°C, ~350-450°C and ~450-1000°C ranges (Fig. S2B). The *ex-situ* FTIR analysis of PS-PEDOT derived char suggests that the first mass loss event is at least partially due to the loss of the ethylenedioxy moiety (C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>) from the PEDOT coating, evidenced by the disappearance of the C-O-C stretching peak (~1075 cm<sup>-1</sup>) in the 300-400°C range (Fig. S2D). The second mass loss event is partially attributed to the decomposition of the PS (C<sub>8</sub>H<sub>8</sub>) fraction,

evidenced by the  $\sim 400^\circ\text{C}$  decomposition onset temperature. It appears that ethylenedioxy abstraction ( $300\text{--}400^\circ\text{C}$ ) and PS decomposition ( $375\text{--}450^\circ\text{C}$ ) events overlap, evidenced by first-derivative peak-overlap in the  $\sim 375\text{--}425^\circ\text{C}$  range (Fig. S8A). The third mass loss event is assigned to Sulfur abstraction from the thiophene ring of PEDOT, evidenced by the disappearance of C-S stretching peaks ( $\sim 985$ ,  $\sim 850$ , and  $\sim 698\text{ cm}^{-1}$ ) in the  $375\text{--}450^\circ\text{C}$  range (Fig. S2D). Variable-temperature TGA suggests that Sulfur abstraction (desulfonation) occurs throughout the pyrolytic process, evidenced by continual mass loss (negative slope) in the  $450\text{--}1000^\circ\text{C}$  range (Fig. S2B).

Bond energy data support the proposed decomposition sequence ( $\text{C}_2\text{H}_4\text{O}_2$ ,  $\text{C}_8\text{H}_8$ , S). The C-O bond ( $\sim 358\text{ kJ mol}^{-1}$ ) is the weakest bond, which explains the abstraction of the ethylenedioxy ( $\text{C}_2\text{H}_4\text{O}_2$ ) moiety starting at  $\sim 300^\circ\text{C}$ . The bond strength of HC- $\text{C}_6\text{H}_5$  ( $\sim 389\text{ kJ mol}^{-1}$ ) in PS, which is rather similar to that of the C-O bond ( $\sim 358\text{ kJ mol}^{-1}$ ) in the  $\text{C}_2\text{H}_4\text{O}_2$ , explains why the decomposition-onset of PS at  $\sim 400^\circ\text{C}$  overlaps with the removal of the  $\text{C}_2\text{H}_4\text{O}_2$ . The aromatic C=S bond ( $\sim 420\text{ kJ mol}^{-1}$ ;  $>$  C-S single bond  $\sim 272\text{ kJ mol}^{-1}$  and  $<$  C=S double bond  $\sim 573\text{ kJ mol}^{-1}$ ) is the strongest bond, which explains the abstraction of S atoms at higher temperatures. Overall, the *ex-situ* TGA/FTIR data suggest that the overall mass loss—and resulting char yield—could be attributed to three primary chemical decomposition events, namely (1) ethylenedioxy abstraction from PEDOT, (2) PS template degradation, and (3) S abstraction from PEDOT.

- **Proposed decomposition pathway (Fig. S6 and Fig. S7):**

Theoretical calculations informed by the above experimental findings can be used to verify the hypothesized decomposition mechanism. Combining insight gained from *ex-situ* data (TGA/FTIR) above and gravimetric composition (wt%)/atomic composition (mol%) of PS-PEDOT, it is possible to predict the expected (1) decomposition profile (thermogram) and (2) residual mass at different stages of pyrolysis, and (3) theoretical char yield of PS-PEDOT. Predicted thermograms are derived by taking averages of the bare template and bare coating thermograms weighted by the gravimetric

composition of PS and PEDOT in PS-PEDOT pairs (Fig. S6; see SI materials and methods section for detailed calculation). The predicted thermograms (Fig. S6A) and theoretical char yields (Fig. S6B) are consistent with experimental observations. This suggests that the char yield of PS-PEDOT is not influenced by template-coating interactions, which could cause deviations from expected decomposition behavior.

To predict the residual mass at different stages of the pyrolytic process, a chemical abstraction technique was used to systematically remove functional groups/atoms (chemical abstraction) based on the above variable-temperature FTIR analysis. Such a calculation can be leveraged to quantify the relative contributions of proposed decomposition events—ethylenedioxy ( $C_2H_4O_2$ ) abstraction, PS ( $C_8H_8$ ) decomposition, and sulfur (S) abstraction—toward the total observed mass loss (Fig. S7; see SI materials and methods section for detailed calculation and data tables). Expected mass loss is predicted by systematically removing atoms/functional groups (ethylenedioxy, PS, S) from the PS-PEDOT precursor of known composition (Fig. S7A-B) and plotting the residual mass after each decomposition event against temperature (Fig. S7C). Expected temperature values are assigned as the point at which complete peak disappearance is observed (Fig. S2D). Prior to chemical abstraction, the PS-PEDOT sample ([EDOT] = 3.0M) under investigation is composed of ~18.9 wt% PS and ~81.1% PEDOT, which corresponds to an atomic composition of 59.1wt% C, 18.6 wt% S, 18.5 wt% O, and 3.8 wt% H (Fig. S7A-B). Starting at 100wt% and then accounting for ~2wt% residual water ( $H_2O$ ), the ethylenedioxy moiety ( $C_2H_4O_2$ ) from the PEDOT fraction is removed first, leaving behind 65.3wt%, which aligns well with experimental observations (~68.9 wt%) (Fig. S7C). This data point is plotted at 390°C because the FTIR signal for C-O-C stretching disappears within the 375-400°C range, the midpoint of which is 390°C. From the residue of the previous abstraction, 96.5wt% of the PS ( $C_8H_8$ ) is removed to account for the small amount of char derived from carbonization of the template



(3.5wt%) under direct ramp conditions (Fig. S3C), leaving behind ~47wt% residual mass. This value is plotted at 450°C as complete PS decomposition is observed by this point (Fig. S2A).

The final abstraction event involves the desulfonation of the PEDOT fraction of PS-PEDOT. From the residue of the previous two abstraction steps, if all S atoms are removed, it will result in ~28.4% residual mass; however, TGA data (Fig. S6A) suggests incomplete desulfonation evidenced by continual mass loss (negative slope) in the 450-1000°C. To quantify the amount of sulfur to be abstracted, XPS analysis is used to quantify the amount of sulfur that gets doped into the pyrolytic carbon at 1000°C. XPS reveals a C:S atomic ratio = 27.8 : 1 for PC-3.0 (see SI materials and methods section for detailed calculation), which is set as a constraint in determining the fraction of sulfur to be abstracted from the previous residue (Fig. S7C). To satisfy this constraint, 85wt% of the S is removed leaving behind ~31.3 wt% residual mass (C/S = 27.4), which is remarkably close to the experimental char yield of 30.9 wt% (Fig. S7D). Overall, the predicted char yield after each proposed decomposition event aligns well with the experimental thermogram, suggesting that systematic chemical abstraction can be helpful to verify the major decomposition events and mechanisms underlying pyrolytic processes.

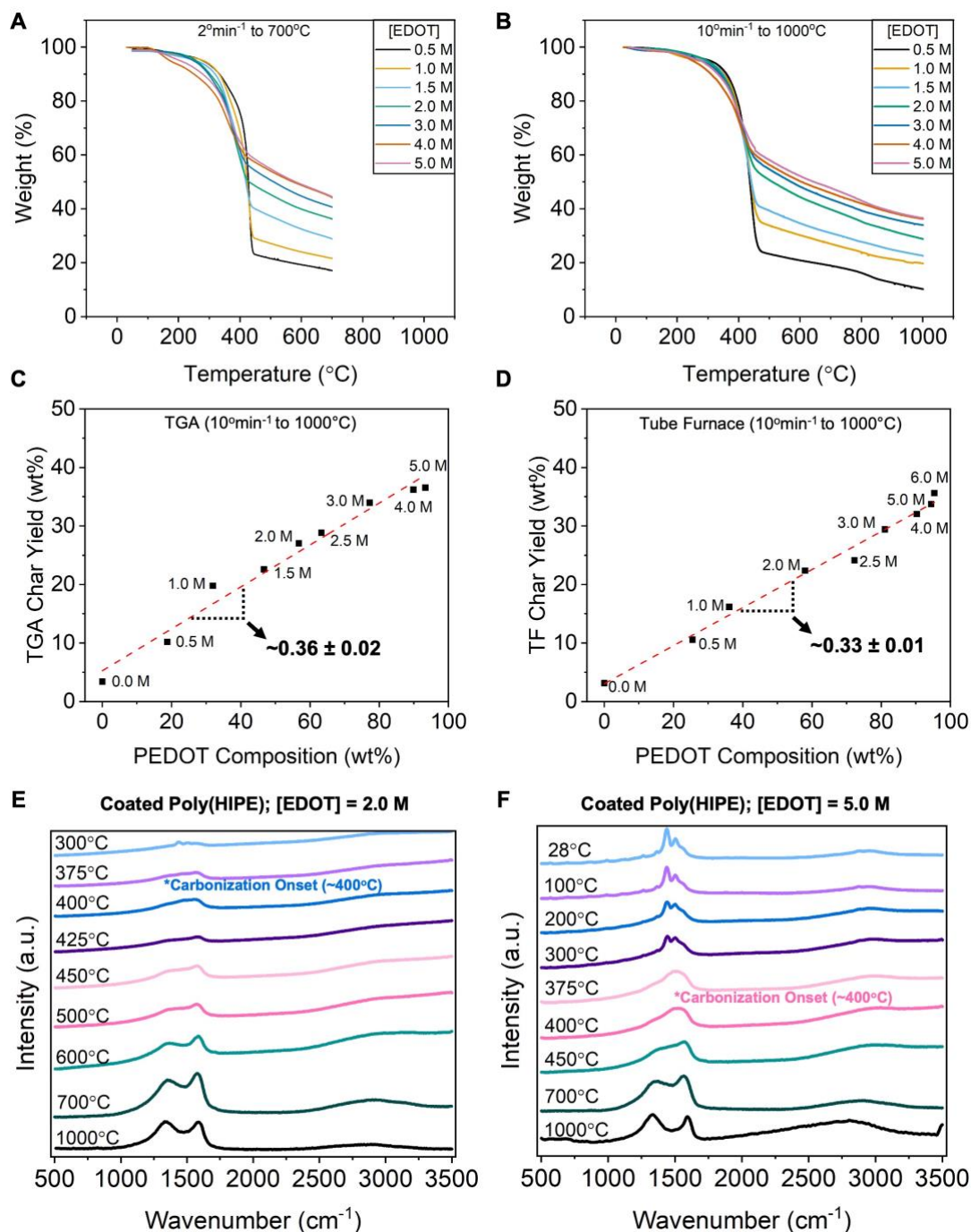
- ***In-situ* TGA-FTIR (Fig. S8):**

To verify if the proposed decomposition pathway ( $C_2H_4O_2$ ,  $C_8H_8$ , S) is chemically feasible, *in-situ* TGA-FTIR provides time-solved spectral information about the identity and elution temperature of gaseous decomposition products formed during the conversion of polymer to carbon (Fig. S8A; see SI instrumentation section for experimental details). In the *in-situ* experiment, the TGA gas outlet is connected to an FTIR equipped with a flow cell designed to accumulate (one spectrum every three minutes) and analyze the gaseous decomposition products as a function of time. The collective spectral information is represented in a stack plot or waterfall diagram (Fig. S8B). The potential peak assignments (Fig. S8B, arrows) in decreasing order of wavenumber are as follows: C-H stretching from

hydrocarbons ( $\sim 3000\text{ cm}^{-1}$ ),  $\text{CO}_2$  ( $\sim 2340\text{-}2360\text{ cm}^{-1}$ ),  $\text{CS}_2$  ( $\sim 2200\text{ cm}^{-1}$ ),  $\text{CO}$  ( $\sim 2150\text{ cm}^{-1}$ ),  $\text{CH}_3\text{COOH}$  ( $\sim 1750\text{ cm}^{-1}$ ),  $\text{H}_2\text{O}$  ( $\sim 1550\text{-}1700\text{ cm}^{-1}$ ),  $\text{SO}_2$  ( $\sim 1360\text{ cm}^{-1}$ ) and hydrocarbons ( $<1000\text{ cm}^{-1}$ ; styrene, toluene, ethylene, etc.).<sup>[6-10]</sup>

In accordance with ex-situ data, the  $\text{CO}_2$  peak intensity increases slowly until  $\sim 250^\circ\text{C}$ , at which point the  $\text{CO}_2$  evolution increases rapidly and reaches a maximum in the  $275\text{-}500^\circ\text{C}$  range. This is consistent with the high rate of carbon expulsion (ethylenedioxy abstraction and PS decomposition) in this temperature range (Fig. S8A; see derivative axis). One of the oxygen sources for forming oxygen-containing gaseous products is presumably the ether ring from PEDOT, which also decomposes in the  $300\text{-}400^\circ\text{C}$  range. Based on the predictive calculations, the atomic composition (mol%) of all theoretical decomposition products from PS-PEDOT-3.0 ( $\text{C}_2\text{H}_4\text{O}_2$ ,  $\text{C}_8\text{H}_8$ , S) is C : O : S : H = 1 : 0.5 : 0.2 : 1.5 (see SI materials and methods section for detailed calculations). Based on this calculation, there are approximately 2 carbon atoms for every oxygen atom, which means that the oxygen from PEDOT alone is insufficient to supply the formation of all the oxygen-containing gaseous products identified. This explains the formation of hydrocarbons such as ethylene, styrene, and toluene. Additionally, since the synthesis of PEDOT is done via chemical oxidative polymerization, overoxidation is a potential side reaction that can introduce oxygen groups to the PS-PEDOT system.<sup>[11,12]</sup> Overoxidation could explain the elution of mainly oxygenated decomposition products despite the limited oxygen supply from the ethylenedioxy moiety. Lastly, the faint but detectable elution of Sulfur containing gases, including  $\text{SO}_2$  and  $\text{CS}_2$ , is consistent with desulfonation as a primary decomposition mechanism and the formation of sulfur-doped carbon.

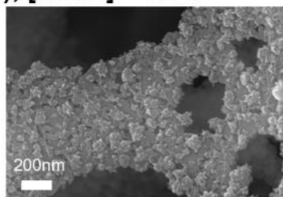
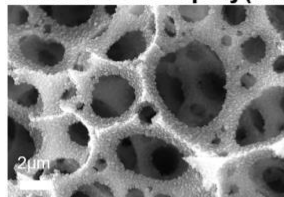
Overall, the data from ex-situ TGA/FTIR, in-situ TGA-FTIR, and predictive calculations are consistent. The ex-situ data provides essential information about the residual mass, while the in-situ data provides valuable information about the decomposition products. The calculations support both these experimental techniques and help verify the proposed pyrolytic mechanism.



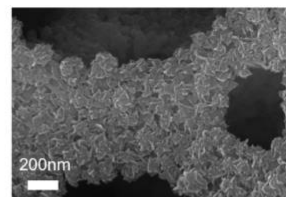
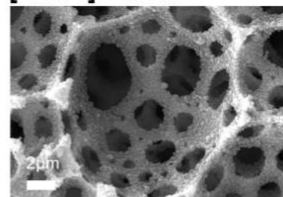
**Fig. S9** Thermograms of PEDOT coated poly(HIPE)s (PS-PEDOT- $x$  for  $x=0.0$  to  $6.0$  M) under (A)  $2^\circ\text{min}^{-1}$  to  $700^\circ\text{C}$  and (B)  $10^\circ\text{min}^{-1}$  to  $1000^\circ\text{C}$ . Gravimetrically determined PEDOT composition (mass measured before and after coating/washing/drying) as correlated with char yield resulting from pyrolysis in the (C) TGA and (D) tube furnace. This suggests that pyrolysis conducted in the TGA and tube furnace yield consistent results, as evidenced by the similar slopes (red dotted lines). Variable-temperature Raman spectra of (E) PS-PEDOT-2.0 ( $2^\circ\text{min}^{-1}$  to  $T^\circ\text{C}$ ) and (F) PS-PEDOT-5.0 ( $10^\circ\text{min}^{-1}$  to  $T^\circ\text{C}$ ) suggest that carbonization onset temperature is independent of both, coating thickness and ramp rate up to  $10^\circ\text{min}^{-1}$ .

## A Before Pyrolysis

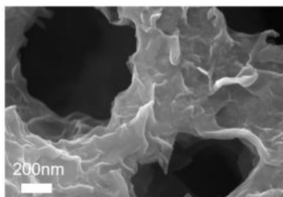
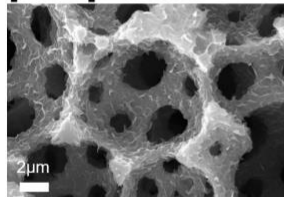
PEDOT coated poly(HIPE); [EDOT] = 1.0M



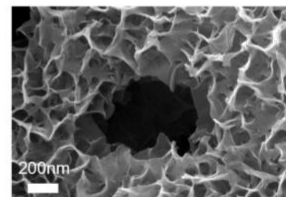
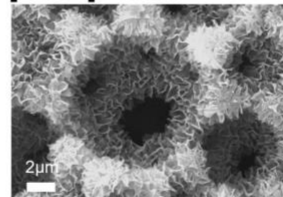
[EDOT] = 2.0M



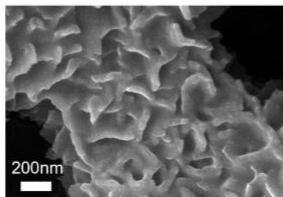
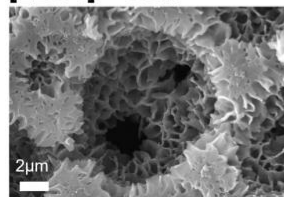
[EDOT] = 2.5M



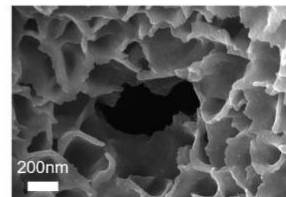
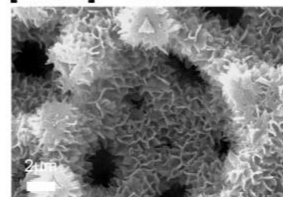
[EDOT] = 3.5M



[EDOT] = 5.0M

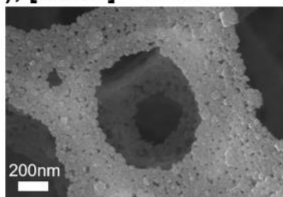
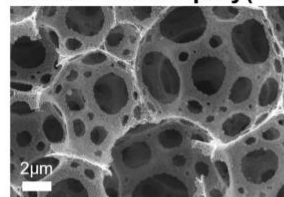


[EDOT] = 6.0M

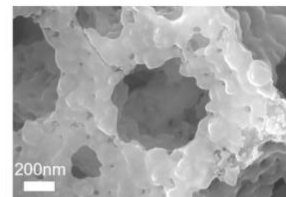
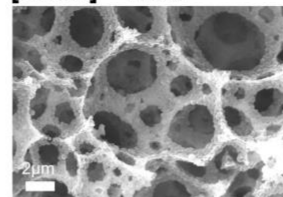


## B After Pyrolysis (Direct Ramp; 10°min<sup>-1</sup> to 1000°C, 2h hold)

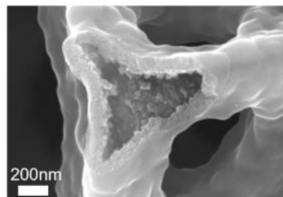
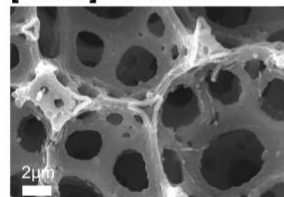
PEDOT coated poly(HIPE); [EDOT] = 1.0M



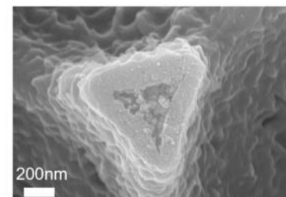
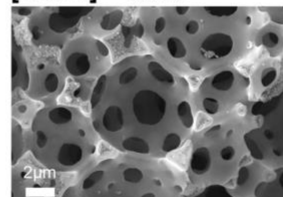
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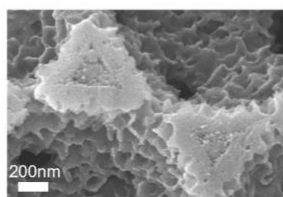
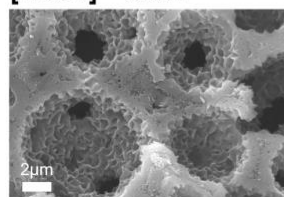
[EDOT] = 2.5M



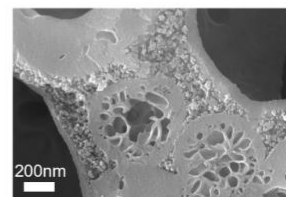
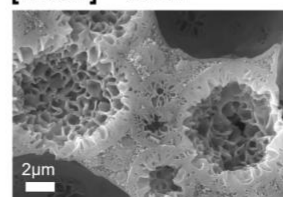
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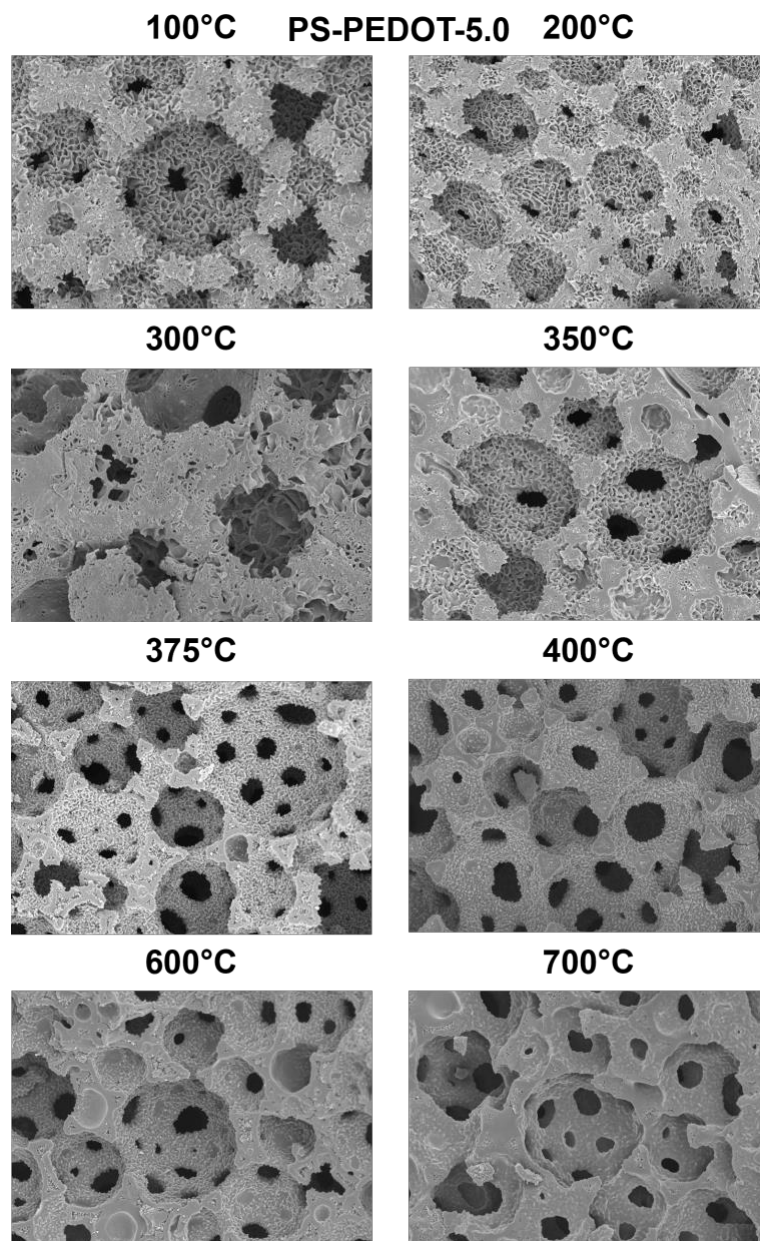
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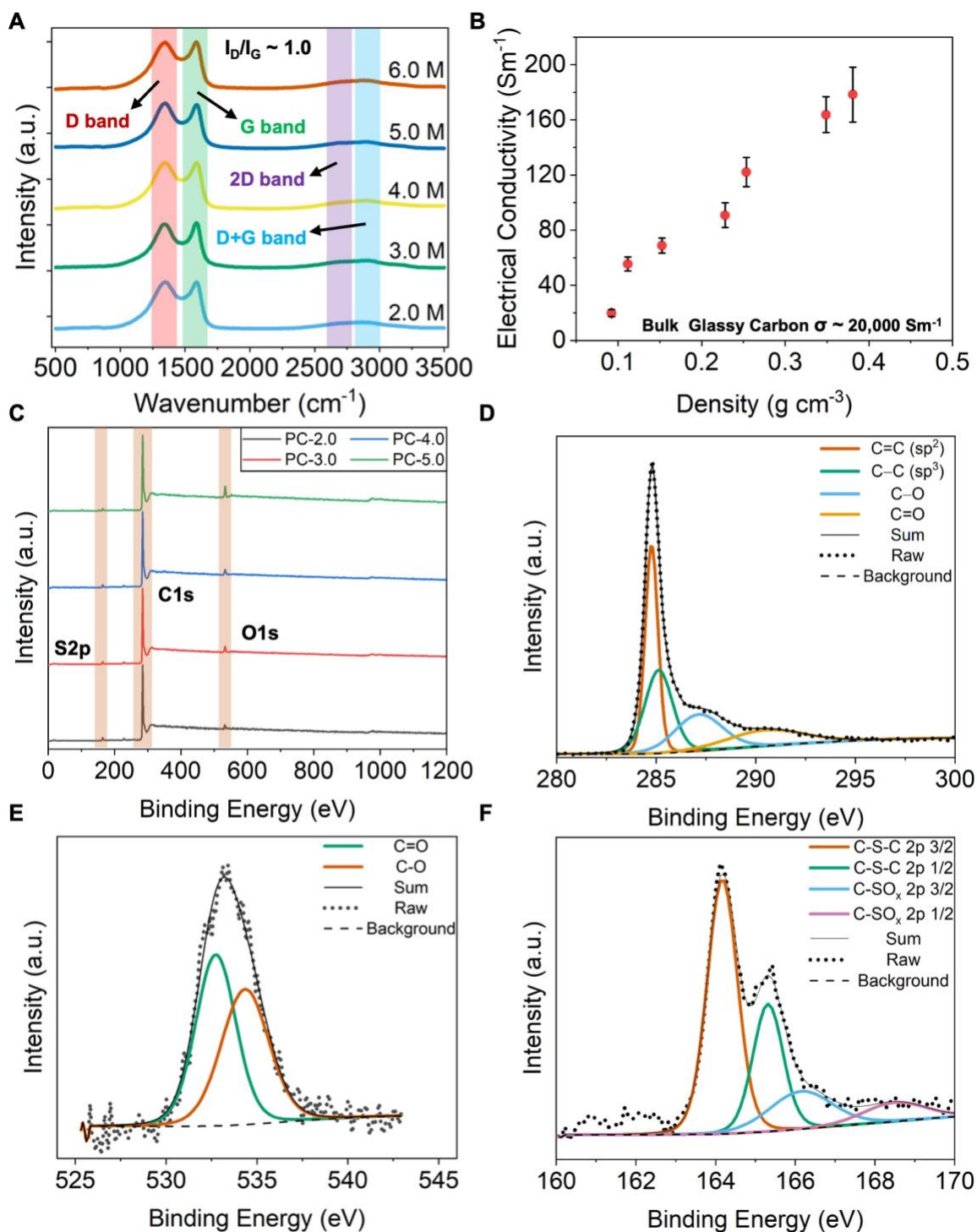
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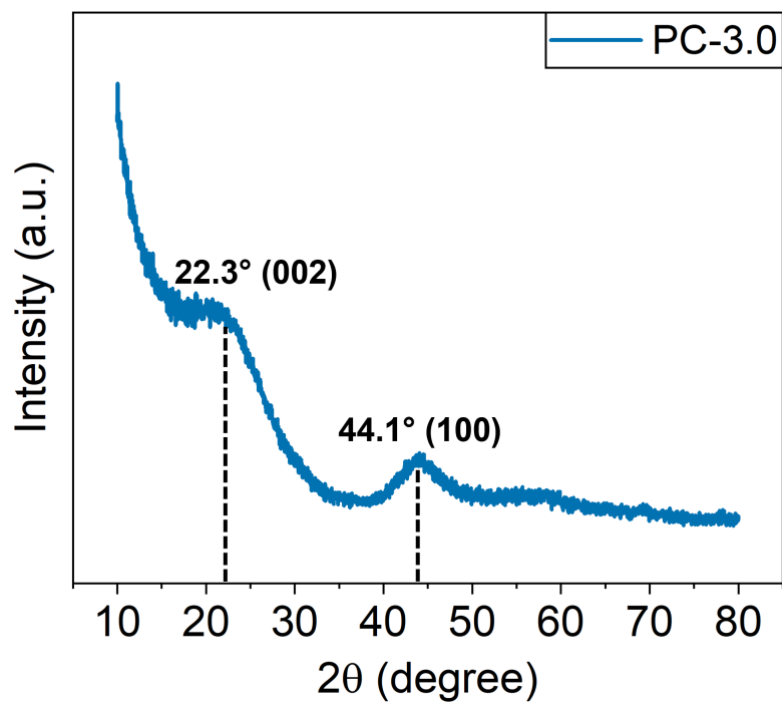
**Fig. S10** SEM of PEDOT coated poly(HIPE) samples **(A)** before pyrolysis (PS-PEDOT-x) and **(B)** after pyrolysis (PC-x) pyrolyzed under “direct ramp” conditions (10°min<sup>-1</sup> to 1000°C, 2h)



**Fig. S11** Variable-temperature SEM characterization of PS-PEDOT-5.0 pyrolyzed in the TGA at several temperatures via the direct ramp protocol ( $10^{\circ}\text{min}^{-1}$  to  $T^{\circ}\text{C}$ ) to further probe the PEDOT morphological transition among samples with thicker coatings. Consistent with PS-PEDOT-3.0 (Fig. S1, Fig. S2D), there appears to be a considerable change in surface morphology occurring in the 300-400°C temperature range. Notably, the PC-5.0 surface morphology at 700°C appears relatively unsmooth, which is likely a result of the non-uniform PEDOT morphology and/or large coating thickness.

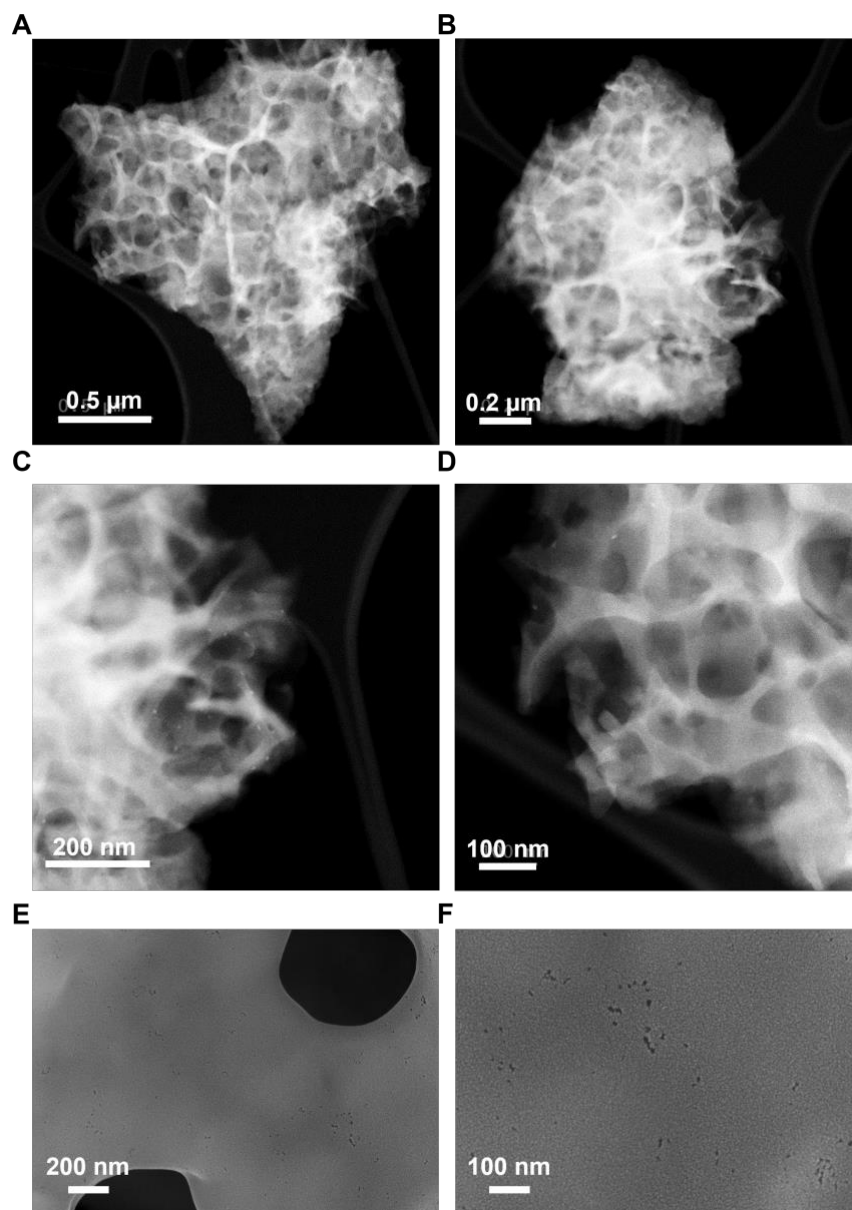


**Fig. S12** (A) Raman spectra of PC-x featuring characteristic D (~1350 cm<sup>-1</sup>) and G (~1590 cm<sup>-1</sup>) bands. (B) Electrical conductivity measurements (Sm<sup>-1</sup>) of bulk pyrolytic carbons (PC-2.0 to 6.0) as a function of density (g cm<sup>-3</sup>) performed via 2-point probe setup with PC-x sandwiched between copper plates. (C) XPS survey spectra, and deconvoluted (D) C1s, (E) O1s and (F) S2p spectra of PC-3.0 (C : S : O = 89.1 : 3.2 : 7.7 % atomic composition).



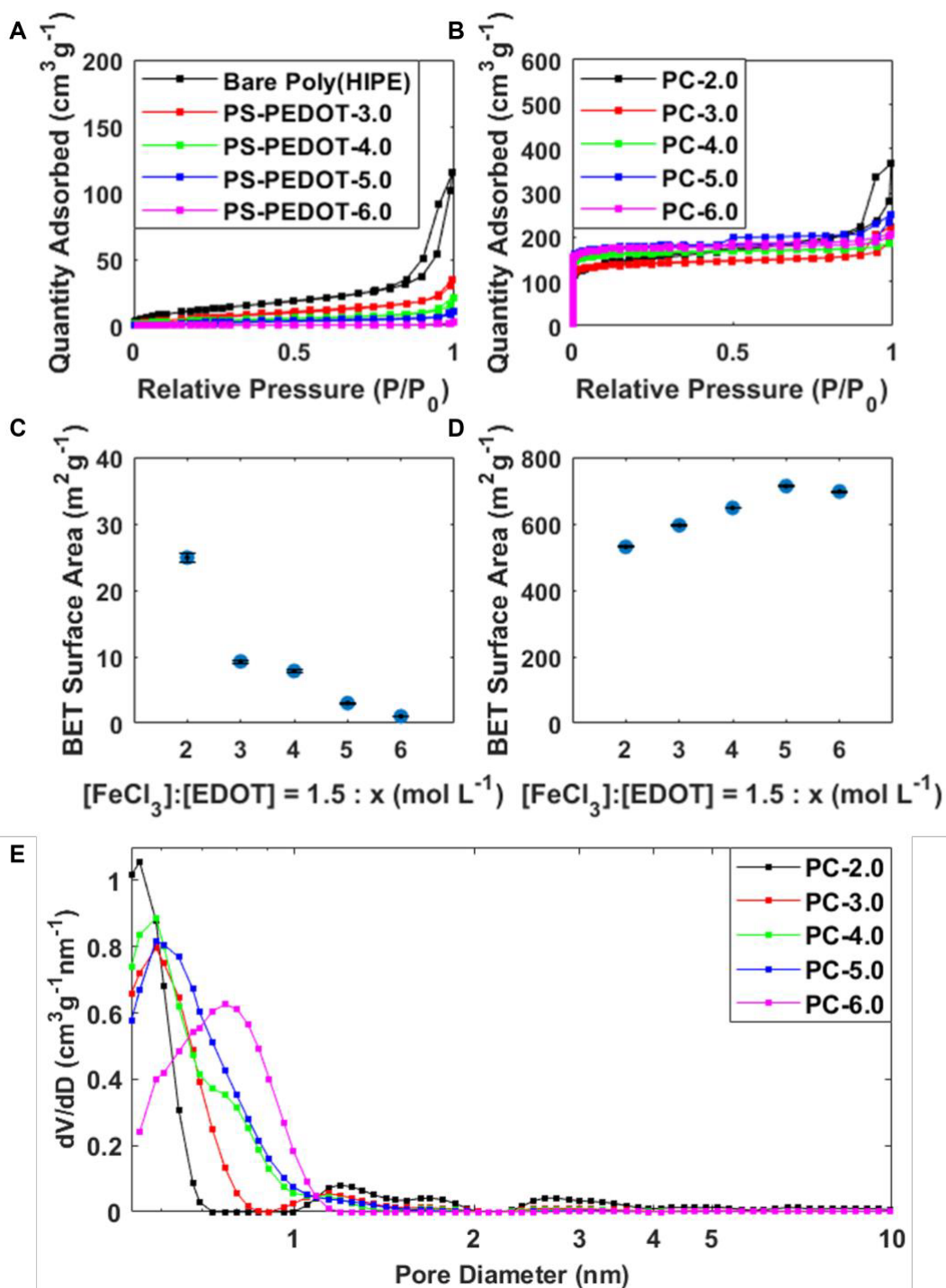
**Fig. S13** XRD pattern of PC-3.0. The two broad peaks around  $\sim 22^\circ$  and  $44^\circ$  are attributed to the (002) and (100) diffraction modes of pyrolytic carbon



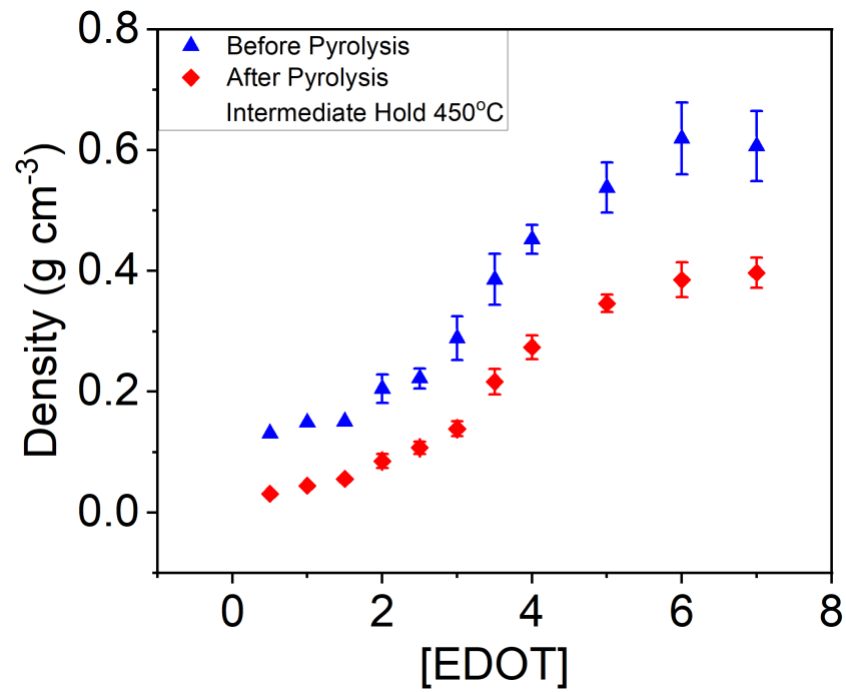


**Fig. S14 (A-D)** Transmission Electron Microscopy (TEM) images of PC-3.5 pyrolyzed under intermediate hold conditions ( $10^{\circ}\text{min}^{-1}$  to  $450^{\circ}\text{C}$ , 1h isotherm,  $10^{\circ}\text{min}^{-1}$  to  $1000^{\circ}\text{C}$ , 2h isotherm). **(E-F)** SEM images of PC-3.0 for comparison. The visible regions of contrast in the SEM images presumably indicate hollow struts.

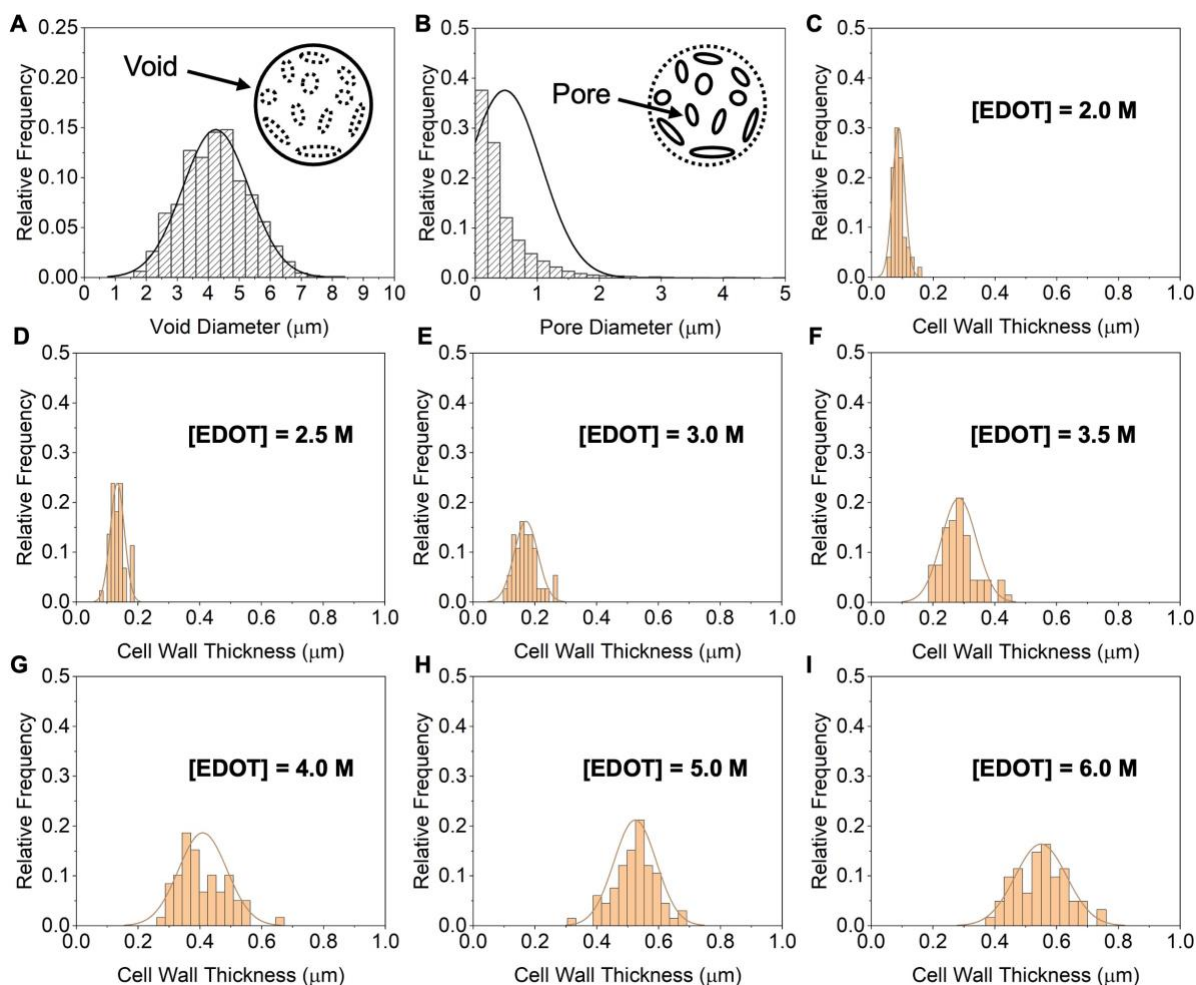




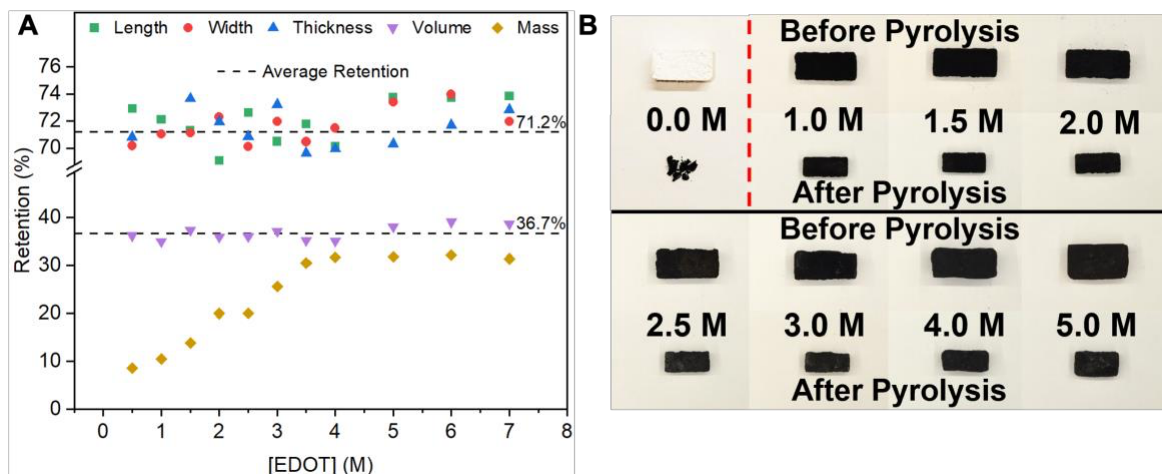
**Fig. S15** Brunauer–Emmett–Teller (BET) analysis of PC-x. N<sub>2</sub> adsorption/desorption isotherms of (A) PS-PEDOT-x and (B) PC-x. BET-derived specific surface area (m<sup>2</sup>g<sup>-1</sup>) of (C) PS-PEDOT-x and (D) PC-x. (E) NLDFT Pore size distributions.



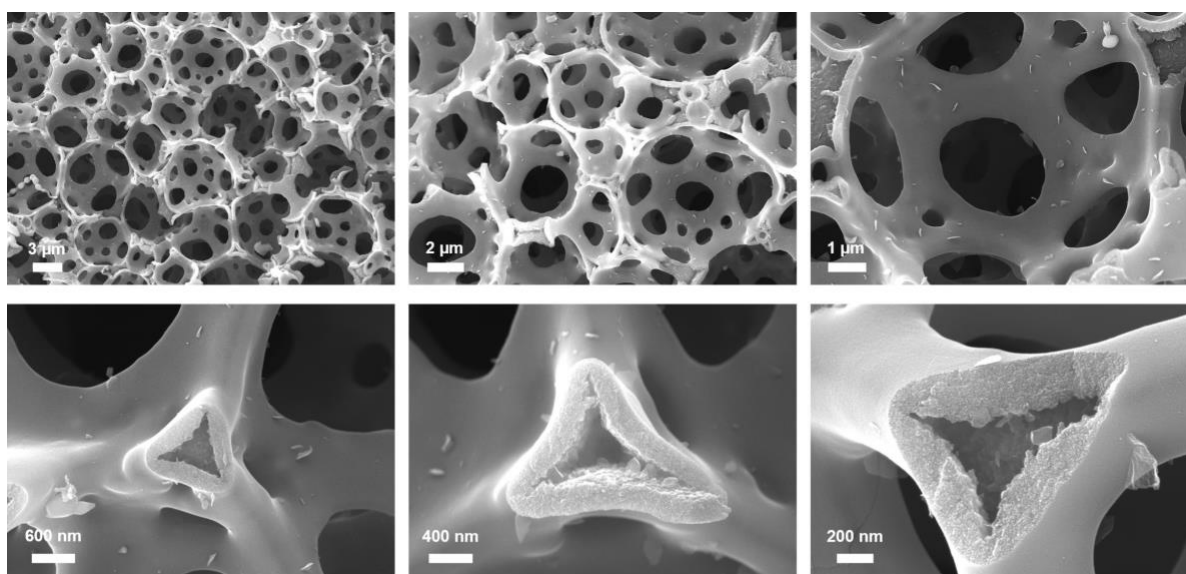
**Fig. S16** Density of PS-PEDOT-x (blue triangles) and PC-x (red diamonds) pyrolyzed under intermediate hold conditions ( $10^{\circ}\text{min}^{-1}$  to  $450^{\circ}\text{C}$ , 1h,  $10^{\circ}\text{min}^{-1}$  to  $1000^{\circ}\text{C}$ , 2h).



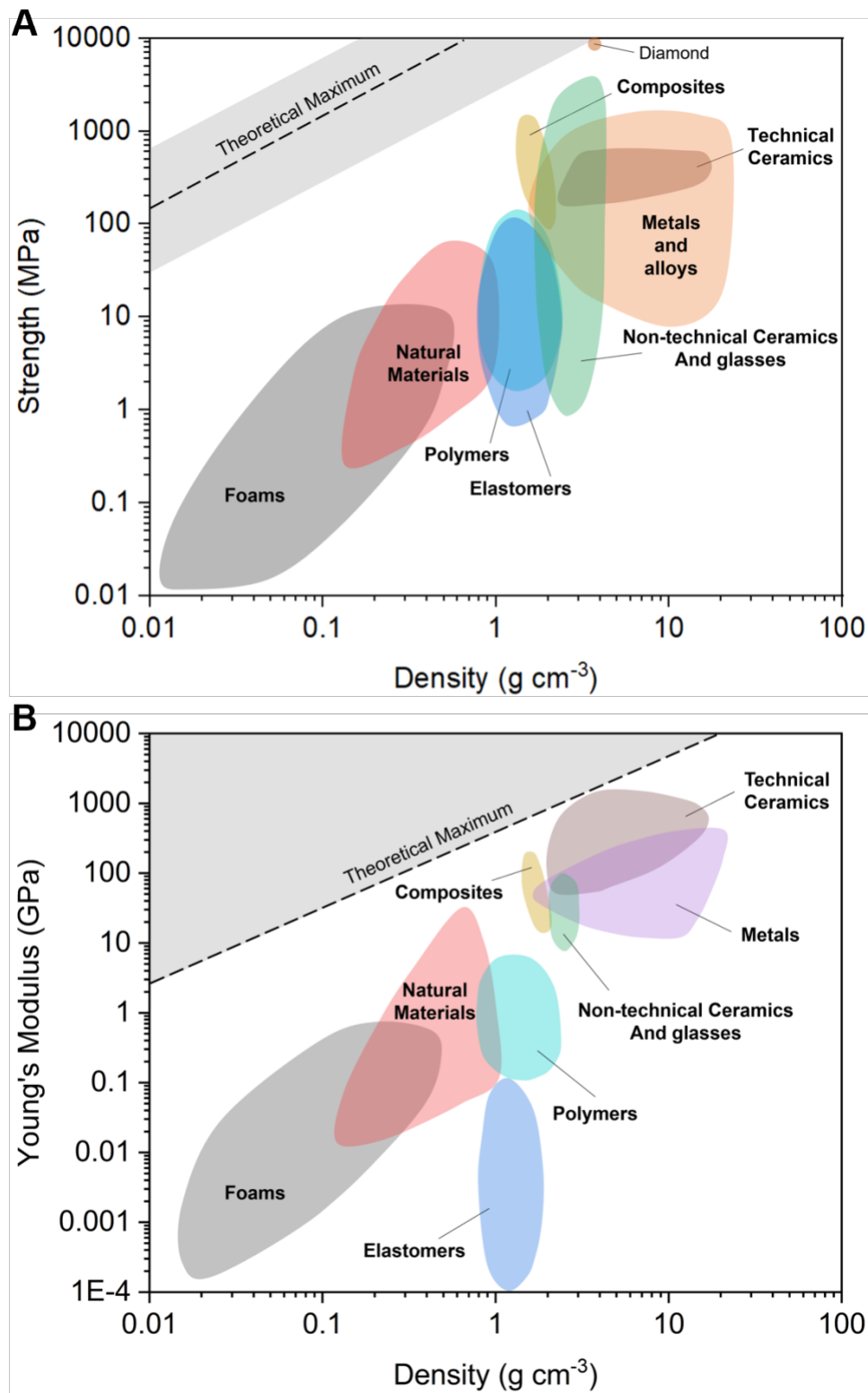
**Fig. S17** SEM image analysis (ImageJ) derived diameter distribution of bare PS-poly(HIPE) (no coating; [EDOT]=0.0M) **(A)** Voids and **(B)** Pores. Considering that the plane of the SEM image cuts through the voids at a random distance from the center, a correction factor of  $4/\pi$  is required ( $d_{\text{void}} = d_{\text{SEM}} \cdot 4/\pi$ ). A similar statistical correction ( $d_{\text{pores}} = (2/\pi)^{0.5} \cdot d_{\text{SEM}}$ ) is needed for window size to account for the angle at which the ellipsoidal windows are viewed in the image. ImageJ derived cell-wall thicknesses of **(C)** PC-2.0, **(D)** PC-2.5, **(E)** PC-3.0, **(F)** PC-3.5, **(G)** PC-4.0, **(H)** PC-5.0 and **(I)** PC-6.0.



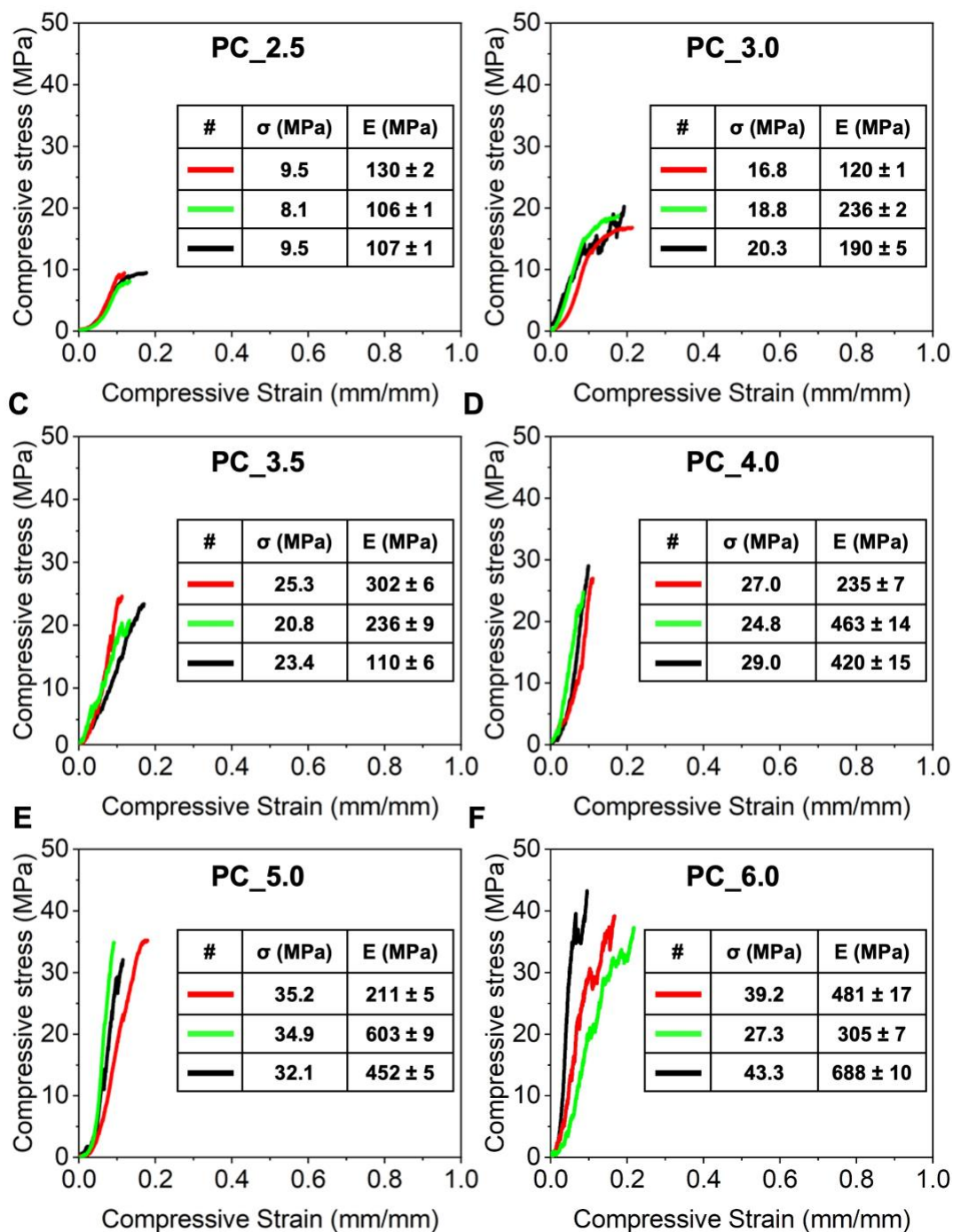
**Fig. S18 (A)** Retention of bulk PC-x properties (mass, length, width, thickness, and volume) pyrolyzed under “Direct Ramp” conditions ( $10^{\circ}\text{min}^{-1}$  to  $1000^{\circ}\text{C}$ , 2h hold) and **(B)** corresponding images of PS-PEDOT-x and PC-x monoliths before and after direct ramp pyrolysis respectively.



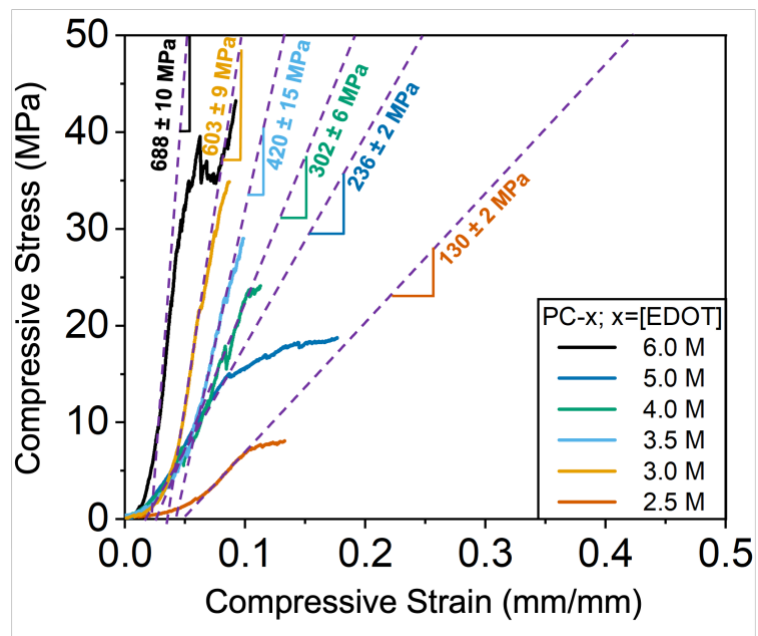
**Fig. S19** SEM images in of macroscale PC-2.5 pyrolyzed under intermediate hold conditions with a slower ramp rate and prolonged isotherms ( $10^{\circ}\text{min}^{-1}$  to  $450^{\circ}\text{C}$ , 2h isotherm,  $2^{\circ}\text{min}^{-1}$  to  $1000^{\circ}\text{C}$ , 4h isotherm) to ensure strut evacuation (at  $450^{\circ}\text{C}$ ) and complete carbonization (at  $1000^{\circ}\text{C}$ ) of the macroscale precursor.



**Fig. S20** Ashby plots of **(A)** Strength versus density and **(B)** Young's Modulus versus density. Materials properties used to create the Ashby charts were obtained from CES EduPack 2019, ANSYS Granta © 2020 Granta Design.

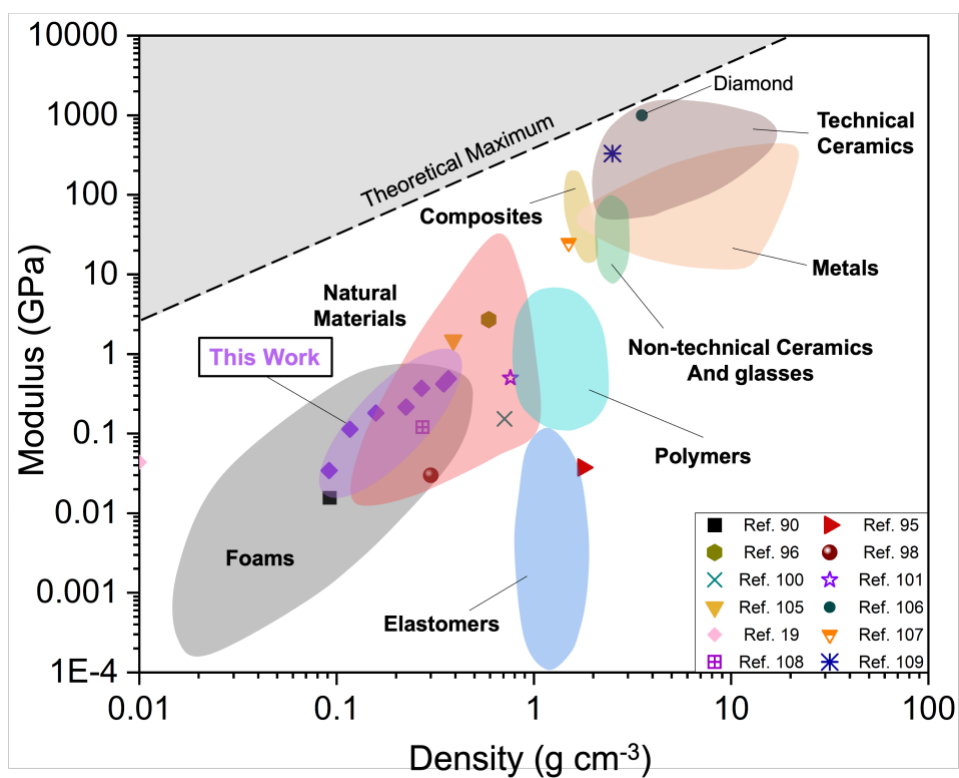


**Fig. S21** Compressive stress-strain curves for PC-x samples (A) PC-2.5, (B) PC-3.0, (C) PC-3.5, (D) PC-4.0, (E) PC-5.0, (F) PC-6.0 plotted up to the point of maximum recorded stress.



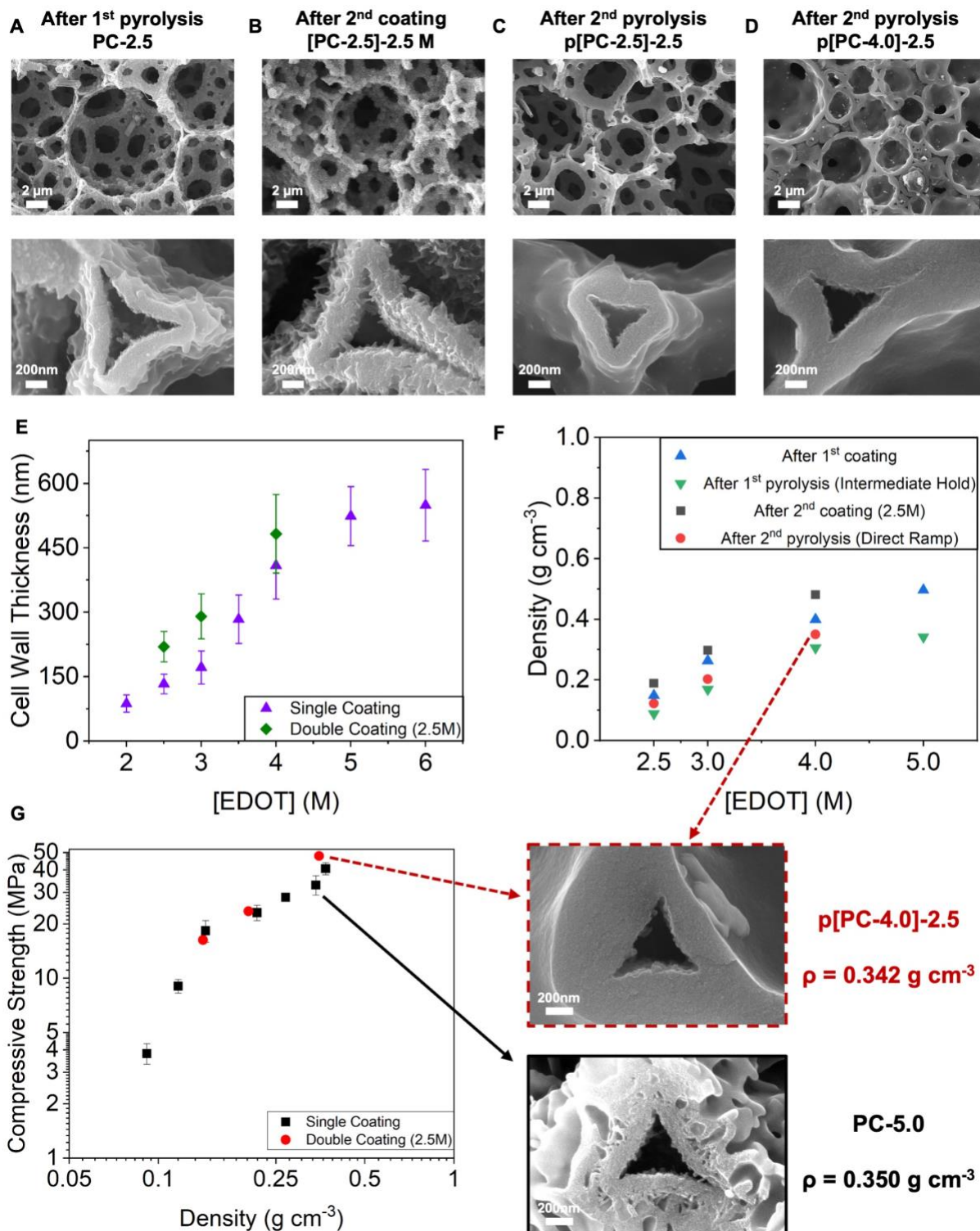
**Fig. S22** Compressive stress-strain curves of representative PC-x samples. Young's Modulus (MPa) values are reported alongside the dotted lines representative of the linear region used to calculate the slope in each stress-strain curve.



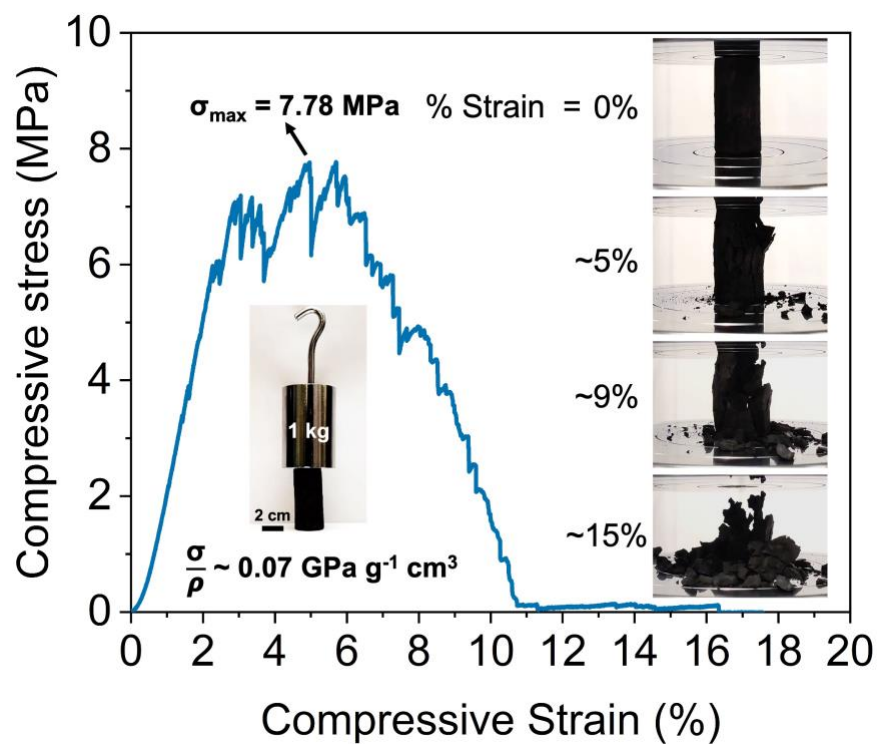


**Fig. S23** Ashby chart comparing the Young's Modulus of PC-x (this work) against other carbonaceous materials. Beyond specified references as seen in the legend, materials property data used to create the Ashby chart were obtained from CES EduPack 2019, ANSYS Granta © 2020 Granta Design. References numbers in the legend refer to those in the main text.

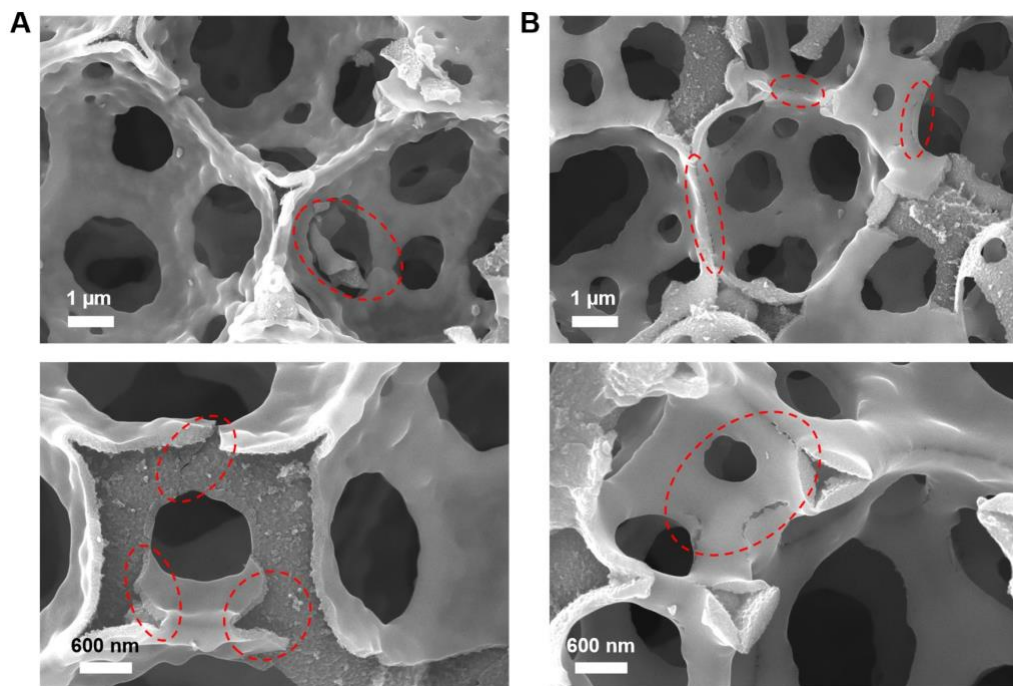




**Fig. S24** SEM images of **(A)** PC-2.5 (1<sup>st</sup> 2.5M PEDOT coating + 1<sup>st</sup> pyrolysis), **(B)** [PC-2.5]-2.5 (1<sup>st</sup> 2.5M PEDOT coating + 1<sup>st</sup> pyrolysis + 2<sup>nd</sup> 2.5M PEDOT coating), **(C)** p[PC-2.5]-2.5 where “p” represents the second pyrolysis (1<sup>st</sup> 2.5M PEDOT coating + 1<sup>st</sup> pyrolysis + 2<sup>nd</sup> 2.5M PEDOT coating + 2<sup>nd</sup> pyrolysis) and **(D)** p[PC-4.0]-2.5 (first 4.0M PEDOT coating + first pyrolysis + second 2.5M PEDOT coating + second pyrolysis). In the above, the first pyrolysis protocol is 10°min<sup>-1</sup> to 450°C, 1h, 10°min<sup>-1</sup> to 1000°C, 2h, and the second pyrolysis protocol is 10°min<sup>-1</sup> to 1000°C, 2h. **(E)** Cell wall thickness measurements for once and twice coated samples. **(F)** Density of p[PC-x]-2.5 tracked across all processing stages from first coating through second pyrolysis. **(G; left)** Compression strength of twice coated samples alongside results from once coated samples (Fig. 4C, main text) for comparison. **(G; right)** SEM images of p[PC-4.0]-2.5 and PC-5.0, which have similar densities but noticeable differences cell wall morphology. That is, PC-5.0 contains plenty of voids within the cell-wall cross-section while p[PC-4.0]-2.5 appears completely dense and smooth.



**Fig. S25** Stress-strain curve of macroscale cylindrical sample of PC-2.5. Inset images on the right show the sample as a function of strain %.



**Fig. S26** SEM images of **(A)** PC-2.5 and **(B)** PC-3.0 monoliths that were strained to a point which is just after the onset linear regime ( $\sim 5\%$  for these samples) but much prior to failure and then relaxed back to 0% strain without inducing catastrophic failure. The marked regions (red dotted ovals) indicate regions where cracks or local regions of fracture were observed.

## **Experimental Materials and Methods**

### **Materials**

Styrene (ST,  $\geq 99\%$  with stabilizer), Divinylbenzene (DVB;  $\geq 80\%$  mixture of isomers), sorbitane monooleate (Span® 80), Potassium Persulfate ( $K_2S_2O_8$ ), Anhydrous Calcium chloride ( $CaCl_2$ ), Iron chloride Hexahydrate ( $FeCl_3 \cdot 6H_2O$ ), Potassium Bromide (KBr), Tetrahydrofuran (THF) and Methanol (MeOH) were purchased from Thermo Fisher Scientific. 3,4-Ethylenedioxythiophene (EDOT) was purchased from AstaTech Inc. ST and DVB were run through a basic alumina plug to remove stabilizer/inhibitor. Besides these, all chemicals were used as received without further purification. All water used was deionized in-house water (DI  $H_2O$ ).

### **Instrumentation**

- **Thermogravimetric analysis (TGA)** was conducted with a TA Instruments Discovery thermogravimetric analyzer using the high-resolution procedure (Hi-Res TGA) with default settings (sensitivity = 1, amplitude  $5^\circ C$ , period 200s, ramp rate =  $2-10^\circ C \text{ min}^{-1}$  to  $T^\circ C$ , resolution = 6) in platinum pans. The ramp rate and isothermal stage durations were varied.
- **Raman spectroscopy (Raman)** was conducted using a Horiba LabRAM HR Evolution confocal Raman microscope equipped with a 50X LWD objective lens, 10% filter, and 532 nm laser.
- **Brunauer–Emmett–Teller (BET)**  $N_2$  gas adsorption/desorption isotherms were measured at 77 K using a Micromeritics 3Flex Adsorption Analyzer. The BET surface area was calculated within the relative pressure ( $P/P_0$ ) range of 0.05–0.2. The pore size distributions were calculated from the adsorption isotherms by nonlocal density functional theory (NLDFIT). The carbon slit pores model for  $N_2$  adsorption at 77 K on carbon was selected to characterize amorphous porous structure

- **X-ray photoelectron spectroscopy (XPS)** – XPS analysis was performed on a Kratos Axis Nova spectrometer using monochromatic Al K $\alpha$  source (1486.6 eV). Spectra were collected using an analysis area of 0.3x0.7mm<sup>2</sup>. Surveys were scanned at 160 eV pass energy (1 eV step size) and high-resolution scans were carried out using 20 eV pass energy (0.1 eV step size). For scan calibrations, C1s peak of adventitious carbon was set at 284.8 eV.
- **Scanning Electron Microscopy (SEM)** was conducted with Carl Zeiss Merlin high-resolution Field Emission Scanning Electron Microscope (FE-SEM). The SEM was operated under the In-Lens mode with an accelerating voltage of 10 kV and a working distance of ~5-7 mm. The samples were placed on copper tape stuck onto stubs and sputter-coated with a thin layer (~4 nm) of Pt/Pd alloy to improve electron conductivity. Pore sizes were analyzed with ImageJ.
- **Transmission electron microscopy (TEM)** was conducted using a JEOL ARM 200F microscope equipped with a cold field emission source operated at 200 kV.
- **Fourier-transform Infrared Spectroscopy (FTIR)** was conducted with a Shimadzu IRTracer-100 Fourier transform infrared spectrometer equipped with ATR (diamond) and transmission modes. Bare PS-poly(HIPE) and PS-PEDOT-x samples were dried in a vacuum oven, diluted with dried KBr (~97 wt%), and pressed into a pellet using a 13mm pellet die (PIKE technologies; part #:161-1900). Spectra were collected between 400–4000 cm<sup>-1</sup> with 44 scans and 4 cm<sup>-1</sup> resolution.
- **TGA-FTIR (in-situ)** analyses were performed in a Netzsch STA 449 F3 Jupiter Simultaneous Thermal Analysis (STA) instrument. A precisely weighed sample is placed in an Alumina crucible. The sample is measured under ultra-high purity Helium gas (25 cm<sup>3</sup>min<sup>-1</sup>). The buoyancy effect for Helium was corrected by measuring the empty crucible under the same measurement conditions used for the sample. The temperature was increased at a rate of 5°min<sup>-1</sup> to 1000°C. The gases are transferred to the FTIR instrumentation via a heated (250°C) transfer line. The FTIR is

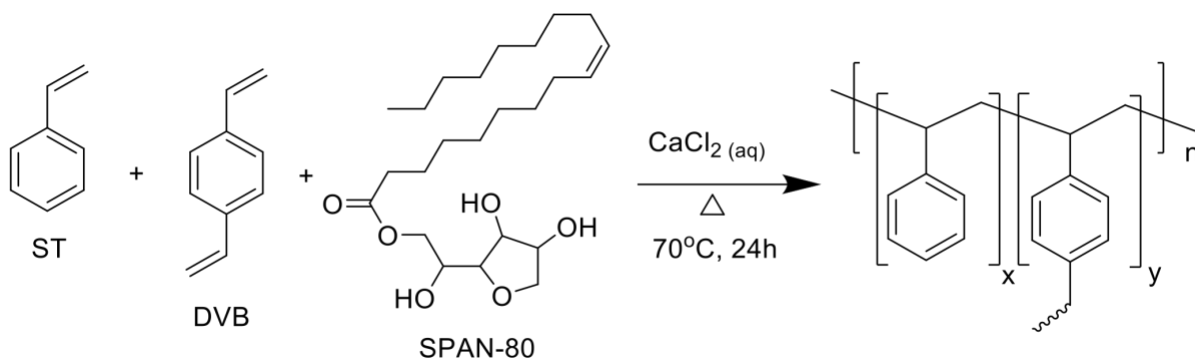
equipped with a flow cell designed to accumulate and analyze the gaseous decomposition products as a function of time/temperature. The FTIR collected a spectrum roughly every 3 minutes. The performance of the thermobalance of the STA is verified by using a certified sample of calcium oxalate monohydrate (European Pharmacopoeia Reference Standard) up to 1000°C.

- **Tube Furnace pyrolysis** was conducted in a Thermo Scientific Lindberg/Blue M Mini-Mite TF55035C Tube Furnace equipped with 1-inch diameter quartz tubes and capable of achieving up to ~1100°C and <50°min<sup>-1</sup>. The tube furnace is installed with a mass flow controller set to deliver ~5-10 sccm of N<sub>2</sub>. The Lindberg furnace was used for pyrolysis of small samples under direct ramp (10°min<sup>-1</sup> to 450°C, 1h isotherm, 10°min<sup>-1</sup> to 1000°C, 2h isotherm)/intermediate hold (10°min<sup>-1</sup> to 450°C, 1h hold, 10°min<sup>-1</sup> to 1000°C, 2h hold) conditions. The cooling rate was set to 2°min<sup>-1</sup> until 500°C and then the furnace was left to cool naturally.
- **Large-Scale Tube Furnace pyrolysis** was conducted in an MTI corporation OTF-1500X-UL Tube Furnace equipped with 3-inch outer diameter mullite tubes and capable of achieving up to ~1500°C and <20°min<sup>-1</sup>. The tube furnace is installed with a gas flow controller set to deliver ~5-10 sccm of N<sub>2</sub>. The MTI furnace was primarily used for the pyrolysis of macroscale samples under intermediate hold conditions (10°min<sup>-1</sup> to 450°C, 2h hold, 2°min<sup>-1</sup> to 1000°C, 4h hold) with a slower ramp rate and prolonged hold times to account for the large precursor size. The cooling rate was set to 2°min<sup>-1</sup> to 500°C and then the furnace was left to cool naturally.
- **Compressive Strength Testing** was conducted with the INSTRON 5800 series materials tester equipped with a 50 kN load cell. Constant strain experiments were conducted on samples at a strain rate of 0.01 mm s<sup>-1</sup> and a sampling interval of 10 Hz.

## Methods

- **Synthesis of PS-poly(HIPE)**

Poly(HIPE)s are synthesized via polymerization of the precursor high internal phase emulsion (HIPE), which is a highly viscous, paste-like, surfactant-stabilized, water-in-oil emulsion that has an internal/droplet/aqueous phase (water, salt) composition of greater than or equal to 74 vol%



**Fig. S27** Crosslinked PS poly(HIPE) chemical reaction scheme.

dispersed within an external/continuous/organic phase (monomer, crosslinker, initiator, surfactant). Subsequent vacuum drying to evacuate the droplet phase results in a polymerized HIPE or poly(HIPE)<sup>[13–16]</sup>. In this system, the external/organic phase composed ~10 vol% of the emulsion and consisted of styrene (ST) monomer (inhibitor removed), divinylbenzene (DVB) crosslinker and sorbitane monooleate (Span® 80) nonionic surfactant (Fig. S27). The internal/aqueous phase composed ~90 vol% of the emulsion and consisted of deionized water (DI H<sub>2</sub>O), calcium chloride (CaCl<sub>2</sub>) stabilizing salt and potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) radical initiator. The precise quantities of the organic and aqueous phase constituents are detailed in Table S1.



| External/Organic Phase |             |             | Internal/Aqueous Phase   |                       |                                                  |
|------------------------|-------------|-------------|--------------------------|-----------------------|--------------------------------------------------|
| Monomer                | Crosslinker | Surfactant  | Water                    | Salt                  | Initiator                                        |
| ST (g)                 | DVB (g)     | Span80 (mL) | DI H <sub>2</sub> O (mL) | CaCl <sub>2</sub> (g) | K <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (g) |
| 1.6                    | 0.160       | 0.35        | 21.0                     | 0.218                 | 0.1                                              |

| Internal Phase      |                    | External Phase      |                    |
|---------------------|--------------------|---------------------|--------------------|
| vol% Internal Phase | wt% Internal Phase | vol% External Phase | wt% External Phase |
| 90.25               | 91.01              | 9.75                | 8.99               |

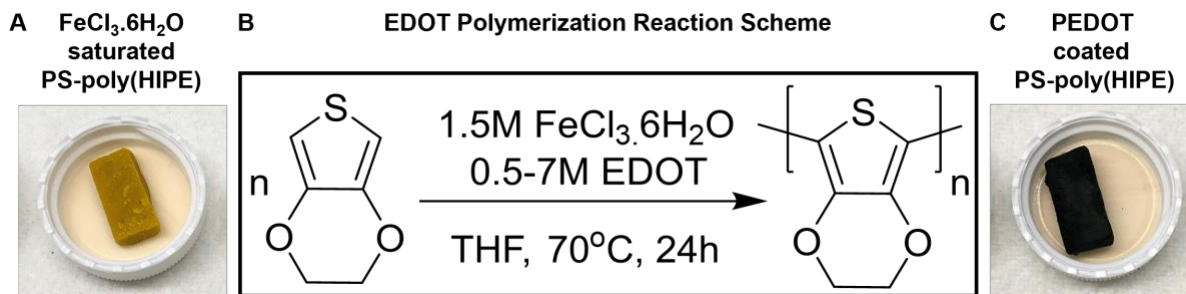
**Table. S1** Materials and composition of chemicals used in PS poly(HIPE) synthesis.

The organic phase was measured into a beaker and the aqueous phase was added to the organic phase at  $\sim 2 \text{ mL min}^{-1}$  using a syringe pump. Initially, during the aqueous addition, the organic phase was stirred using an overhead stirrer ( $\sim 300 \text{ rpm}$ ) to better disperse the water droplets. As more of the aqueous phase was incorporated into the emulsion, a concentrated emulsion began to form, and the stir rate was increased to  $\sim 500 \text{ rpm}$ . When the volumetric ratio of the aqueous to organic phase reaches at least 74%, the emulsion is known as a HIPE. The HIPE was then contained and tightly sealed in a 40 mL vial and placed in a convection oven (open to air) at  $70^\circ\text{C}$  for curing/polymerization of ST/DVB. After 24h of curing, the PS-poly(HIPE) was vacuum dried for 24h to extract the internal phase. The PS-poly(HIPE) was subject to washing via Soxhlet extraction with water for 24h to remove aqueous impurities and methanol for an additional 24h to remove organic impurities. The PS-poly(HIPE) was then dried under vacuum at  $70^\circ\text{C}$  for 24h resulting in a plug-shaped monolith contained in a vial. The PS-poly(HIPE) is removed from the vial and cut into  $\sim 0.5 \text{ cm}$  thick cylinders which were further divided into  $\sim 1 \text{ cm}$  long cuboids.

- **Synthesis of PEDOT-coated PS-poly(HIPE) (PS-PEDOT-x)**

The PS-poly(HIPE) samples were soaked in 1.5M solutions of iron chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) redox initiator in tetrahydrofuran (THF) solvent for 24 hours. THF was the chosen solvent for two reasons: (i) the initiator is highly soluble in THF and (ii) THF has low surface tension which allows for facile infiltration into the tortuous architecture of the PS-poly(HIPE). The samples were removed

from the redox initiator solutions and dried for 15 minutes in a desiccator connected to an in-house vacuum line to ensure that the initiator crystallizes along the interior of the PS-poly(HIPE). If the samples are over-dried, they start to de-swell non-uniformly and cause irregularities in the geometry of the resulting monolith. 10mL monomer solutions of 3,4-Ethylenedioxythiophene (EDOT) in THF of desired concentration were prepared in 40mL vials, flushed with N<sub>2</sub> for 15min, capped and sealed tightly, and then heated on a hot plate at 70°C. The dried initiator-saturated samples were immersed in the 70°C monomer solutions of EDOT in THF for 24h. The yellow monoliths (Fig. S28A) turned blue-black soon after making contact with the EDOT solution, indicative of the polymerization reaction (Fig. S28B). After 24h, the black samples were removed from the vials, washed via Soxhlet extraction with methanol for 24h, and then dried under vacuum at 70°C for 24h resulting in black monoliths of PS-PEDOT-x where x = [EDOT] (M) (Fig. S28C). Note that for [EDOT] ≥ 4.0, the monoliths get buried within a dense PEDOT puck after the 24h reaction. Intact removal of these monoliths can be done by adding THF to the vial and shaking to loosen the sample from the PEDOT puck and gently scraping off any excess PEDOT on the monolith exterior. To vary the PEDOT coating thickness, the monomer concentration [EDOT] was varied from 0.0-6.0M while keeping the initiator concentration [FeCl<sub>3</sub>·6H<sub>2</sub>O] constant at 1.5M during the soaking stage.



**Fig. S28** Synthesis of PS-PEDOT-x. **(A)** FeCl<sub>3</sub>·6H<sub>2</sub>O saturated PS-poly(HIPE) dried for 15 minutes in a desiccator. **(B)** EDOT polymerization reaction scheme. **(C)** PEDOT coated PS-poly(HIPE) with [EDOT]=3.0M (PS-PEDOT-3.0) after washing and drying.

- **Synthesis of porous carbons (PC-x)**

The as-obtained PEDOT-coated PS-poly(HIPE) samples (PS-PEDOT-x) were sanded down in two rounds using coarse and fine-grain sandpaper to flatten out all the faces of the monolith and remove any PEDOT that formed on the outside of PS-PEDOT-x, especially at  $[\text{EDOT}] \geq 4.0\text{M}$ . Before pyrolysis, the sample dimensions were measured using vernier calipers and recorded. The samples were placed in an alumina boat with small supports at both ends of the boat such that they were slightly elevated above the surface of the boat during pyrolysis to ensure uniform heat transport and prevent crack formation. The alumina boat can accommodate two samples simultaneously, with sufficient space between each piece. The alumina boat is placed inside a clear fused quartz tube ( $\sim 20$  mm inner diameter by  $\sim 25$  mm outer diameter by  $\sim 0.7$  m length made by Technical Glass Products, Inc). The tube was placed in a tube furnace (Lindberg/Blue Mini-Mite model) and flushed with ultrahigh purity  $\text{N}_2$  for at least 30 minutes to purge oxygen. The flow rate of  $\text{N}_2$  was set to  $\sim 10 \text{ cm}^3 \text{ min}^{-1}$  using a mass flow controller and the pyrolysis protocol—"Direct ramp"  $10^\circ\text{C min}^{-1}$  to  $1000^\circ\text{C}$ , 2h hold or "Intermediate Hold"  $10^\circ\text{C min}^{-1}$  to  $450^\circ\text{C}$ , 1h hold,  $10^\circ\text{C min}^{-1}$  to  $1000^\circ\text{C}$ , 2h hold—was programmed into the furnace. Pyrolysis of macroscale samples was done at slower ramp rates and prolonged hold times ( $10^\circ\text{min}^{-1}$  to  $450^\circ\text{C}$ , 2h isotherm,  $2^\circ\text{min}^{-1}$  to  $1000^\circ\text{C}$ , 4h isotherm) to ensure complete strut evacuation (at  $450^\circ\text{C}$ ) and carbonization (at  $1000^\circ\text{C}$ ). Once the pyrolysis was completed, the furnace was left to slowly cool ( $2^\circ\text{min}^{-1}$ ) back down to  $500^\circ\text{C}$  to prevent stress-induced crack formation. The samples were washed via Soxhlet extraction for 24h with a water/methanol mixture (25:75 vol%/vol%) and then dried.

- **Density measurement and property retention calculation**

The monolithic or bulk density of a given PS-PEDOT-x or PC-x monolith is calculated by dividing the gravimetrically determined mass by the monolithic volume (length × width × height cm<sup>3</sup>, not accounting for the void space).

$$\rho = \frac{m \text{ (g)}}{V \text{ (cm}^3\text{)}}$$

The dimensions are determined using triplicate measurements made using vernier calipers. The relative density of PC-x is determined by dividing the monolithic density of the porous carbon by the bulk density of glassy carbon (~1.3-1.5 g cm<sup>-3</sup>).<sup>[17]</sup>

The dried PC-x sample dimensions are measured after pyrolysis and the following values are recorded: char yield (mass retention %), dimension/volume retention (%), bulk density (g cm<sup>-3</sup>), and relative density (non-dim). Property (mass, dimension, volume, density) retention values were calculated using the following:

$$\text{Property Retention \%} = \frac{\text{Property after pyrolysis}}{\text{Property before pyrolysis}} \times 100 \%$$

- **Measurement of mechanical properties:**

The stress-strain response of a given PC-x sample is measured using the INSTRON 5800 series materials tester equipped with a 50kN load cell. The PC-x monolith (~1.0 x 1.0 x 0.5 cm<sup>3</sup>) is placed in between two metal plates. The top is brought down such that it is close to the top surface of the PC-x sample. The top plate is then moved in small increments until a stress response is detected, indicating plate-sample contact. The load is set to apply zero force and the top plate is set to strain the sample monolith at 0.01 mm s<sup>-1</sup>. This process is repeated for all PC-x samples and the stress-strain measurements are plotted in Figure S21. The resulting stress-strain curves are offset such that the detected stress response starts at zero strain.

- **Compressive strength calculation**

Compressive strength ( $\text{N/m}^2$ ) is defined as the maximum compressive engineering stress prior to failure/collapse. All stress-strain curves are plotted up to the point of maximum recorded stress and the corresponding values are recorded in Table S2.

- **Young's modulus calculation**

The young's modulus of PC-x samples is measured by fitting the linear region of the stress-strain curves with a straight line and calculating the slope thereof (Figure S22). Each of the curves has a dotted line going through the linear region used to calculate the slope ( $E \sim \text{MPa}$ ). Young's modulus values are recorded alongside each dotted line. Any non-linearities observed at lower strains—also known as “toe” regions—can be attributed to surface roughness and structural imperfections in the PC-x monoliths, which can manifest in plate-sample contact variations between experiments.

- **Average mechanical property calculation**

The average compressive strength and young's modulus are calculated by taking the mean of triplicate measurements (Table S3). The error values are calculated by taking the sample standard deviation

**Specific mechanical property calculation**

The specific strength/modulus ( $\text{MPa g}^{-1}\text{cm}^3$ ) of a given PC-x sample is calculated by dividing strength/modulus (MPa) by density ( $\text{g cm}^{-3}$ ) (Table S3). The average specific strength/modulus is calculated by taking the mean of triplicate measurements. The error values are calculated by taking the sample standard deviation of measurements.

- **Relative mechanical property calculation**

The relative strength/modulus (non-dim) of PC-x (Table S3) is calculated by dividing the mechanical properties of PC-x (strength  $\sigma$  and modulus  $E$ ) by the mechanical properties of bulk pyrolytic carbon

$$(\sigma_{\text{rel}} = \sigma_{\text{meas}}/\sigma_s \text{ and } E_{\text{rel}} = E_{\text{meas}}/E_s)^{[18,19]}$$

| [EDOT]<br>[M] | $\rho$<br>[g/cm <sup>3</sup> ] | $\rho/\rho_s$<br>[%] | $\sigma$<br>[MPa] | $\sigma/\rho$<br>[MPa/g cm <sup>-3</sup> ] | $\sigma/\sigma_s$<br>[%] | E<br>[MPa] | E/ $\rho$<br>[MPa/g cm <sup>-3</sup> ] | E/ $E_s$<br>[%] |
|---------------|--------------------------------|----------------------|-------------------|--------------------------------------------|--------------------------|------------|----------------------------------------|-----------------|
| 2.0           | 0.09                           | 6.1                  | 4.0               | 44.4                                       | 0.16                     | 41.6       | 455.9                                  | 0.17            |
| 2.0           | 0.07                           | 4.6                  | 3.2               | 47.0                                       | 0.13                     | 28.3       | 411.2                                  | 0.11            |
| 2.0           | 0.11                           | 7.6                  | 4.1               | 36.3                                       | 0.17                     | 33.3       | 291.5                                  | 0.13            |
| 2.5           | 0.12                           | 7.9                  | 9.5               | 79.9                                       | 0.38                     | 130.3      | 1098.1                                 | 0.52            |
| 2.5           | 0.10                           | 6.7                  | 8.1               | 80.9                                       | 0.32                     | 105.7      | 1051.8                                 | 0.42            |
| 2.5           | 0.13                           | 8.7                  | 9.5               | 72.5                                       | 0.38                     | 106.5      | 812.5                                  | 0.43            |
| 3.0           | 0.17                           | 11.3                 | 20.3              | 119.0                                      | 0.81                     | 189.9      | 1116.3                                 | 0.76            |
| 3.0           | 0.14                           | 9.4                  | 18.8              | 132.6                                      | 0.75                     | 235.9      | 1664.7                                 | 0.94            |
| 3.0           | 0.16                           | 10.8                 | 16.8              | 103.7                                      | 0.67                     | 119.8      | 737.9                                  | 0.48            |
| 3.5           | 0.22                           | 14.4                 | 23.4              | 108.3                                      | 0.94                     | 109.9      | 508.6                                  | 0.44            |
| 3.5           | 0.22                           | 14.4                 | 20.8              | 96.5                                       | 0.83                     | 236.4      | 1097.0                                 | 0.95            |
| 3.5           | 0.24                           | 16.1                 | 25.3              | 104.4                                      | 1.01                     | 301.8      | 1246.3                                 | 1.21            |
| 4.0           | 0.24                           | 16.2                 | 24.8              | 102.2                                      | 0.99                     | 463.3      | 1910.1                                 | 1.85            |
| 4.0           | 0.26                           | 17.6                 | 27.0              | 102.3                                      | 1.08                     | 234.8      | 889.5                                  | 0.94            |
| 4.0           | 0.30                           | 20.1                 | 29.0              | 96.1                                       | 1.16                     | 420.3      | 1391.6                                 | 1.68            |
| 5.0           | 0.33                           | 22.3                 | 32.1              | 95.9                                       | 1.28                     | 452.2      | 1351.7                                 | 1.81            |
| 5.0           | 0.37                           | 24.5                 | 34.9              | 95.1                                       | 1.39                     | 603.4      | 1644.9                                 | 2.41            |
| 5.0           | 0.35                           | 23.0                 | 35.2              | 102.0                                      | 1.41                     | 210.7      | 610.2                                  | 0.84            |
| 6.0           | 0.41                           | 27.6                 | 44.1              | 106.6                                      | 1.76                     | 687.8      | 1662.4                                 | 2.75            |
| 6.0           | 0.33                           | 22.0                 | 39.9              | 121.0                                      | 1.60                     | 480.8      | 1456.3                                 | 1.92            |
| 6.0           | 0.36                           | 24.1                 | 38.0              | 105.2                                      | 1.52                     | 305.1      | 844.8                                  | 1.22            |

**Table. S2** Mechanical properties (under compression) of representative PC-x samples.

| [EDOT]<br>[M] | $\rho$<br>[g/cm <sup>3</sup> ] | $\rho/\rho_s$<br>[%] | $\langle\sigma\rangle$<br>[MPa] | $\sigma/\rho$<br>[GPa/g cm <sup>-3</sup> ] | $\sigma/\sigma_s$<br>[%] | $\langle E \rangle$<br>[MPa] | E/ $\rho$<br>[GPa/g cm <sup>-3</sup> ] | E/ $E_s$<br>[%] |
|---------------|--------------------------------|----------------------|---------------------------------|--------------------------------------------|--------------------------|------------------------------|----------------------------------------|-----------------|
| 2.0           | 0.09                           | 6.1                  | 3.8                             | 0.04                                       | 0.15                     | 34.4                         | 0.39                                   | 0.14            |
| 2.5           | 0.12                           | 7.8                  | 9.0                             | 0.08                                       | 0.36                     | 114.2                        | 0.99                                   | 0.46            |
| 3.0           | 0.16                           | 10.5                 | 18.6                            | 0.12                                       | 0.75                     | 181.9                        | 1.17                                   | 0.73            |
| 3.5           | 0.22                           | 15.0                 | 23.2                            | 0.10                                       | 0.93                     | 216.0                        | 0.95                                   | 0.86            |
| 4.0           | 0.27                           | 18.0                 | 26.9                            | 0.10                                       | 1.08                     | 372.8                        | 1.40                                   | 1.49            |
| 5.0           | 0.35                           | 23.3                 | 34.1                            | 0.10                                       | 1.36                     | 422.1                        | 1.20                                   | 1.69            |
| 6.0           | 0.37                           | 24.6                 | 40.7                            | 0.11                                       | 1.63                     | 491.2                        | 1.32                                   | 1.96            |

**Table. S3** Average/relative/specific mechanical properties of representative PC-x samples.

### Predictive residual mass and char yield calculations

- Predicted char yield based on a weighted average of pure component thermograms (Fig. S6):
  - Char yield from bare PS = CY(PS)
  - Char yield from bare PEDOT = CY(PEDOT)

| Temperature (°C) | 700°C | 1000°C |
|------------------|-------|--------|
| <b>CY(PS)</b>    | 3.87  | 3.27   |
| <b>CY(PEDOT)</b> | 41.74 | 37.55  |

$$\text{CY(PS-PEDOT-x)} = [\text{PS}_x \cdot \text{CY(PS)}] + [\text{PEDOT}_{1-x} \cdot \text{CY(PEDOT)}]$$

- Gravimetric composition of PS-PEDOT-x (Fig. S7A):

| [EDOT] (M)     | wt% PS | wt% PEDOT |
|----------------|--------|-----------|
| [EDOT] = 2.0 M | 42.02  | 57.98     |
| <b>2.5</b>     | 27.73  | 72.27     |
| <b>3.0</b>     | 18.93  | 81.07     |
| <b>4.0</b>     | 9.72   | 90.28     |
| <b>5.0</b>     | 5.58   | 94.42     |
| <b>6.0</b>     | 4.67   | 95.33     |

- Elemental contributions (wt% C, S, O, H) of PS and PEDOT in PS-PEDOT-x (Fig. S7B):

| Elemental contribution (wt%) | C(PS) | C(PEDOT) | O(PEDOT) | S(PEDOT) | H(PS) | H(PEDOT) |
|------------------------------|-------|----------|----------|----------|-------|----------|
| <b>2.0</b>                   | 38.8  | 29.8     | 13.2     | 13.3     | 3.3   | 1.7      |
| <b>2.5</b>                   | 25.6  | 37.1     | 16.5     | 16.5     | 2.1   | 2.1      |
| <b>3.0</b>                   | 17.5  | 41.7     | 18.5     | 18.6     | 1.5   | 2.3      |
| <b>4.0</b>                   | 9.0   | 46.4     | 20.6     | 20.7     | 0.8   | 2.6      |
| <b>5.0</b>                   | 5.1   | 48.5     | 21.6     | 21.6     | 0.4   | 2.7      |
| <b>6.0</b>                   | 4.3   | 49.0     | 21.8     | 21.8     | 0.4   | 2.7      |

\*S(PS) and O(PS) are equal to zero as PS does not contain any sulfur or oxygen atoms.

- XPS-derived atomic composition of PS-PEDOT-3.0:

| [EDOT] (M) | Area under the curve |       |        | C (mol %) | S (mol%) | O (mol %) | C/S (Molar ratio) |
|------------|----------------------|-------|--------|-----------|----------|-----------|-------------------|
|            | C1s                  | S2p   | O1s    |           |          |           |                   |
| <b>2</b>   | 3782.7               | 154.4 | 291.2  | 89.5      | 3.7      | 6.9       | 24.5              |
| <b>3</b>   | 11183.3              | 402.1 | 967.8  | 89.1      | 3.2      | 7.7       | 27.8              |
| <b>4</b>   | 12480.0              | 412.3 | 1193.2 | 88.6      | 2.9      | 8.5       | 30.3              |

\*XPS compositions derived by calculating the ratio of area under the curve (Fig. S12C-F).

- Stepwise predictive decomposition mechanism (Fig. S7C):

| Element   | 0.33*C(PEDOT)                                                  | O(PEDOT) | H(PEDOT) | C(PS)                                            | H(PS) | S(PEDOT)           |
|-----------|----------------------------------------------------------------|----------|----------|--------------------------------------------------|-------|--------------------|
| [EDOT](M) | C <sub>2</sub> H <sub>4</sub> O <sub>2</sub><br>(100% removed) |          |          | C <sub>8</sub> H <sub>8</sub><br>(96.5% removed) |       | S<br>(85% removed) |
| 2.0       | 90.1                                                           | 76.8     | 75.2     | 37.8                                             | 34.6  | 23.3               |
| 2.5       | 87.6                                                           | 71.1     | 69.0     | 44.3                                             | 42.3  | 28.2               |
| 3.0       | 86.1                                                           | 67.6     | 65.3     | 48.4                                             | 47.0  | 31.2               |
| 4.0       | 84.5                                                           | 63.9     | 61.3     | 52.7                                             | 51.9  | 34.4               |
| 5.0       | 83.8                                                           | 62.3     | 59.5     | 54.6                                             | 54.2  | 35.8               |
| 6.0       | 83.7                                                           | 61.9     | 59.2     | 55.0                                             | 54.6  | 36.1               |

- Cumulative predictive decomposition mechanism (Fig. S7C):

| Moiety abstracted                            | Initial | Residual Water<br>(~2%) | Ether<br>(C <sub>2</sub> O <sub>2</sub> H <sub>4</sub> ) | PS<br>(C <sub>8</sub> H <sub>8</sub> ) | Sulfur<br>(S) |
|----------------------------------------------|---------|-------------------------|----------------------------------------------------------|----------------------------------------|---------------|
| Temperature at which moiety fully abstracted | 50°C    | 200°C                   | 380°C                                                    | 450°C                                  | 1000°C        |
| 2.0                                          | 100     | 98                      | 75.2                                                     | 34.6                                   | 23.3          |
| 2.5                                          | 100     | 98                      | 69.0                                                     | 42.3                                   | 28.2          |
| 3.0                                          | 100     | 98                      | 65.3                                                     | 47.0                                   | 31.2          |
| 4.0                                          | 100     | 98                      | 61.3                                                     | 51.9                                   | 34.4          |
| 5.0                                          | 100     | 98                      | 59.5                                                     | 54.2                                   | 35.8          |
| 6.0                                          | 100     | 98                      | 59.2                                                     | 54.6                                   | 36.1          |

- Predicted atomic composition of PC-3.0 based on the chemical abstraction method (Fig. S7D):

| PC-3.0      | mol%             | mol%            |
|-------------|------------------|-----------------|
| Composition | Before Pyrolysis | After Pyrolysis |
| C           | 47.3             | 94.6            |
| O           | 11.1             | 0.0             |
| S           | 5.6              | 3.5             |
| H           | 36.1             | 2.0             |

\*C : S atomic ratio for PC-3.0 ~ 27.4 : 1

- Predicted atomic composition (mol%) of proposed decomposition products (Fig. S7D):

| Atomic composition of decomposition products | C (mol) | O (mol) | S (mol) | H (mol) | C (mol%) | O (mol%) | S (mol%) | H (mol%) |
|----------------------------------------------|---------|---------|---------|---------|----------|----------|----------|----------|
| 2.0                                          | 5.1     | 1.1     | 0.5     | 6.2     | 39.9     | 8.4      | 3.6      | 48.2     |
| 2.5                                          | 4.3     | 1.4     | 0.6     | 5.7     | 35.6     | 11.9     | 5.1      | 47.5     |
| 3.0                                          | 3.7     | 1.7     | 0.7     | 5.4     | 32.3     | 14.6     | 6.2      | 46.9     |
| 4.0                                          | 3.1     | 2.0     | 0.8     | 5.0     | 28.1     | 18.0     | 7.7      | 46.2     |
| 5.0                                          | 2.7     | 2.1     | 0.9     | 4.8     | 25.9     | 19.8     | 8.4      | 45.8     |
| 6.0                                          | 2.7     | 2.1     | 0.9     | 4.8     | 25.4     | 20.3     | 8.6      | 45.7     |



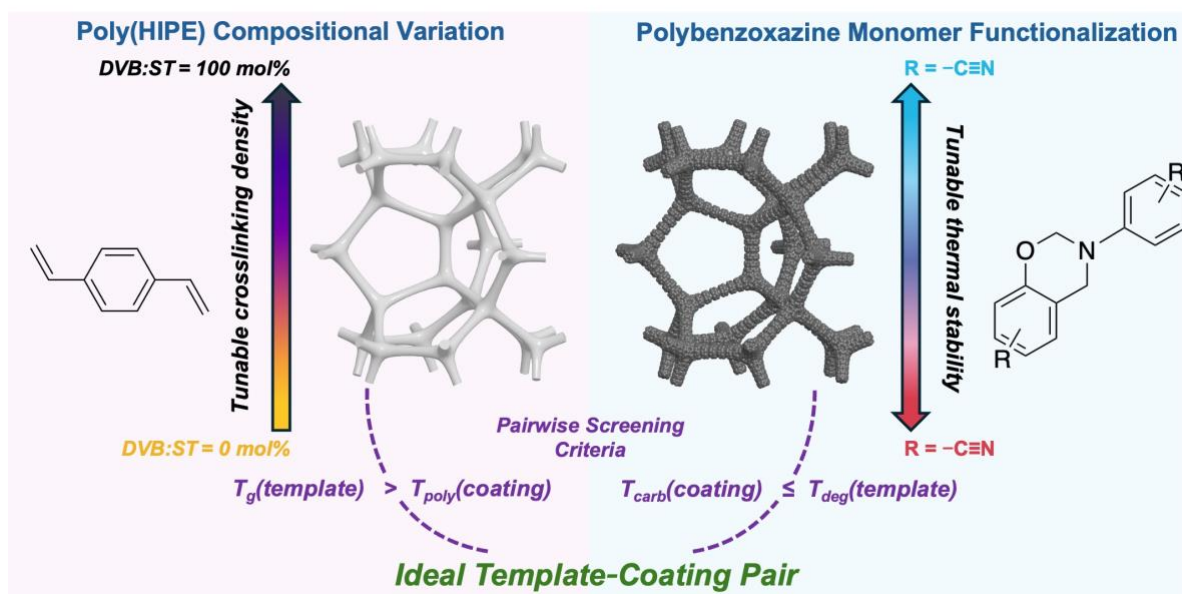
## References – Supporting Information

- [1] V. S. Deshpande, M. F. Ashby, N. A. Fleck, *Acta Materialia* 2001, 49, 1035.
- [2] N. A. Fleck, V. S. Deshpande, M. F. Ashby, *Proc. R. Soc. A* 2010, 466, 2495.
- [3] M. F. Ashby, Society of Automotive Engineers, Eds., *Metal Foams: A Design Guide*, Butterworth-Heinemann, Woburn, MA, 2000.
- [4] P. Dhavalikar, J. Sheno, K. Salhadar, M. Chwatko, G. Rodriguez-Rivera, J. Cheshire, R. Foudazi, E. Cosgriff-Hernandez, *Polymers* 2021, 13, 1479.
- [5] R. Mravljak, O. Bizjak, M. Podlogar, A. Podgornik, *Polymer Testing* 2021, 93, 106590.
- [6] S. W. Sharpe, T. J. Johnson, R. L. Sams, P. M. Chu, G. C. Rhoderick, P. A. Johnson, *Appl Spectrosc* 2004, 58, 1452.
- [7] Y. Maréchal, *The Journal of Chemical Physics* 1987, 87, 6344.
- [8] J. Mullens, J. Yperman, R. Carleer, D. Franco, L. C. Van Poucke, J. Van der Biest, *Applied Clay Science* 1993, 8, 91.
- [9] S. Singh, C. Wu, P. T. Williams, *Journal of Analytical and Applied Pyrolysis* 2012, 94, 99.
- [10] J. L. Gurman, L. Baier, B. C. Levin, *Fire Mater.* 1987, 11, 109.
- [11] J. C. Thiéblemont, J. L. Gabelle, M. F. Planche, *Synthetic Metals* 1994, 66, 243.
- [12] J. Fan, S. S. Rezaie, M. Facchini-Rakovich, D. Gudi, C. Montemagno, M. Gupta, *Organic Electronics* 2019, 66, 148.
- [13] N. R. Cameron, *Polymer* 2005, 46, 1439.
- [14] M. S. Silverstein, N. R. Cameron, M. A. Hillmyer, Eds., in *Porous Polymers*, John Wiley & Sons, Inc., Hoboken, NJ, USA, 2011, pp. i–xii.

- [15] I. Pulko, P. Krajnc, *Macromol. Rapid Commun.* 2012, 33, 1731.
- [16] M. S. Silverstein, *Progress in Polymer Science* 2014, 39, 199.
- [17] O. J. A. Schueller, S. T. Brittain, C. Marzolin, G. M. Whitesides, *Chem. Mater.* 1997, 9, 1399.
- [18] G. M. Jenkins, K. Kawamura, *Polymeric Carbons: Carbon Fibre, Glass and Char*, Cambridge University Press, Cambridge, 2011.
- [19] J. X. Zhao, R. C. Bradt, P. L. Walker, *Carbon* 1985, 23, 15.

## CHAPTER 3

Designing thermally compatible template-coating pairs toward dimensionally stable 3D porous carbons with tunable density\*



\*Note: portions of this chapter were taken from a first-authored manuscript submitted (as of June 2025) to *Advanced Functional Materials*.

### **3.1 Abstract**

The macroscale fabrication of three-dimensional (3D) porous carbons with adjustable density and hierarchical architecture is crucial for emerging applications in energy storage, chemical separations, and lightweight structural materials. The pyrolytic conversion of polymer precursors is a common route to 3D porous carbon architectures, which typically relies on a single porous polymer precursor to function both as the structural blueprint and the carbon source. However, this approach can lead to substantial volume reduction, poor mass retention, and loss of architectural features, necessitating compromises between structural inheritance, dimensional stability, and control of density during pyrolysis. Here we utilize a template-coating platform that separates these conflicting requirements, facilitating independent optimization of mass and architecture. Specifically, a series of polybenzoxazine coatings were investigated to target early carbonization, minimal degradation, and high char yield. Concurrently, a complementary series of hierarchically porous polystyrene template architectures with tunable thermal properties was developed to meet synthetic and thermal compatibility criteria. The optimized template-coating combination results in porous carbons that retain the architectural features of the template while maintaining dimensional integrity of ca. 90% (< 10% linear shrinkage). By adjusting the coating weight fraction and pyrolysis temperature, we demonstrated a broad range of bulk densities ( $\sim 0.1 - 0.7 \text{ g cm}^{-3}$ ) while preserving structural and dimensional integrity (> 80 % volume retention). Importantly, these materials occupy a previously inaccessible region in the density-retention landscape, showcasing low-density porous carbons with minimal shrinkage (< 20 vol%). This work presents a versatile design platform for the macroscale fabrication of structurally and dimensionally stable 3D porous carbons, allowing deterministic control over density across a wide range.

**Keywords:** porous carbon foam, pyrolytic carbon, porous polymer, template-coating pair, macroscale, dimensional stability, specific strength

## **3.2 Introduction**

Density is a fundamental parameter in material selection, influencing key performance metrics such as the strength-to-weight ratio, thermal conductivity, and fracture resistance<sup>[1]</sup>. In designing porous materials for specific applications, the porous materials architecture—the spatial arrangement of mass—is equally important. This highlights the need for materials with tunable hierarchical features spanning several orders of magnitude in length scale<sup>[2–6]</sup>. Among these, three-dimensional (3D) porous carbons represent a distinct subset of porous materials whose architecture and density can be deliberately tuned across length scales, enabling precise control over structure–property relationships. Unlike conventional porous carbons, typically derived from biomass pyrolysis<sup>[7,8]</sup>, 3D porous carbons, such as foams, are derived from engineered precursors using techniques like emulsion templating, 3D printing, and self-assembly<sup>[9]</sup>. Inspired by the structural hierarchy of natural materials such as bone and wood<sup>[10,11]</sup>, 3D porous carbons integrate tunable architecture with hierarchical porosity, featuring interconnected micropores ( $< 2$  nm), mesopores ( $2 - 50$  nm), and macropores ( $> 50$  nm), which enables enhanced structural control across multiple scales and access to a wide range of densities<sup>[12–15]</sup>.

At the macroscale, the form factor of the precursor determines the overall shape and bulk volume<sup>[16]</sup>, as illustrated by carbon fibers derived from the pyrolysis of electrospun polyacrylonitrile (PAN)<sup>[17]</sup>, carbon foams derived from the pyrolysis of emulsion-templated froths<sup>[18]</sup>, and carbon nanolattices obtained from the pyrolysis of 3D-printed polymer microlattices<sup>[19]</sup>. At the microscale, porosity—defined by void volume and pore distribution—can be customized using techniques such as sacrificial particle leaching to create macropores, polymer microphase separation to generate mesopores<sup>[20–22]</sup>, and surface activation to produce nanopores<sup>[23,24]</sup>. At the nanoscale, skeletal density represents the internal packing of the carbon framework and can be adjusted through precursor chemistry<sup>[25–27]</sup> and pyrolysis conditions<sup>[28–30]</sup>. Researchers have leveraged this synthetic versatility to

develop lightweight 3D porous carbons, with densities ranging from  $\sim 0.005 \text{ g cm}^{-3}$  to  $\sim 0.9 \text{ g cm}^{-3}$ , which enables their use in emerging applications such as energy storage<sup>[31–34]</sup>, plastic upcycling<sup>[35,36]</sup>, CO<sub>2</sub> capture<sup>[37–39]</sup>, electrochemical separations<sup>[40–42]</sup>, and impact mitigation<sup>[43–47]</sup>.

3D porous carbon structures are typically produced by pyrolyzing single polymer precursors in a two-stage process involving an initial thermal decomposition ( $\sim 200 - 400 \text{ }^{\circ}\text{C}$ ) to yield a carbon-rich matrix, followed by carbonization ( $> 400 \text{ }^{\circ}\text{C}$ ), which promotes dehydrogenation and structural ordering. Using a porous polymer as the precursor to 3D porous carbons can be challenging as they often undergo severe shrinkage, warpage, or collapse during pyrolysis (Fig. 1A)<sup>[48–52]</sup>. To address this, thermal stabilization techniques, such as resin impregnation<sup>[53]</sup> and hyper-crosslinking<sup>[54–58]</sup>, have been employed to improve char yield and mitigate shrinkage<sup>[59–62]</sup>. However, these treatments—particularly those involving harsh chemistries like sulfonation<sup>[63–66]</sup>—can induce distortions in the precursor architecture, resulting in porous carbon with less controllable geometry and bulk density.

Mechanical stabilization approaches provide an alternative pathway by reinforcing the polymer matrix with carbon-based fillers like carbon dots<sup>[67]</sup>, reduced graphene oxide (rGO) flakes<sup>[68–71]</sup>, carbon fibers<sup>[72,73]</sup>, or Co nanoparticles<sup>[74]</sup>. These fillers can enhance structural retention and suppress shrinkage at the macroscale but often suffer from inhomogeneous dispersion, leading to stress concentration, microcracking, and compromised pore architecture. While carbon fillers remain embedded in the final structure, resulting in inflated densities that are challenging to tune, non-carbon fillers like silica nanoparticles, which can be etched away after pyrolysis, can be used to improve porosity and lower density<sup>[75–77]</sup>. However, this introduces added processing complexity and can diminish mechanical stability. Collectively, these trade-offs underscore the challenges in the macroscale fabrication of application-specific 3D porous carbons: maintaining architecture and dimensional integrity while achieving tunable control over the final product density.

As a route to overcome these limitations a template-coating pair design framework was introduced that resolves the coupled constraints faced by single precursors (Fig. 1B)<sup>[78]</sup>. Instead of relying on a single precursor to serve as both the structural blueprint and the primary carbon source, the template-coating approach delineates these functions into a two-component system comprising a structurally robust template and a high-char-yield coating. In this initial work the template (a polystyrene-based poly(high internal phase emulsion), PolyHIPE) serves as the architectural blueprint, defining the macroscopic geometry and hierarchical pore distribution, while a conformal coating (poly(3,4-ethylenedioxythiophene, PEDOT) acts as the primary carbon source, specifically designed to imprint and transcribe the template architecture into pyrolytic carbon. By independently adjusting the coating thickness (to control mass retention) and pyrolysis temperature (to control volume retention), this framework allows for bottom-up control over the mass and volume contributions to bulk density.

Building on this strategy, the current work advances the template-coating approach by investigating the use of polybenzoxazine coatings paired with various hierarchically porous poly(HIPE) templates. Specifically, a series of polybenzoxazine coatings was investigated to target early carbonization, minimal degradation, and high char yield. Concurrently, a complementary series of hierarchically porous polystyrene template architectures with tunable thermal properties was developed to meet synthetic and thermal compatibility criteria. The objective is to identify the most thermally compatible template-coating pair, effectively decoupling the trade-offs that often limit conventional single-precursor pyrolysis. The optimized pair yields porous carbons with complete structural inheritance and exceptional dimensional stability (~80% volume retention). Systematic studies on coating concentration and pyrolysis temperature reveal how these parameters influence the final bulk density, which ranges from approximately 0.1 to 0.7 g cm<sup>-3</sup>, while demonstrating dimensional retention exceeding 90%. Crucially, the resulting materials occupy a previously inaccessible region of

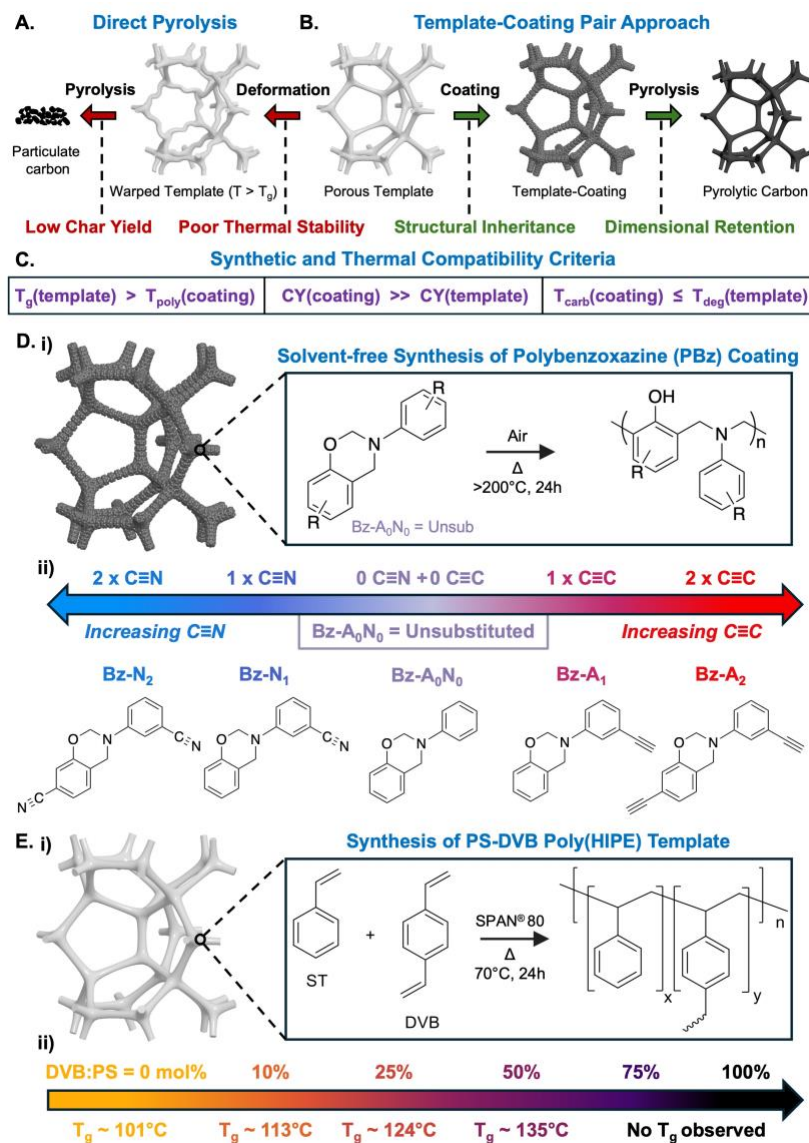
the density–retention landscape, successfully achieving low density alongside low shrinkage. This work establishes a generalizable and scalable platform for crafting dimensionally stable 3D porous carbons with precisely tunable architecture and density suitable for various applications.

### **3.3 Results and Discussion**

#### **3.3.1 Template-Coating Compatibility Criteria**

Template-coating pairs must satisfy both synthetic and thermal compatibility criteria to produce structurally and dimensionally stable 3D porous carbons with tunable mass density (Fig. 1C). Synthetic compatibility ensures that the coating integrates effectively with the template architecture without inducing structural deformation before pyrolysis. This requires that the glass transition temperature of the template ( $T_g(\text{template})$ ) exceeds the polymerization temperature of the coating ( $T_{\text{poly}}(\text{coating})$ ) to prevent softening and subsequent pore collapse during the coating synthesis (i.e.,  $T_{\text{poly}}(\text{coating}) < T_g(\text{template})$ ). Additional thermal compatibility requirements are necessary to preserve the structural features during the pyrolysis of the template-coating pair. Firstly, given that the coating acts as the primary carbon source, it must exhibit a significantly higher char yield compared to the template, which serves as the structural blueprint (i.e.,  $\text{CY}(\text{coating}) \gg \text{CY}(\text{template})$ ). This requirement maximizes the mass retention of the precursor as carbon and minimizes structural deformation resulting from mass loss. Additionally, it is essential that the coating undergo carbonization before the inevitable degradation and collapse of the template, that is,  $T_{\text{carb}}(\text{coating}) \leq T_{\text{deg}}(\text{template})$ . The following section explains how these criteria guide the design and composition of the template and coating.





**Figure 1.** Template-coating pair design strategy and compatibility criteria for tunable porous carbon fabrication. **A)** Illustration of the challenges faced by a porous polymer during direct pyrolysis, often leading to structural deformation and catastrophic collapse due to low char yield and uncontrolled shrinkage. **B)** Depiction of the template-coating pair design strategy, highlighting the roles of the structural blueprint (template) and carbon source (coating). This approach enables the fabrication of dimensionally stable porous carbons with independently tunable architecture and density. **C)** Schematic representation of the synthetic and thermal compatibility criteria, presented as inequalities between measurable thermal properties—including polymerization temperature, glass transition temperature, carbonization onset, and degradation onset. These criteria facilitate the selection of compatible template-coating pairs by ensuring that the coating polymerizes without distorting the template and carbonizes before template degradation, thus preserving structural integrity throughout the synthesis and pyrolysis processes. **D)** (i) Reaction scheme illustrating the ring-opening polymerization of benzoxazine monomers into polybenzoxazine polymer coatings, (ii) monomeric benzoxazine derivatives that incorporate acetylene and nitrile groups to optimize char yield and thermal stability. **E)** (i) Synthetic scheme for the PS-DVB poly(HIPE) template series, (ii) in which compositional tuning of the DVB content used to modulate crosslinking density for compatibility with the polybenzoxazine coatings.

### 3.3.2 Template-Coating Materials Selection

Prior work using this approach employed PS-PEDOT template-coating systems and demonstrated that achieving specific porous carbon densities necessitates precise control over both mass (char yield) and volume (dimensional retention) contributions, parameters primarily influenced by the coating. As such, the pyrolysis of PS–PEDOT template-coating pairs with varying coating thicknesses resulted in high volume retention of up to 50% and mass retention ranging from 15% to 35%, affording access to a range of densities ( $\sim 0.04 - 0.4 \text{ g cm}^{-3}$ )<sup>[78]</sup>. Since bulk density scales with the ratio of char yield to volume retention, increasing the char yield extends the upper bound of accessible densities, while increasing the volume retention decreases bulk density. Accordingly, the first aim was to design a coating system that achieves exceptional char yield and volume retention.

To realize this vision, the coating—acting as the primary carbon source—should exhibit (1) delayed thermal degradation and high thermal stability to maximize char yield and (2) early carbonization to maximize volume retention. Polybenzoxazines (PBz) are a subclass of phenolic resins recognized for their high aromatic content, outstanding char yield<sup>[79–81]</sup>, and thermal tunability<sup>[82,83]</sup>. The synthesis of benzoxazine monomers typically involves a Mannich-like condensation reaction between a phenol, paraformaldehyde, and an aniline, forming a heterocyclic structure that contains oxygen and nitrogen atoms within a six-membered ring (Fig. 1D i)<sup>[84]</sup>. These benzoxazine monomers can undergo thermally induced ring-opening polymerization reactions without the need for an added initiator or catalyst. Furthermore, the functionalization of benzoxazine monomers presents a promising strategy for tailoring the thermal degradation properties of polybenzoxazines<sup>[85]</sup>. Various functional groups, including furan, allyl, nitrile, acetylene, and aldehyde, can be utilized to tune crucial parameters, such as char yield, degradation onset temperature, and activation energy of degradation, all of which significantly impact the thermal stability of the resulting polymer<sup>[86]</sup>. Notably, the incorporation of acetylene<sup>[87–89]</sup> and nitrile<sup>[90–93]</sup> functional groups has been shown to enhance the rigidity of

polybenzoxazine networks through cross-linking reactions, resulting in exceptional thermal stability and high char yields.

Building on these insights, the current work features a series of benzoxazine monomers, designated by PBz-A<sub>m</sub>N<sub>n</sub> (A = acetylene (–C≡C), N = nitrile (–C≡N), m/n = number of A/N groups): PBz-A<sub>0</sub>N<sub>0</sub> (unsubstituted), PBz-A<sub>1</sub>, PBz-A<sub>2</sub>, PBz-N<sub>1</sub>, PBz-N<sub>2</sub> (Fig. 1D ii), were prepared that contain acetylene and nitrile groups incorporated on one or both of the aromatic rings. All Bz-A<sub>m</sub>N<sub>n</sub> were synthesized via a solventless procedure and purified before polymerization (see Methods Section of the Supporting Information for detailed synthesis). Notably, benzoxazines undergo ring-opening polymerization in the 180 – 250°C range, temperatures that far exceed the T<sub>g</sub> of the styrene/10 wt% divinylbenzene(DVB) based poly(HIPE)s used in the prior study. Poly(HIPE)s are viable sacrificial template candidates owing to their high porosity (> 90 vol%), low density (< 0.1 g cm<sup>-3</sup>), and synthetic tunability<sup>[94,95]</sup>. To experimentally validate the significance of synthetic compatibility, a polystyrene/10 wt% DVB poly(HIPE) (T<sub>g</sub>~101°C) was infiltrated with Bz-A<sub>1</sub> and subjected to thermal curing at 190°C to form a conformal coating PBz-A<sub>1</sub> (Fig. S1). As anticipated, the coated sample underwent catastrophic deformation on account of template softening, confirming that the synthetic compatibility condition (i.e., T<sub>g</sub>(template) > T<sub>poly</sub>(coating)) is essential for structural preservation.

Thus, a series of PS-DVB poly(HIPE)s were prepared (Fig. 1E i) to push the template T<sub>g</sub> beyond the coating polymerization temperature (Fig. 1E ii). The templates are hereby designated by PS-DVB-x, where x is the DVB mol% in the organic phase, ranging from x=0% (pure PS poly(HIPE)) to x=100% (pure DVB poly(HIPE)). The resulting series of PS-DVB-x was subjected to SEM to confirm the presence of interconnected voids and hierarchical pores (Fig. S2). DSC analysis confirmed that DVB content significantly elevates T<sub>g</sub> of the PS-DVB poly(HIPE) templates and that > 75 mol% DVB results in poly(HIPE)s with no discernible T<sub>g</sub> by DSC (Fig. S3)<sup>[96]</sup>. This results in a series of

poly(HIPE) templates with varying  $T_g$ , enabling a study of how template architecture, both with and without the coating, is translated into pyrolytic carbon.

### 3.3.3 Degradation Behavior of Polybenzoxazine Coatings

The thermal degradation behavior of PBz- $A_mN_n$  was evaluated using thermogravimetric analysis (TGA; see the Methods Section of the Supporting Information for additional details). Each PBz- $A_mN_n$  polymer was subjected to a direct ramp TGA protocol ( $5\text{ }^\circ\text{min}^{-1}$  to  $700\text{ }^\circ\text{C}$ ), and the resulting thermograms (Fig. 2A) show three key parameters: (1) char yield (CY, wt%), (2) degradation temperature range ( $T_{\text{deg}}$   $^\circ\text{C}$ ), and (3) degradation activation energy ( $E_a$   $\text{kJmol}^{-1}$ ). For qualitative comparison, the degradation profile of PS-DVB-100 (i.e., the most crosslinked and thermally robust template candidate) is included alongside those of PBz- $A_mN_n$  coatings in Figure 2A. These results are summarized in Figure 2B, allowing for a direct comparison of how acetylene and nitrile ( $-\text{C}\equiv\text{N}$ ) substitution influence the thermal stability of polybenzoxazine coatings.

The char yield (CY)—mass retention at  $700\text{ }^\circ\text{C}$  (Fig. 2A)—of the PBz- $A_mN_n$  coatings follows the trend  $\text{PBz-}A_0N_0 < \text{PBz-}N_1 < \text{PBz-}A_1 < \text{PBz-}N_2 < \text{PBz-}A_2$ , with  $\text{PBz-}A_0N_0$  exhibiting the lowest CY value ( $\approx 51\text{ wt}\%$ ) and  $\text{PBz-}A_2$  the highest ( $\approx 81\text{ wt}\%$ ). The data shows that both acetylene and nitrile substitution enhance mass retention during pyrolysis (Fig. 2B; bar labels) and that increasing the degree of substitution leads to higher char yields. The data also show that acetylenes contribute more substantially to char formation than nitriles. Beyond high char yield, delayed degradation is advantageous for minimizing premature volatilization and supporting structural preservation during pyrolysis. Figure 2B (left y-axis) shows a bar graph in which each bar delineates the entire degradation temperature range for each PBz- $A_mN_n$  coating candidate. The bottom of each bar indicates the degradation onset ( $T_{\text{deg}}[\text{onset}]$ ), an “x” inside each bar marks the peak degradation temperature ( $T_{\text{deg}}[\text{peak}]$ ), and the top of the bar represents the degradation endset ( $T_{\text{deg}}[\text{endset}]$ ). The degradation

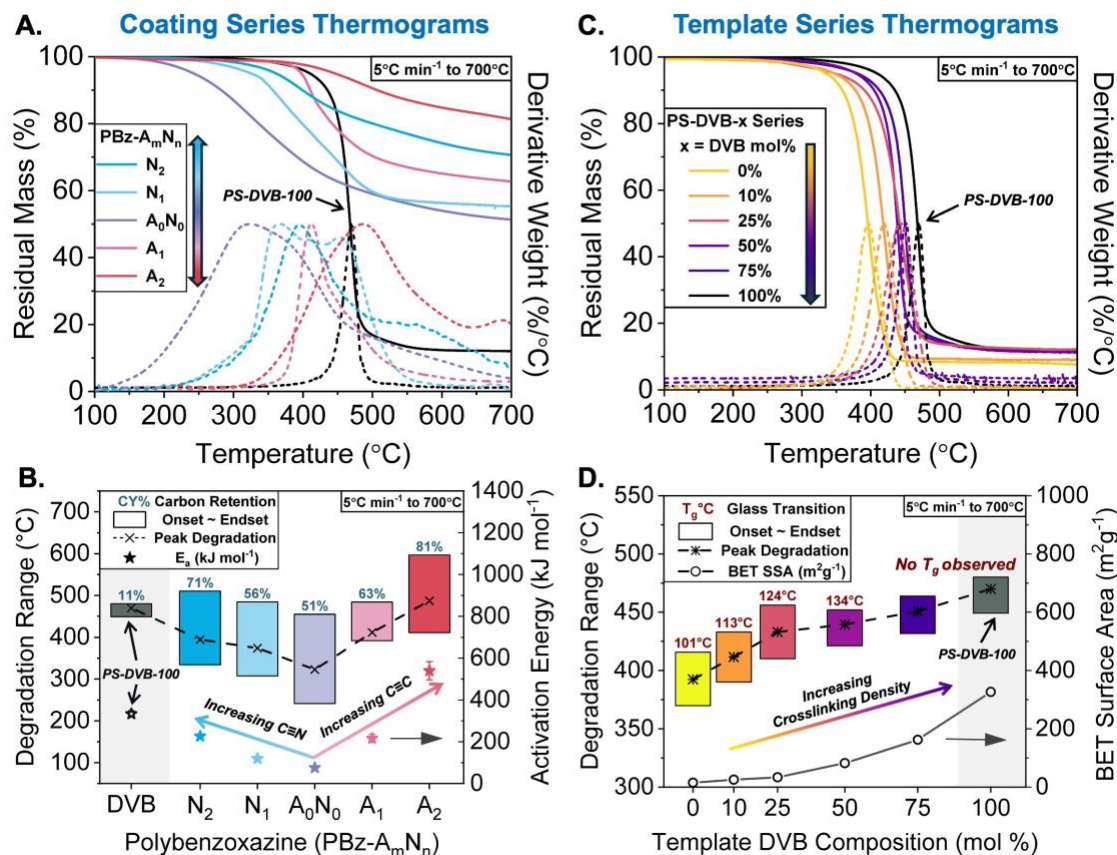
temperature range  $T_{\text{deg}}[\text{onset, peak, endset}]$  follows the same trend as the CY, with PBz-A<sub>0</sub>N<sub>0</sub> exhibiting the lowest peak temperature ( $\sim 326$  °C) and PBz-A<sub>2</sub> the highest ( $\sim 479$  °C). Consistent with the literature, the trends  $T_{\text{deg}}[\text{PBz-A}_0\text{N}_0 < \text{PBz-N}_1 < \text{PBz-N}_2]$  and  $T_{\text{deg}}[\text{PBz-A}_0\text{N}_0 < \text{PBz-A}_1 < \text{PBz-A}_2]$  suggest that increasing the degree of nitrile or acetylene substitution systematically raises  $T_{\text{deg}}$ , confirming that functionalization leads to improved thermal stability<sup>[97,98]</sup>. In line with the trend in CY,  $T_{\text{deg}}[\text{PBz-N}_2 < \text{PBz-A}_2]$  suggests that acetylene substitution stabilizes the polymer against thermal degradation to a greater extent than nitrile substitution.

The activation energy ( $E_a$  kJ mol<sup>-1</sup>) represents the minimum energy required to initiate thermal degradation and is, therefore, expected to correlate with the trend observed in degradation onset. Two TGA protocols were leveraged to evaluate this parameter: high-resolution ramp TGA (HR-TGA) and modulated TGA (Mod-TGA). HR-TGA was conducted at multiple ramp rates ( $\beta = 2 - 20$  °C min<sup>-1</sup>) to extract ramp-averaged peak decomposition temperatures and calculate activation energy using the Kissinger model ( $E_a^{\text{Kiss}}$  kJ mol<sup>-1</sup>) (Fig. S4; see the Methods Section of the Supporting Information for additional details). The strong correlation between  $E_a$  and  $T_{\text{deg}}$  further supports the expected relationship between the energy barrier and delayed degradation (Fig. S5A). Within the acetylene-substituted series, the  $E_a$  trend is  $\text{PBz-A}_0\text{N}_0 < \text{PBz-A}_1 < \text{PBz-A}_2$  suggests that increasing the number of acetylenes progressively raises the decomposition barrier. Nitrile substitution also increases  $E_a$ , as reflected in the trend  $\text{PBz-N}_1 < \text{PBz-A}_1 < \text{PBz-N}_2 < \text{PBz-A}_2$ , although to a lesser extent than acetylenes.

For comparison, Mod-TGA (Fig. S5B) applies an oscillatory ramp to minimize thermal lag and baseline drift and enables model-free estimation of activation energy ( $E_a^{\text{Mod}}$ ; see the Methods Section of the Supporting Information for additional details). Both methods produced consistent trends, with  $E_a^{\text{Kiss}}$  and  $E_a^{\text{Mod}}$  following the order  $\text{PBz-A}_0\text{N}_0 < \text{PBz-N}_1 < \text{PBz-A}_1 < \text{PBz-N}_2 < \text{PBz-A}_2$  (Fig. S5C). Represented by star symbols in Figure 2B (right y-axis), PBz-A<sub>0</sub>N<sub>0</sub> ( $\sim 76$  kJ mol<sup>-1</sup>) requires

the least energy to initiate decomposition, and PBz-A<sub>2</sub> requires the most ( $\sim 540 \text{ kJ mol}^{-1}$ ). This sevenfold increase underscores the substantial improvement in thermal stability induced by acetylene or nitrile moieties.

Taken together, these results confirm that PBz-A<sub>2</sub> exhibits the most favorable decomposition profile among the PBz-A<sub>m</sub>N<sub>n</sub> series, combining the highest char yield ( $\sim 81 \text{ wt}\%$ ), peak degradation temperature ( $\sim 479 \text{ }^{\circ}\text{C}$ ), and degradation activation energy ( $\sim 540 \text{ kJ mol}^{-1}$ ). These attributes make PBz-A<sub>2</sub> the strongest coating candidate for structural preservation during pyrolysis and for enabling tunable porous carbon density. Accordingly, PBz-A<sub>2</sub> was selected as the primary coating candidate for compatibility screening with the PS-DVB-x template series.



**Figure 2.** Thermal characterization of coating and template candidates for compatibility screening. **A)** TGA thermograms for the polybenzoxazine coating series (PBz-A<sub>m</sub>N<sub>n</sub>) alongside the PS-DVB-100 template control demonstrate variations in thermal degradation behavior and residual mass among the functionalized compositions. **B)** A summary of the thermal degradation characteristics for the PBz-A<sub>m</sub>N<sub>n</sub> series, including degradation temperature ranges (bars), char yields at 700 °C (bar labels), and activation energies derived from Kissinger analysis (stars). **C)** TGA thermograms for the PS-DVB-x poly(HIPE) template series exhibit the impact of crosslinking density on degradation onset and mass retention, emphasizing the sacrificial behavior of these materials during pyrolysis. **D)** A summary of the PS-DVB-x template properties, including degradation temperature ranges (bars), glass transition temperatures (bar labels), and BET surface areas (open circles). The systematic variation within the PS-DVB-x series facilitates the selection of an optimal template based on thermal resilience and compatibility.

### 3.3.4 Degradation Behavior of Poly(HIPE) Templates

To evaluate the thermal degradation behavior of the PS-DVB-x poly(HIPE) templates, thermogravimetric analysis (TGA) was conducted under nitrogen using a direct ramp of  $5\text{ }^{\circ}\text{min}^{-1}$  to  $700\text{ }^{\circ}\text{C}$ . The resulting TGA thermograms and their corresponding first derivatives are shown in Figure 2C, providing a clear visualization of the thermal degradation behavior across the PS-DVB-x series. The first derivative curves indicate a distinct shift in the degradation profile as the DVB content increases, suggesting enhanced thermal stability due to a higher crosslinking density. Additionally, the char yield at  $700^{\circ}\text{C}$  increased slightly with added DVB content, ranging from approximately 8 wt% (pure PS) to 11 wt% (pure DVB) (Fig. 2C). Notably, the char yield for all PS-DVB-x templates was significantly lower than that of any PBz-A<sub>m</sub>N<sub>n</sub> coating and particularly lower than that of the primary coating candidate, PBz-A<sub>2</sub> ( $\sim 81\text{ wt}\%$ ), thus satisfying the thermal compatibility requirement that  $\text{CY}(\text{template}) \ll \text{CY}(\text{coating})$ .

Figure 2D shows the degradation window for each PS-DVB-x template. Each bar represents the full degradation temperature range, with the bottom marking the onset and the top marking the endset. As expected, the onset and endset temperatures increase monotonically from PS-DVB-0 ( $\sim 369 - 415\text{ }^{\circ}\text{C}$ ) to PS-DVB-100 ( $\sim 448 - 480\text{ }^{\circ}\text{C}$ ). The consistent shift to higher temperatures reflects the enhanced thermal stability imparted by greater crosslink density in the polymer network.

While templates PS-DVB-10 through PS-DVB-50 showed improved thermal behavior with increasing DVB content, only PS-DVB-75 and PS-DVB-100 exhibited no detectable  $T_g$  below  $200\text{ }^{\circ}\text{C}$ , suggesting that these templates would not exhibit significant deformation at the ring-opening polymerization temperature of the PBz-A<sub>m</sub>N<sub>n</sub> coatings ( $\sim 190\text{ }^{\circ}\text{C}$ ). Among these, PS-DVB-100 featured the highest specific surface area ( $\sim 300\text{ m}^2\text{g}^{-1}$ ), which could facilitate more uniform coating infiltration and enhanced interfacial contact during curing (Fig. 2D, right y-axis). Based on its superior



thermal stability and highest specific surface area, PS-DVB-100 was selected as the primary template candidate for pairing.

### 3.3.5 Verification of Template-Coating Compatibility

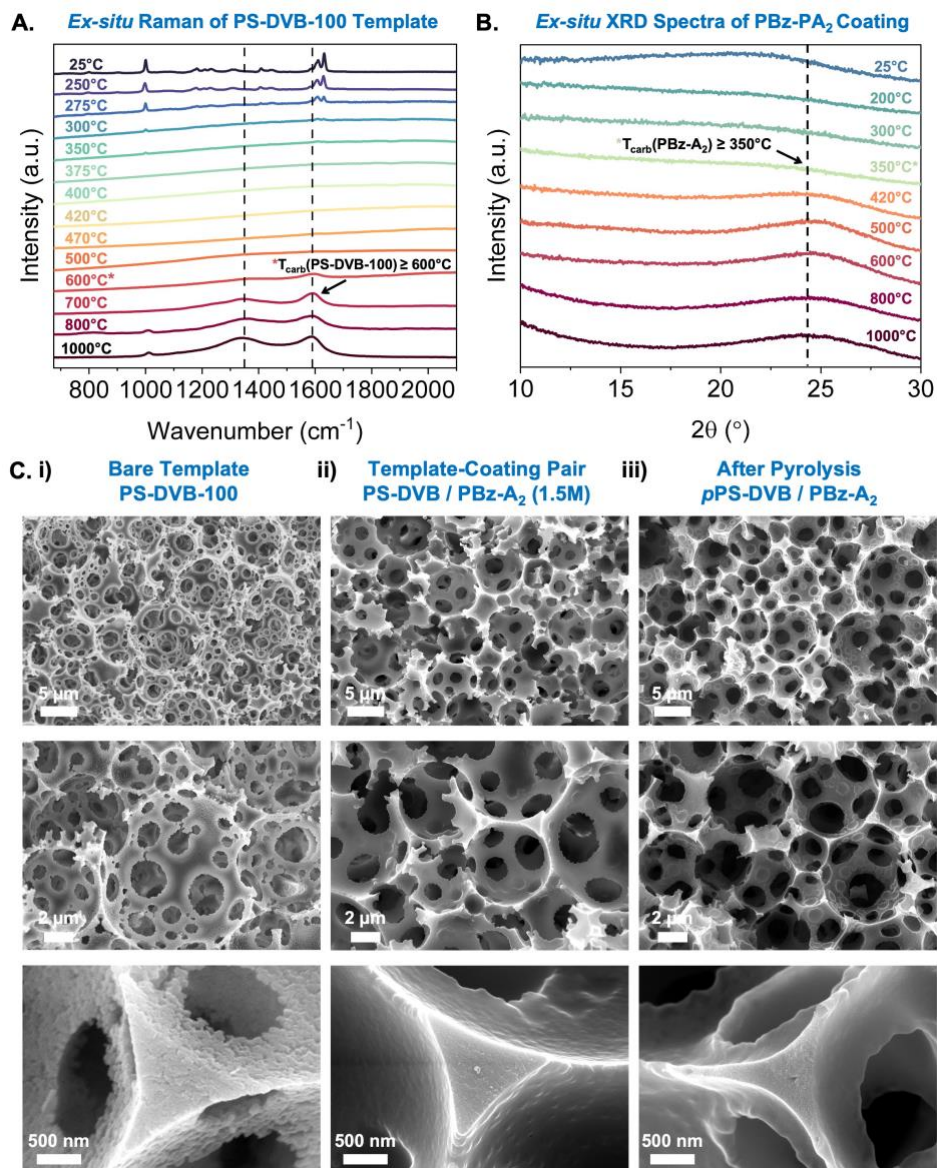
The individual characterization of the degradation behavior of the PBz-A<sub>m</sub>N<sub>n</sub> coatings (Section 2.3) and PS-DVB-x templates (Section 2.4) revealed PBz-A<sub>2</sub> and PS-DVB-100 as a viable candidate pair. When considered together, PS-DVB-100 does not display a T<sub>g</sub> before the ring-opening polymerization temperature of PBz-A<sub>2</sub> (~190 °C), and PBz-A<sub>2</sub> exhibits significantly higher char yield (~81 wt%) than PS-DVB-100 (~11 wt%). To validate the final thermal compatibility condition—that PBz-A<sub>2</sub> undergoes carbonization before PS-DVB-100 undergoes degradation (~450 °C)—the carbonization onset temperatures of the template and coating candidates were determined via *ex-situ* variable-temperature experiments.

In these *ex-situ* experiments, PS-DVB-100 and PBz-A<sub>2</sub> with known initial mass and dimensions were placed into a furnace and heated at 5 °C min<sup>-1</sup> to a target temperature (T<sub>pyrolysis</sub> °C), varying from 200 to 800 °C (Fig. S6). Each sample was held isothermally at its target temperature for 30 minutes to eliminate thermal lag artifacts and allow it to equilibrate to the furnace temperature. After cooling, the samples were recovered and characterized using spectroscopic (Raman spectroscopy, X-ray diffraction (XRD)) and microscopic (Scanning Electron Microscopy (SEM)) techniques to evaluate structural and dimensional stability evolution.

Variable-temperature Raman spectroscopy was conducted on PS-DVB-100 to determine its carbonization onset temperature (T<sub>carb</sub>), defined as the temperature at which the characteristic G band (~1582 cm<sup>-1</sup>) and D band (~1350 cm<sup>-1</sup>) first appear. As illustrated in Figure 3A, T<sub>carb</sub> for PS-DVB-100 is ~600 °C, significantly above its degradation onset (~450 °C). This confirms that the template does not undergo carbonization before decomposition, which explains its low char yield. In contrast, PBz-

A<sub>2</sub> proved unsuitable for Raman analysis due to rapid laser-induced carbonization occurring even at minimal laser power at room temperature (Fig. S7), indicating a high propensity for carbonization<sup>[79,85]</sup>. To address this issue, variable-temperature X-ray diffraction (XRD) was performed, where T<sub>carb</sub> is identified by the emergence of a broad diffraction peak centered around 24°, characteristic of the (002) diffraction mode in disordered pyrolytic carbon. This peak signifies the formation and stacking of graphitic carbon ribbon domains within an amorphous carbon matrix<sup>[99]</sup>. As depicted in Figure 3B, the T<sub>carb</sub> for PBz-A<sub>2</sub> is ~350°C, confirming that the coating carbonizes well before the template degrades. It is hypothesized that satisfaction of this final thermal compatibility condition (i.e., T<sub>carb</sub>(coating) ≤ T<sub>deg</sub>(template)) should enable good structural inheritance by allowing the coating to harden and form a carbon shell prior to template degradation and imminent collapse.

Having satisfied the synthetic and thermal compatibility criteria, a series of PBz-A<sub>2</sub> coated PS-DVB-100 poly(HIPE)s, herein referred to as PS-DVB/PBz-A<sub>2</sub>, was created using the following procedure. Uniformly cut PS-DVB-100 poly (HIPE) template pieces (Fig. 3C i) were soaked in a solution of PBz-A<sub>2</sub> in chloroform (1.5 M) for 24 hours under house vacuum to facilitate monomer penetration. The infiltrated samples were thermally cured in an air-circulating oven at 200°C for 24 hours, followed by Soxhlet extraction with methanol and vacuum drying. SEM analysis of the PS-DVB/PBz-A<sub>2</sub> before pyrolysis (Fig. 3C ii) confirms the formation of a smooth, conformal coating uniformly covering the template's internal surface without observable strut deformation. Following pyrolysis, SEM analysis of the *p*PS-DVB/PBz-A<sub>2</sub> (where “p” indicates pyrolysis) confirms complete preservation of the original template architecture, with pore connectivity and strut morphology remaining visually intact (Fig. 3C iii).



**Figure 3.** Verification of carbonization onset and structural inheritance through spectroscopic and microscopic characterization. **A)** Variable-temperature Raman spectra of PS-DVB-100 demonstrate the emergence of the characteristic D and G bands ( $\sim 1350$  cm<sup>-1</sup> and  $\sim 1582$  cm<sup>-1</sup>, respectively) at  $\sim 600$  °C, confirming that template carbonization commences only after degradation ( $\sim 450$  °C). **B)** Variable-temperature XRD spectra of PBz-A<sub>2</sub> exhibit a broad peak near 24 ° (002) at  $\sim 350$  °C, indicating the formation of disordered graphitic carbon and suggesting that early carbonization occurs before template degradation. **C)** SEM images illustrating **(i)** the pristine PS-DVB-100 template, **(ii)** PS-DVB/PBz-A<sub>2</sub> following coating (1.5M) and curing, which displays a smooth and conformal polybenzoxazine layer while maintaining intact porosity and strut morphology, and **(iii)** pPS-DVB/PBz-A<sub>2</sub> (after pyrolysis) confirms structural inheritance and volume preservation of the original template architecture.

### 3.3.6 Structural Evolution of Template-Coating Pairs

With qualitative structural inheritance confirmed post-pyrolysis, a detailed quantitative analysis was carried out to evaluate the dimensional stability of the optimized pair across multiple length scales. First, the mass retention evolution profile of *p*PS-DVB/PBz-A<sub>2</sub>—composed of ~90 wt% PS-DVB-100 and 10 wt% PBz-A<sub>2</sub> before pyrolysis—and the bare *p*PS-DVB-100 template as a function of pyrolysis temperature (5 °min<sup>-1</sup> to T°C, 30-minute isotherm) was quantified. Figure 4A shows a substantially higher char yield for the pair (~80 wt%) relative to the bare PS-DVB-100 template (~11 wt%), clearly underscoring the vital role of the coating in enhancing the char yield while the template functions as the structural blueprint.

Next, the shrinkage behavior upon pyrolysis was quantified at the macroscale by tracking bulk dimensions as a function of pyrolysis temperature. Figure 4B plots dimensional retention (Characteristic length  $L/L_0$ ) and volume retention ( $V/V_0$ ) for the optimized pair and the bare PS-DVB-100 template. For the bare template, volume retention closely follows its mass retention curve, indicating that mass loss primarily drives bulk shrinkage. As thermal degradation progresses, the rapid depletion of template material results in diminishing structural integrity, leading to shrinkage and severe structural collapse. In contrast, the optimized pair exhibits excellent dimensional stability (~90% retention). These results demonstrate the efficacy of the template-coating design strategy in preserving both the structural integrity and dimensional fidelity of 3D porous carbon architectures during pyrolytic conversion.

To confirm structural inheritance at the microscale, SEM analyses of the bare *p*PS-DVB-100 template and the *p*PS-DVB/PBz-A<sub>2</sub> template-coating pair across various pyrolysis temperatures were conducted. Figure 4C shows representative SEM images of the bare *p*PS-DVB-100 template at four key stages of pyrolytic conversion: 300°C, 470°C (degradation), 600°C (carbonization), and 800 °C.

After a 30-minute hold at 300 °C, the PS-DVB-100 template appears visually intact. However, because PS-DVB-100 undergoes extensive degradation before carbonization, there is insufficient mass to support the template architecture. This degradation-driven collapse becomes evident by 470 °C, where the original void morphology is destroyed, rendering the template architecture unrecognizable. By 600 °C, after degradation is complete, the minimal residual carbon (~12 wt%) shows signs of structural hardening consistent with the onset of carbonization, corroborated by the faint D and G bands emerging in variable-temperature Raman spectra at this temperature (Fig. 3A). By 800 °C, the pyrolyzed *p*PS-DVB-100 sample is destroyed where the retained pyrolytic carbon exists only in the form of thin, disconnected shards.

Figure 4D shows the SEM images of the *p*PS-DVB/PBz-A<sub>2</sub> pair at four key pyrolysis temperatures: 300 °C, 470 °C, 600 °C, and 800 °C. In contrast to the bare template, the pair undergoes early carbonization and delayed degradation, demonstrating complete structural preservation throughout the pyrolysis process. During the carbonization of *p*PS-DVB/PBz-A<sub>2</sub>, the coating transforms into a carbonaceous network comprising crystalline sp<sup>2</sup>-hybridized carbon domains within an amorphous sp<sup>2</sup>-hybridized carbon matrix (Fig. S8). This transformation effectively hardens the structure and enhances the resistance of the template-coating pair to thermal decomposition, thereby preserving the architecture and dimensions throughout pyrolysis.

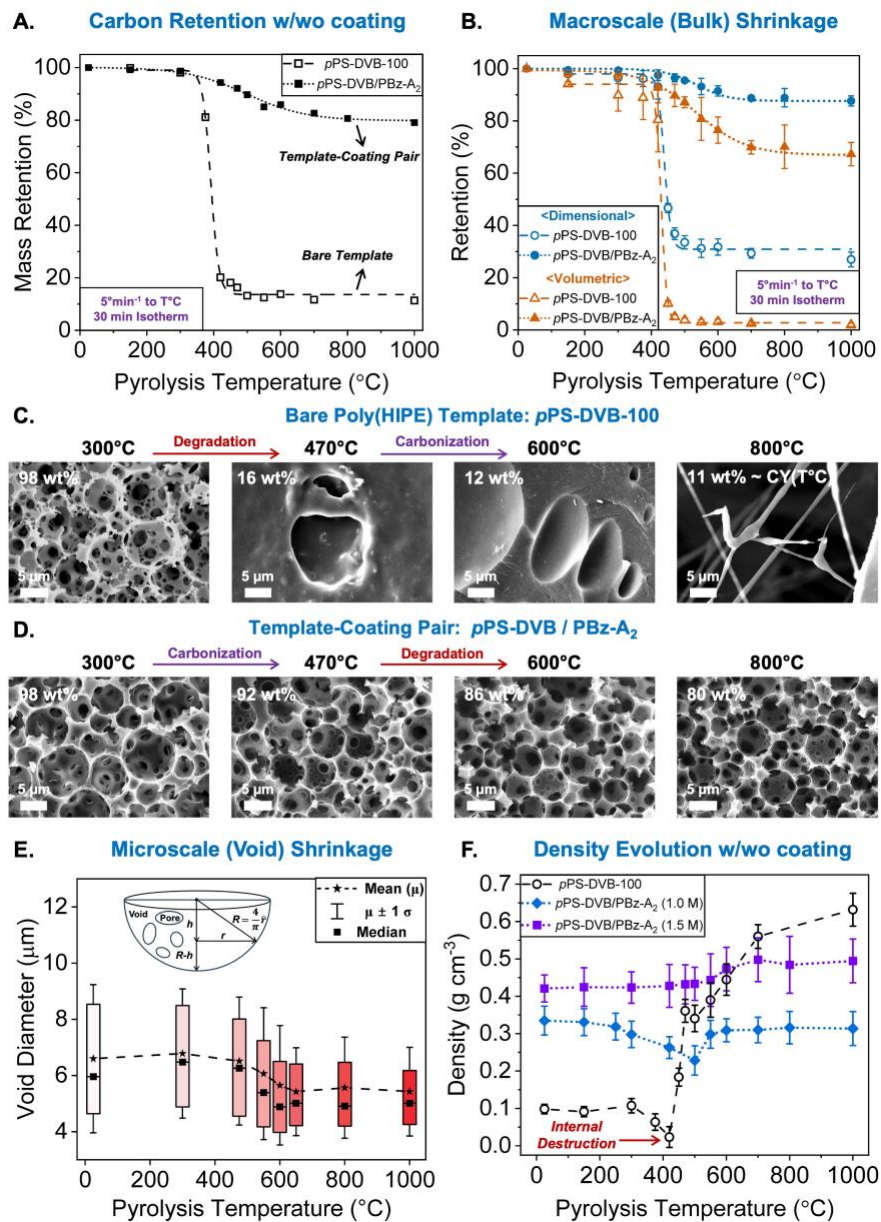
To quantify shrinkage at the microscale, the evolution of the void diameter in *p*PS-DVB/PBz-A<sub>2</sub> was analyzed as a function of pyrolysis temperature using automated SEM image analysis (Fig. 4E; See Appendix Section of the Supporting Information). A standard correction factor of  $4/\pi$  was applied to compensate for the statistical bias where spherical pores intersected by a 2D imaging plane appear smaller unless sectioned through their centers; integrating over all sectioning positions results in an average measured radius of  $R \cdot \pi/4$ . By applying this correction, it is possible to estimate the true void

diameters from 2D SEM image projections (Fig. 4E, inset). The corrected void diameter distributions at various pyrolysis temperatures (light red to dark red) are illustrated as a bar chart, with each bar indicating the interquartile range, star symbols denoting medians, and square symbols denoting means. Initially, the mean and median void diameters are approximately 6.0  $\mu\text{m}$  and 6.5  $\mu\text{m}$ , respectively. Following pyrolysis at 800  $^{\circ}\text{C}$ , these values decrease to 5.0  $\mu\text{m}$  and 5.6  $\mu\text{m}$ , reflecting a void dimension retention of  $\sim 85\%$  and a void volume retention of  $\sim 65\%$ . This shrinkage is predominantly observed within the 400–700  $^{\circ}\text{C}$  range, which coincides with the primary degradation window, underscoring the relationship between polymer decomposition and structural contraction. Compared to the bulk volume loss ( $\sim 30\text{ vol}\%$ ), the  $\sim 16\%$  void volume loss implies the creation of internal free volume during the pyrolysis process. This differential shrinkage may result from morphological changes in the strut cross-sections, which appear triangular before pyrolysis but resemble more concave triangular shapes after pyrolysis (Fig. 3C; bottom), thus enhancing internal free space while maintaining external dimensions.

To probe the effects of mass and volume retention on bulk density, Figure 4F plots the density evolution of the *p*PS-DVB-100 template and *p*PS-DVB/PBz-A<sub>2</sub> as a function of pyrolysis temperature. The initial, pre-pyrolysis density of the template ( $\sim 0.1\text{ g cm}^{-3}$  at 25  $^{\circ}\text{C}$ ; Fig. 4F: black circles) sharply decreases, reaching a minimum of  $\sim 0.02\text{ g cm}^{-3}$  by 420  $^{\circ}\text{C}$ . This drop corresponds to rapid mass loss due to degradation, consistent with the collapse observed in SEM (Fig. 4C). As degradation progresses, the rapid mass loss is quickly followed by structural destruction and volume loss (Fig. S9), resulting in a steep density increase between 500–700  $^{\circ}\text{C}$ , ultimately plateauing around  $\sim 0.63\text{ g cm}^{-3}$  by 1000  $^{\circ}\text{C}$ . In contrast, *p*PS-DVB/PBz-A<sub>2</sub> exhibits a significantly higher initial density ( $\sim 0.43\text{ g cm}^{-3}$  at 25  $^{\circ}\text{C}$ ; Fig. 4F: purple squares), reflecting the substantially higher coating weight fraction ( $\sim 90\text{ wt}\%$ ). As pyrolysis proceeds, the density increases gradually and reaches  $\sim 0.50\text{ g cm}^{-3}$  at 800  $^{\circ}\text{C}$ , with the most densification occurring in the 500–700  $^{\circ}\text{C}$  range, coinciding with the shrinkage window identified

previously. Overall,  $p$ PS-DVB/PBz-A<sub>2</sub> experiences a mass loss of ~20% and a volume loss of ~30%, resulting in a net increase in bulk density of ~16%.

For additional comparison, a PS-DVB/PBz-A<sub>2</sub> pair with a lower coating weight fraction—synthesized using [Bz-A<sub>2</sub>] = 1.0 M and composed of ~30 wt% PS-DVB-100 and ~70 wt% PBz-A<sub>2</sub>—displays a density profile (Fig. 4F: blue diamonds) that closely follows the weighted average of its two pyrolytic constituents— $p$ PS-DVB-100 and  $p$ PBz-A<sub>2</sub>. These findings confirm the ability to independently adjust the density of porous carbons through variations in coating weight fraction and pyrolysis temperature, or a combination of both.



**Figure 4.** Temperature evolution of structural and dimensional retention observed in thermally Compatible template-coating pairs. **A)** Mass retention profiles for the bare template and the template-coating pair as a function of pyrolysis temperature, illustrating the contrasting degradation behavior and char yield of pPS-DVB-100 and pPS-DVB/PBz-A<sub>2</sub> (synthesized using [Bz-A<sub>2</sub>] = 1.5 M). This emphasizes the distinct roles of the coating as a carbon source and the template as a sacrificial scaffold. **B)** Assessment of dimensional and volume retention for the optimized pair compared to the bare template across various pyrolysis temperatures, revealing that the shrinkage evolution profile aligns with the mass loss profile. SEM images of the **C)** bare pPS-DVB-100 template and **D)** pPS-DVB/PBz-A<sub>2</sub> pair at four critical temperatures (300 °C, 470 °C, 600 °C, 800 °C) illustrate the importance of the coating in maintaining structural integrity. **E)** A quantitative analysis of void diameter in pPS-DVB/PBz-A<sub>2</sub> as a function of pyrolysis temperature, with an inset displaying the correction factor for projected estimations through image analysis. **F)** Bulk density as a function of pyrolysis temperature, confirming the capability to independently control density through coating weight fraction and pyrolysis temperature.



### 3.3.7 Tuning the Properties of Porous Carbons

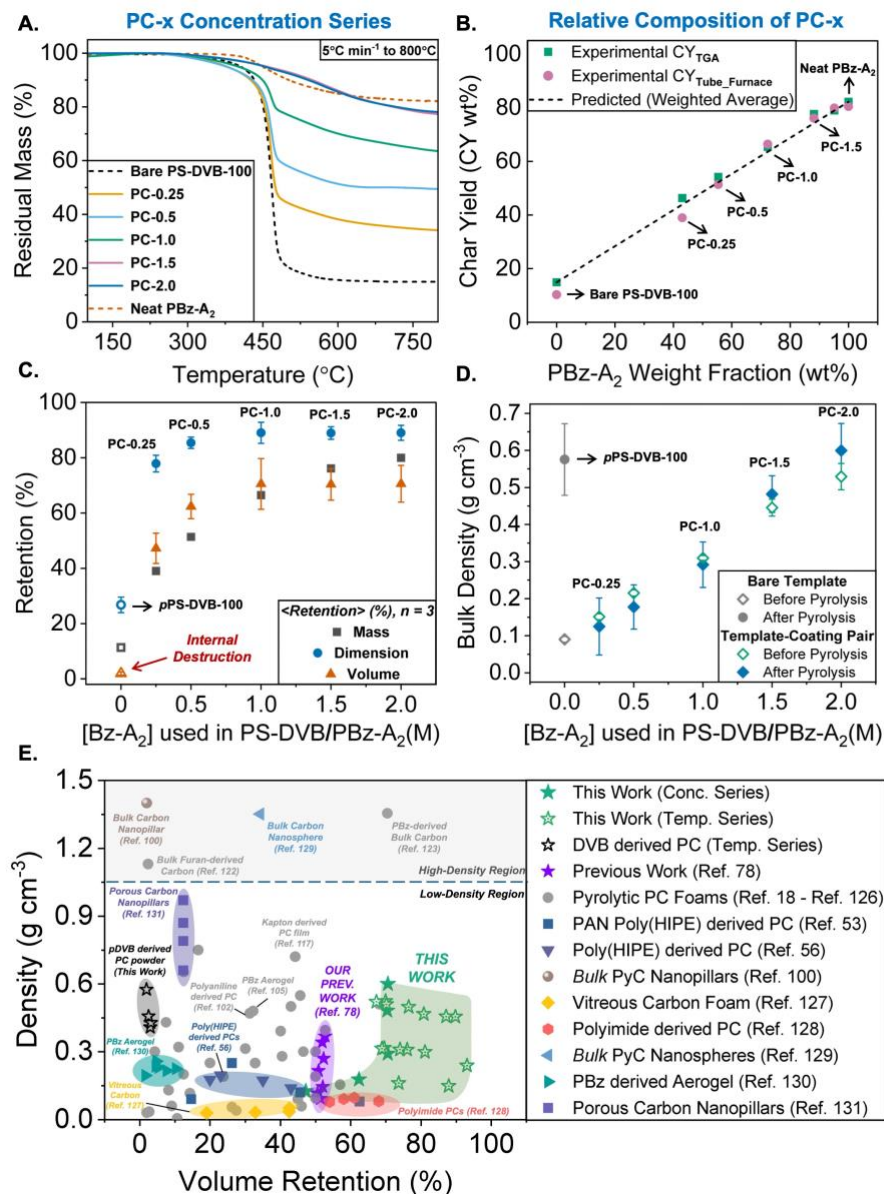
Having established the compatibility and performance of the PS-DVB/PBz-A<sub>2</sub> template-coating pair, the next goal was to investigate how tuning the carbon content modulates the key properties of the resulting porous carbon. Specifically, the concentration of the coating monomer solution was varied from 0.25 M to 2.0 M to control the weight fraction of the PBz-A<sub>2</sub> coating relative to the PS-DVB-100 template. The resulting pyrolytic carbons are herein denoted by “PC-x,” where “PC” represents porous carbon and “x” indicates the benzoxazine monomer solution concentration (in M) used to synthesize the PS-DVB/PBz-A<sub>2</sub> precursor.

Figure 5A shows the thermograms of the PC-x samples across this concentration range alongside those of the bare PS-DVB-100 template and neat PBz-A<sub>2</sub> coating. The char yield increases monotonically from ~40 wt% (PC-0.25) to ~80 wt% (PC-2.0), indicating progressively higher carbon content with increasing weight fraction of the coating. The experimentally measured char yields were compared with theoretical values calculated as weighted averages of the constituent components (pure PS-DVB-100 and neat PBz-A<sub>2</sub>). As shown in Figure 5B, experimental and predicted values align closely, suggesting that no unexpected side reactions (e.g., recondensation of volatiles) influence mass retention.

Figure 5C shows the evolution of dimensional and volume retention with increasing coating concentration. Both metrics increase monotonically up to PC-1.0, beyond which they plateau. This suggests a minimum carbon threshold is required to fully reinforce the architecture during pyrolysis. Figure 5D presents the densities of each sample before and after pyrolysis. The bare template exhibits a drastic transformation, with density increasing from ~0.09 g cm<sup>-3</sup> before pyrolysis to ~0.60 g cm<sup>-3</sup> after pyrolysis due to catastrophic mass and volume loss (>99%), indicative of uncontrolled degradation and complete architectural collapse. In contrast, even a small weight fraction of PBz-A<sub>2</sub>

coating (PC-0.25) significantly shifts the outcome: the coating suppresses collapse, enables density control, and preserves the pore architecture. As coating weight fraction increases, density increases systematically and predictably, reaching  $\sim 0.70 \text{ g cm}^{-3}$  for PC-2.0—demonstrating the utility of this strategy to continuously tune bulk density across a wide range without compromising structural inheritance. These results establish coating weight fraction as an effective lever to independently tune carbon density over a wide range within the lightweight materials regime.

To provide context for these results, the PC-x materials are benchmarked against various porous carbons reported in the literature, as shown in a shrinkage-density map (Fig. 5E and Table S1 of the Supporting Information), where the x- and y-axes represent dimensional retention (%) and bulk density ( $\text{g cm}^{-3}$ ), respectively<sup>[18,26,49,51–53,55,56,62,69,70,78,92,100–132]</sup>. Most porous carbons derived from single-component precursors, filled polymers, or crosslinked resins appear as discrete points on this map, indicating that mass retention and volume retention are deeply intertwined properties (Fig. S10). These systems lack independent control over the carbon source and structural blueprint, resulting in a final density dictated by the singular precursor's chemistry and the conflicting constraints imposed by it. In contrast, the template-coating framework delineates these influences by differentiating the roles of the carbon source and the structural blueprint. The PC-x materials occupy a unique region in the lower-right quadrant, characterized by high retention (low shrinkage) and tunable densities ( $\sim 0.1 - 0.7 \text{ g cm}^{-3}$ ). Besides concentration, pyrolysis temperature serves as a secondary tuning parameter. As discussed in Section 2.5 (Fig. 2E), lowering the pyrolysis temperature creates even higher-retention porous carbons by minimizing carbon loss, thereby preserving structural integrity. These two parameters—coating weight fraction and pyrolysis temperature—provide orthogonal control over the bulk density, facilitating the design of finely tailored porous carbon architectures suitable for a wide range of applications.



**Figure 5.** Modulating the properties of Poly(HIPE)-Polybenzoxazine derived porous carbons through coating concentration. **A)** TGA thermograms for PC-x template-coating pairs, alongside bare template and neat coating controls, illustrate a progressive increase in char yield with coating weight fraction. **B)** A comparison of experimental char yields with theoretically predicted values for each concentration affirms that mass retention is a weighted average of contributions from the coating (primary carbon source) and template, with no indications of unexpected synergistic effects. **C)** The evolution of dimensional and volume retention as a function of benzoxazine monomer concentration during the coating polymerization stage shows a dramatic enhancement until a plateau is reached at 1.0 M, suggesting a minimum carbon threshold is necessary for fully stabilizing the architecture during pyrolysis. **D)** Density profiles before and after pyrolysis across the coating concentration series illustrate the tunability of final carbon density, ranging from approximately 0.1 to 0.7 g cm<sup>-3</sup>. **E)** A density-retention map benchmarks the PC-x series against reported porous carbons derived from various precursors<sup>[18,26,49,51–53,55,56,62,69,70,78,92,100–132]</sup> (data compiled in Table S1 of the Supporting Information), emphasizing the unique capability of the template-coating strategy to achieve low-density, high-retention porous carbons.

### **3.4 Conclusion**

The macroscale fabrication of 3D porous carbons with adjustable density and hierarchical architecture is critical for applications in energy storage, separations, and lightweight structural materials. However, conventional approaches based on single-polymer precursors require the same material to serve as both the structural scaffold and the carbon source, linking mass retention to structural fidelity. As a result, pyrolysis often leads to severe shrinkage, warping, or collapse, which limits control over both the structural hierarchy and the final density of the pyrolytic product. Presented herein is a template-coating platform that separates these conflicting requirements by decoupling the carbon source from the structural scaffold. A series of polybenzoxazine coatings engineered for early carbonization, minimal degradation, and high char yield is developed, alongside a complementary series of hierarchically porous polystyrene templates with tunable thermal properties. Using defined synthetic and thermal compatibility criteria, the most compatible pair is screened and identified, enabling the macroscale fabrication of 3D porous carbons that retain structural and dimensional integrity under the harsh conditions imposed by pyrolysis. By adjusting the coating weight fraction and pyrolysis temperature, a broad range of densities ( $\sim 0.1 - 0.7 \text{ g cm}^{-3}$ ) is achieved, while ensuring complete structural inheritance and exceptional dimensional stability ( $> 90\%$  dimensional retention). Notably, the resulting materials occupy a previously inaccessible region of the density–shrinkage landscape, showcasing low-density porous carbons with minimal shrinkage, challenging an enduring trade-off in macroscale 3D porous carbon fabrication. Crucially, these density limits are not intrinsic—they can be pushed further by exploring alternative template and coating chemistries. This work establishes a generalizable and scalable template-coating design framework for fabricating lightweight 3D porous carbons with deterministic control over shape, size, porosity, and density suitable for various mechanical and electrochemical applications.

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### **3.6 References**

- [1] M. F. Ashby, *Materials Selection in Mechanical Design*, Butterworth-Heinemann, Amsterdam ; Cambridge, MA, **2017**.
- [2] J. Jiang, H. Wang, J. Lin, F. Wang, Z. Liu, L. Wang, Z. Li, Y. Li, Y. Li, Z. Lu, *Nat Commun* **2025**, *16*, 3018.
- [3] D. Nepal, S. Kang, K. M. Adstedt, K. Kanhaiya, M. R. Bockstaller, L. C. Brinson, M. J. Buehler, P. V. Coveney, K. Dayal, J. A. El-Awady, L. C. Henderson, D. L. Kaplan, S. Keten, N. A. Kotov, G. C. Schatz, S. Vignolini, F. Vollrath, Y. Wang, B. I. Yakobson, V. V. Tsukruk, H. Heinz, *Nat. Mater.* **2023**, *22*, 18.
- [4] Y. M. Wang, T. Voisin, J. T. McKeown, J. Ye, N. P. Calta, Z. Li, Z. Zeng, Y. Zhang, W. Chen, T. T. Roehling, R. T. Ott, M. K. Santala, P. J. Depond, M. J. Matthews, A. V. Hamza, T. Zhu, *Nature Mater* **2018**, *17*, 63.
- [5] M. Bechthold, J. C. Weaver, *Nat Rev Mater* **2017**, *2*, 17082.
- [6] A. Papadopoulou, J. Laucks, S. Tibbits, *Nat Rev Mater* **2017**, *2*, 17078.
- [7] X. Zhu, L. Lin, M. Pang, C. Jia, L. Xia, G. Shi, S. Zhang, Y. Lu, L. Sun, F. Yu, J. Gao, Z. He, X. Wu, A. Li, L. Wang, M. Wang, K. Cao, W. Fu, H. Chen, G. Li, J. Zhang, Y. Wang, Y. Yang, Y.-G. Zhu, *Nat Commun* **2024**, *15*, 3218.
- [8] Y. Wang, M. Zhang, X. Shen, H. Wang, H. Wang, K. Xia, Z. Yin, Y. Zhang, *Small* **2021**, *17*, 2008079.
- [9] H. Sun, J. Zhu, D. Baumann, L. Peng, Y. Xu, I. Shakir, Y. Huang, X. Duan, *Nat Rev Mater* **2019**, *4*, 45.
- [10] P. Fratzl, R. Weinkamer, *Progress in Materials Science* **2007**, *52*, 1263.
- [11] R. Lakes, *Nature* **1993**, *361*, 511.

- [12] P. R. Onffroy, S. Chiovoloni, H. L. Kuo, M. A. Saccone, J. Q. Lu, J. M. DeSimone, *JACS Au* **2024**, *4*, 3706.
- [13] Y. M. Eggeler, K. C. Chan, Q. Sun, A. D. Lantada, D. Mager, R. Schwaiger, P. Gumbsch, R. Schröder, W. Wenzel, J. G. Korvink, M. Islam, *Adv Funct Materials* **2024**, *34*, 2302068.
- [14] B. Chen, Q. Ma, C. Tan, T. Lim, L. Huang, H. Zhang, *Small* **2015**, *11*, 3319.
- [15] H. Liu, S. Wu, N. Tian, F. Yan, C. You, Y. Yang, *J. Mater. Chem. A* **2020**, *8*, 23699.
- [16] R. Llamas-Unzueta, J. A. Menéndez, L. A. Ramírez-Montoya, J. Viña, A. Argüelles, M. A. Montes-Morán, *Carbon* **2021**, *175*, 403.
- [17] E. Frank, L. M. Steudle, D. Ingildeev, J. M. Spörl, M. R. Buchmeiser, *Angew Chem Int Ed* **2014**, *53*, 5262.
- [18] M. Jalalian, Q. Jiang, A. Coulon, M. Storb, R. Woodward, A. Bismarck, *Materials & Design* **2019**, *168*, 107658.
- [19] J. Bauer, L. R. Meza, T. A. Schaedler, R. Schwaiger, X. Zheng, L. Valdevit, *Adv. Mater.* **2017**, *29*, 1701850.
- [20] J. N. Pagaduan, S. Samitsu, J. Varma, T. Emrick, R. Katsumata, *ACS Appl. Polym. Mater.* **2022**, *4*, 4329.
- [21] Z. Zhou, T. Liu, A. U. Khan, G. Liu, *Sci. Adv.* **2019**, *5*, eaau6852.
- [22] T. Kowalewski, N. V. Tsarevsky, K. Matyjaszewski, *J. Am. Chem. Soc.* **2002**, *124*, 10632.
- [23] T. Wang, R. Pan, M. L. Martins, J. Cui, Z. Huang, B. P. Thapaliya, C.-L. Do-Thanh, M. Zhou, J. Fan, Z. Yang, M. Chi, T. Kobayashi, J. Wu, E. Mamontov, S. Dai, *Nat Commun* **2023**, *14*, 4607.
- [24] M. Sevilla, N. Díez, A. B. Fuertes, *ChemSusChem* **2021**, *14*, 94.
- [25] F. Xu, D. Wu, R. Fu, B. Wei, *Materials Today* **2017**, *20*, 629.

- [26] M. Inagaki, N. Ohta, Y. Hishiyama, *Carbon* **2013**, *61*, 1.
- [27] C. Chen, E. B. Kennel, A. H. Stiller, P. G. Stansberry, J. W. Zondlo, *Carbon* **2006**, *44*, 1535.
- [28] H. You, J. Hui, Y. Zhou, K. Vittore, J. Zhang, L. E. Chaney, S. Chinta, Y. Zhao, G. Lim, D. Lee, E. A. Ainsworth, J. B. Dunn, V. P. Dravid, M. C. Hersam, S. J. Rowan, *Small* **2024**, *20*, 2406669.
- [29] Y. Wang, Z. Chen, L. Yang, T. Xu, H. Wu, J. Zhang, L. He, *Ceramics International* **2024**, *50*, 31548.
- [30] J. R. Gissinger, S. R. Zavada, J. G. Smith, J. Kemppainen, I. Gallegos, G. M. Odegard, E. J. Siochi, K. E. Wise, *Carbon* **2023**, *202*, 336.
- [31] K. Narita, M. A. Citrin, H. Yang, X. Xia, J. R. Greer, *Adv. Energy Mater.* **2021**, *11*, 2002637.
- [32] L. E. Asp, K. Bouton, D. Carlstedt, S. Duan, R. Harnden, W. Johannisson, M. Johansen, M. K. G. Johansson, G. Lindbergh, F. Liu, K. Peuvot, L. M. Schneider, J. Xu, D. Zenkert, *Adv Energy Sustain Res* **2021**, *2*, 2000093.
- [33] J. Yin, W. Zhang, N. A. Alhebshi, N. Salah, H. N. Alshareef, *Small Methods* **2020**, *4*, 1900853.
- [34] J. Lai, A. Nsabimana, R. Luque, G. Xu, *Joule* **2018**, *2*, 76.
- [35] C. Jehanno, J. W. Alty, M. Roosen, S. De Meester, A. P. Dove, E. Y.-X. Chen, F. A. Leibfarth, H. Sardon, *Nature* **2022**, *603*, 803.
- [36] H. Weldekidan, A. K. Mohanty, M. Misra, *ACS Environ. Au* **2022**, *2*, 510.
- [37] H. Li, M. E. Zick, T. Trisukhon, M. Signorile, X. Liu, H. Eastmond, S. Sharma, T. L. Spreng, J. Taylor, J. W. Gittins, C. Farrow, S. A. Lim, V. Crocellà, P. J. Milner, A. C. Forse, *Nature* **2024**, *630*, 654.
- [38] R. L. Siegelman, E. J. Kim, J. R. Long, *Nat. Mater.* **2021**, *20*, 1060.



- [39] S. Rufer, M. P. Nitzsche, S. Garimella, J. R. Lake, K. K. Varanasi, *Nat Commun* **2024**, *15*, 9429.
- [40] T. Liu, J. Serrano, J. Elliott, X. Yang, W. Cathcart, Z. Wang, Z. He, G. Liu, *Science Advances* **2020**, *6*, eaaz0906.
- [41] P. Srimuk, X. Su, J. Yoon, D. Aurbach, V. Presser, *Nat Rev Mater* **2020**, *5*, 517.
- [42] M. E. Suss, V. Presser, *Joule* **2018**, *2*, 10.
- [43] W. Song, X. Pan, X. Wang, H. Wang, J. Li, D. Li, X. Ma, F. Yin, *Adv Funct Materials* **2025**, *35*, 2415937.
- [44] J. U. Surjadi, Y. Zhou, S. Huang, L. Wang, M. Li, S. Fan, X. Li, J. Zhou, R. H. W. Lam, Z. Wang, Y. Lu, *Matter* **2022**, S2590238522004672.
- [45] J. Bauer, M. Sala-Casanovas, M. Amiri, L. Valdevit, *Sci. Adv.* **2022**, *8*, eabo3080.
- [46] C. M. Portela, B. W. Edwards, D. Veyssset, Y. Sun, K. A. Nelson, D. M. Kochmann, J. R. Greer, *Nat. Mater.* **2021**, *20*, 1491.
- [47] J. Bauer, A. Schroer, R. Schwaiger, O. Kraft, *Nature Mater* **2016**, *15*, 438.
- [48] K. Nakanishi, S. Hofmann, *APL Materials* **2020**, *8*, 021106.
- [49] H. Steldinger, A. Esposito, K. Brunnengräber, J. Gläsel, B. J. M. Etzold, *Adv. Sci.* **2019**, *6*, 1901340.
- [50] T. Zhang, R. A. Sanguramath, S. Israel, M. S. Silverstein, *Macromolecules* **2019**, *52*, 5445.
- [51] W. Hu, F. Xie, Y. Li, Z. Wu, K. Tian, M. Wang, L. Pan, L. Li, *Langmuir* **2017**, *33*, 13364.
- [52] D. Wang, N. L. Smith, P. M. Budd, *Polymer International* **2005**, *54*, 297.
- [53] N. Cohen, M. S. Silverstein, *Polymer* **2011**, *52*, 282.
- [54] R. Castaldo, I. Berezovska, M. S. Silverstein, G. Gentile, *ACS Appl. Polym. Mater.* **2023**, *5*, 6920.

- [55] S. Kovačič, B. Schafzahl, N. B. Matsko, K. Gruber, M. Schmuck, S. Koller, S. A. Freunberger, C. Slugovc, *ACS Appl. Energy Mater.* **2022**, acsaem.2c02787.
- [56] R. T. Woodward, A. Jobbe-Duval, S. Marchesini, D. B. Anthony, C. Petit, A. Bismarek, *Polymer* **2017**, *115*, 146.
- [57] D.-Y. Kang, C. Kim, G. Park, J. H. Moon, *Sci Rep* **2015**, *5*, 18185.
- [58] D. J. Malik, A. W. Trochimczuk, S. Ronka, *PLoS ONE* **2012**, *7*, e43354.
- [59] C. Jouanne, T. N. Pham-Truong, C. Vancaeyzeele, F. N. Muya, K. Pokpas, P. G. L. Baker, P. H. Aubert, *ChemElectroChem* **2024**, *11*, e202300689.
- [60] H. Li, Z. Li, Y. Peng, Z. Jiang, X. Xiao, *Polymer Testing* **2024**, *136*, 108489.
- [61] P. Blyweert, V. Nicolas, J. Macutkevicius, V. Fierro, A. Celzard, *ACS Sustainable Chem. Eng.* **2022**, *10*, 7702.
- [62] A. Szczurek, V. Fierro, A. Pizzi, A. Celzard, *Carbon* **2014**, *74*, 352.
- [63] P. Smith, A. G. Obando, A. Griffin, M. Robertson, E. Bounds, Z. Qiang, *Advanced Materials* **2023**, *35*, 2208029.
- [64] U. M. Patil, R. V. Ghorpade, M. S. Nam, A. C. Nalawade, S. Lee, H. Han, S. C. Jun, *Sci Rep* **2016**, *6*, 35490.
- [65] H. D. Asfaw, R. Younesi, M. Valvo, J. Maibach, J. Ångström, C.-W. Tai, Z. Bacsik, M. Sahlberg, L. Nyholm, P. K. Edström, *ChemistrySelect* **2016**, *1*, 784.
- [66] S. Israel, I. Gurevitch, M. S. Silverstein, *Polymer* **2015**, *72*, 453.
- [67] X.-R. Zhang, T.-B. Song, T.-L. He, Q.-L. Ma, Z.-F. Wu, Y.-G. Wang, H.-M. Xiong, *Adv. Funct. Mater.* **2025**, DOI <https://doi.org/10.1002/adfm.202419219>.
- [68] S. Zheng, Y. Wang, X. Wang, H. Lu, *Polymer Testing* **2024**, *135*, 108469.

- [69] R. T. Woodward, F. Markoulidis, F. De Luca, D. B. Anthony, D. Malko, T. O. McDonald, M. S. P. Shaffer, A. Bismarck, *J. Mater. Chem. A* **2018**, *6*, 1840.
- [70] R. T. Woodward, D. W. H. Fam, D. B. Anthony, J. Hong, T. O. McDonald, C. Petit, M. S. P. Shaffer, A. Bismarck, *Carbon* **2016**, *101*, 253.
- [71] R. Woodward, F. De Luca, A. Roberts, A. Bismarck, *Materials* **2016**, *9*, 776.
- [72] S. Park, Z. Cao, D. H. Sung, K. K. Fu, *Advanced Energy Materials* **2023**, *13*, 2301704.
- [73] P. Smith, J. Hu, A. Griffin, M. Robertson, A. Güillen Obando, E. Bounds, C. B. Dunn, C. Ye, L. Liu, Z. Qiang, *Nat Commun* **2024**, *15*, 838.
- [74] H. Liu, F. Lei, W. Xu, Q. Li, C. Lei, C. Xiong, N. Tian, C. You, Y. Yang, *ACS Nano* **2025**, *19*, 1198.
- [75] N. Díez, M. Sevilla, A. B. Fuertes, *Carbon* **2021**, *178*, 451.
- [76] J. Wang, H. Zhu, B. Li, S. Zhu, *Chemistry A European J* **2018**, *24*, 16426.
- [77] M. S. Silverstein, H. Tai, A. Sergienko, Y. Lumelsky, S. Pavlovsky, *Polymer* **2005**, *46*, 6682.
- [78] A. Suresh, S. J. Rowan, C. Liu, *Advanced Materials* **2023**, *35*, 2206416.
- [79] C. Shaer, L. Oppenheimer, A. Lin, H. Ishida, *Polymers* **2021**, *13*, 3775.
- [80] Y. Lu, **2021**.
- [81] Y. Gao, F. Huang, Y. Zhou, L. Du, *J of Applied Polymer Sci* **2013**, *128*, 340.
- [82] R. Yang, Q. Chen, W. Sheng, K. Zhang, **2024**.
- [83] Z. Brunovska, R. Lyon, H. Ishida, *Thermochimica Acta* **2000**, 357–358, 195.
- [84] H. Yan, Z. Zhan, H. Wang, J. Cheng, Z. Fang, *ACS Appl. Polym. Mater.* **2021**, *3*, 3392.
- [85] H. Y. Low, H. Ishida, *J. Polym. Sci. B Polym. Phys.* **1999**, *37*, 647.

- [86] J. Hacaloğlu, T. Uyar, H. Ishida, in *Handbook of Benzoxazine Resins*, Elsevier, **2011**, pp. 287–305.
- [87] W. Wen, W. Luo, G. Chen, X. Fang, Y. Zhou, Q. Ran, *High Performance Polymers* **2025**, 37, 230.
- [88] C. Liu, M. Sun, B. Zhang, X. Zhang, J. Li, Q. Li, *J of Applied Polymer Sci* **2017**, 134, app.44547.
- [89] H. J. Kim, Z. Brunovska, H. Ishida, *Polymer* **1999**, 40, 6565.
- [90] L. Chen, D. Ren, S. Chen, K. Li, M. Xu, X. Liu, *Polymer Testing* **2019**, 74, 127.
- [91] H. Zhang, Z. Lu, *e-Polymers* **2010**, 10, DOI 10.1515/epoly.2010.10.1.1578.
- [92] L. Zhang, M. Liu, S. Roy, E. K. Chu, K. Y. See, X. Hu, *ACS Appl. Mater. Interfaces* **2016**, 8, 7422.
- [93] Z. Brunovska, H. Ishida, *J. Appl. Polym. Sci.* **1999**, 73, 2937.
- [94] N. R. Cameron, D. C. Sherrington, *J. Mater. Chem.* **1997**, 7, 2209.
- [95] P. Hailey, I. M. Huxham, B. Rowatt, D. C. Sherrington, L. Tetley, *Macromolecules* **1991**, 24, 117.
- [96] R. Sanetra, B. N. Kolarz, A. Wlochowicz, **n.d.**
- [97] Y. Xu, J. Dai, Q. Ran, Y. Gu, *Polymer* **2017**, 123, 232.
- [98] H. Jin Kim, Z. Brunovska, H. Ishida, *Polymer* **1999**, 40, 1815.
- [99] G. M. Jenkins, K. Kawamura, *Nature* **1971**, 231, 175.
- [100] X. Zhang, L. Zhong, A. Mateos, A. Kudo, A. Vyatsikh, H. Gao, J. R. Greer, X. Li, *Nat. Nanotechnol.* **2019**, 14, 762.
- [101] S. Yu, Z. Chen, Y. Wang, R. Luo, Y. Pan, *J Porous Mater* **2018**, 25, 527.

- [102] J. W. F. To, Z. Chen, H. Yao, J. He, K. Kim, H.-H. Chou, L. Pan, J. Wilcox, Y. Cui, Z. Bao, *ACS Cent. Sci.* **2015**, *1*, 68.
- [103] M. Mazaj, M. Bjelica, E. Žagar, N. Z. Logar, S. Kovačič, *ChemSusChem* **2020**, *13*, 2089.
- [104] M. Jalalian, Q. Jiang, M. Birot, H. Deleuze, R. T. Woodward, A. Bismarck, *Reactive and Functional Polymers* **2018**, *132*, 145.
- [105] P. Lorjai, S. Wongkasemjit, T. Chaisuwan, *Materials Science and Engineering: A* **2009**, *527*, 77.
- [106] C. J. Zúñiga Ruiz, A. Szczurek, A. Martínez De Yuso Arisa, J. C. Ronda, V. Cádiz, V. Fierro, A. Celzard, *Carbon* **2015**, *95*, 919.
- [107] Q. Lin, S. Dong, L. Qu, C. Fang, K. Luo, *Journal of Analytical and Applied Pyrolysis* **2014**, *106*, 164.
- [108] A. Foulet, M. Birot, R. Backov, G. Sonnemann, H. Deleuze, *Materials Today Communications* **2016**, *7*, 108.
- [109] K. Kapilov-Buchman, L. Portal, Y. Zhang, N. Fechner, M. Antonietti, M. S. Silverstein, *J. Mater. Chem. A* **2017**, *5*, 16376.
- [110] M. Xiang, H. Wu, H. Liu, J. Huang, Y. Zheng, L. Yang, P. Jing, Y. Zhang, S. Dou, H. Liu, *Adv Funct Materials* **2017**, *27*, 1702573.
- [111] M. A. Aslam, W. Ding, S. Ur Rehman, A. Hassan, Y. Bian, Q. Liu, Z. Sheng, *Applied Surface Science* **2021**, *543*, 148785.
- [112] R. Llamas-Unzueta, J. A. Menéndez, M. Suárez, A. Fernández, M. A. Montes-Morán, *Additive Manufacturing* **2022**, *59*, 103083.
- [113] K. Xiao, L. Ding, G. Liu, H. Chen, S. Wang, H. Wang, *Advanced Materials* **2016**, *28*, 5997.
- [114] Q. Liang, Z. Li, X. Yu, Z. Huang, F. Kang, Q. Yang, *Advanced Materials* **2015**, *27*, 4634.

- [115] T. N. Pham, T. Sharifi, R. Sandström, W. Siljebo, A. Shchukarev, K. Kordas, T. Wågberg, J.-P. Mikkola, *Sci Rep* **2017**, *7*, 6112.
- [116] S. Wang, N. Xiao, Y. Zhou, Z. Ling, M. Li, J. Qiu, *Carbon* **2016**, *105*, 224.
- [117] Y. Li, B. Shen, X. Pei, Y. Zhang, D. Yi, W. Zhai, L. Zhang, X. Wei, W. Zheng, *Carbon* **2016**, *100*, 375.
- [118] Y. Sun, S. Luo, H. Sun, W. Zeng, C. Ling, D. Chen, V. Chan, K. Liao, *Carbon* **2018**, *136*, 299.
- [119] M. Islam, J. Flach, R. Martinez-Duarte, *Carbon* **2018**, *133*, 140.
- [120] J. Men, J. Feng, Y. Jiang, L. Li, Y. Hu, J. Feng, *ACS Appl. Nano Mater.* **2024**, *7*, 7132.
- [121] Q. X. Huang, R. P. Wang, W. J. Li, Y. J. Tang, Y. Chi, J. H. Yan, *Energy Fuels* **2014**, *28*, 6398.
- [122] J. Kemppainen, I. Gallegos, A. S. Krieg, J. R. Gissinger, K. E. Wise, M. Kowalik, J. A. King, S. Gowtham, A. Van Duin, G. M. Odegard, *ACS Appl. Eng. Mater.* **2023**, *1*, 2555.
- [123] S. Zhang, Q. Ran, Q. Fu, Y. Gu, *Materials Chemistry and Physics* **2019**, *236*, 121806.
- [124] J. E. Mosquera, L. Delevingne, F. Delbecq, E. Daouk, A. Drelich, K. Saleh, R. Gautier, M. Leturia, *RSC Adv.* **2025**, *15*, 6783.
- [125] S. Wang, W.-C. Li, L. Zhang, Z.-Y. Jin, A.-H. Lu, *J. Mater. Chem. A* **2014**, *2*, 4406.
- [126] F. Su, C. K. Poh, J. S. Chen, G. Xu, D. Wang, Q. Li, J. Lin, X. W. Lou, *Energy Environ. Sci.* **2011**, *4*, 717.
- [127] M. Letellier, C. Delgado-Sanchez, M. Khelifa, V. Fierro, A. Celzard, *Carbon* **2017**, *116*, 562.
- [128] J. Li, Y. Ding, N. Yu, Q. Gao, X. Fan, X. Wei, G. Zhang, Z. Ma, X. He, *Carbon* **2020**, *158*, 45.

- [129] J. Kim, D. Lee, C. Kim, H. Lee, S. Baek, J. H. Moon, *Proc. Natl. Acad. Sci. U.S.A.* **2023**, *120*, e2222050120.
- [130] V. A. Edlabadkar, S. Gorla, R. U. Soni, A. B. M. S. U. Doulah, J. Gloriod, S. Hackett, N. Leventis, C. Sotiriou-Leventis, *Chem. Mater.* **2023**, *35*, 432.
- [131] Z. Li, A. Bhardwaj, J. He, W. Zhang, T. T. Tran, Y. Li, A. McClung, S. Nuguri, J. J. Watkins, S.-W. Lee, *Nat Commun* **2024**, *15*, DOI 10.1038/s41467-024-52359-6.
- [132] S. Scott, J. Chew, J. Barnard, A. Burrows, M. Smith, S. Tennison, S. Perera, *Adv Funct Materials* **2023**, *33*, 2213715.

## **CHAPTER 3 – SUPPORTING INFORMATION**

### **List of Figures**

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### **Materials and Methods**

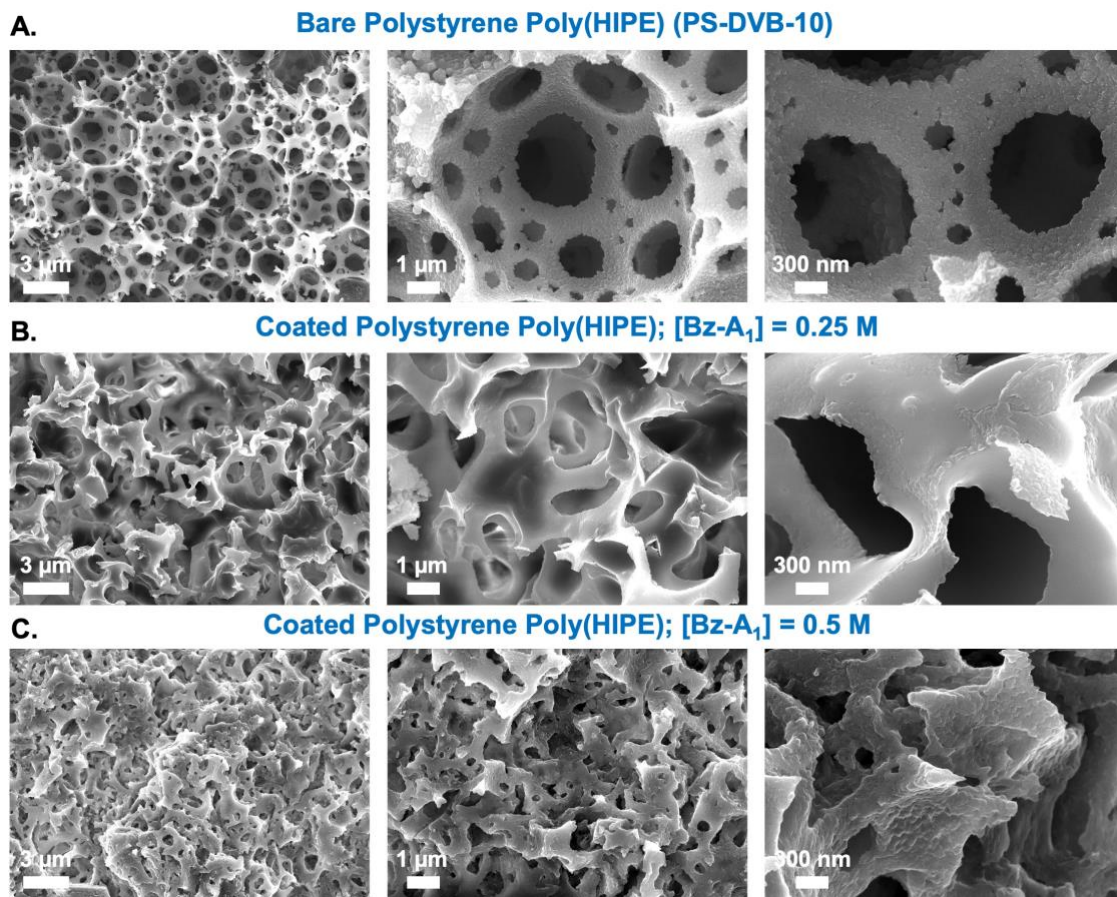
**Figure S11** – PS-DVB Poly(HIPE) Reaction Scheme

**Figure S12** – <sup>1</sup>H-NMR spectra of acetylene-substituted benzoxazine monomers

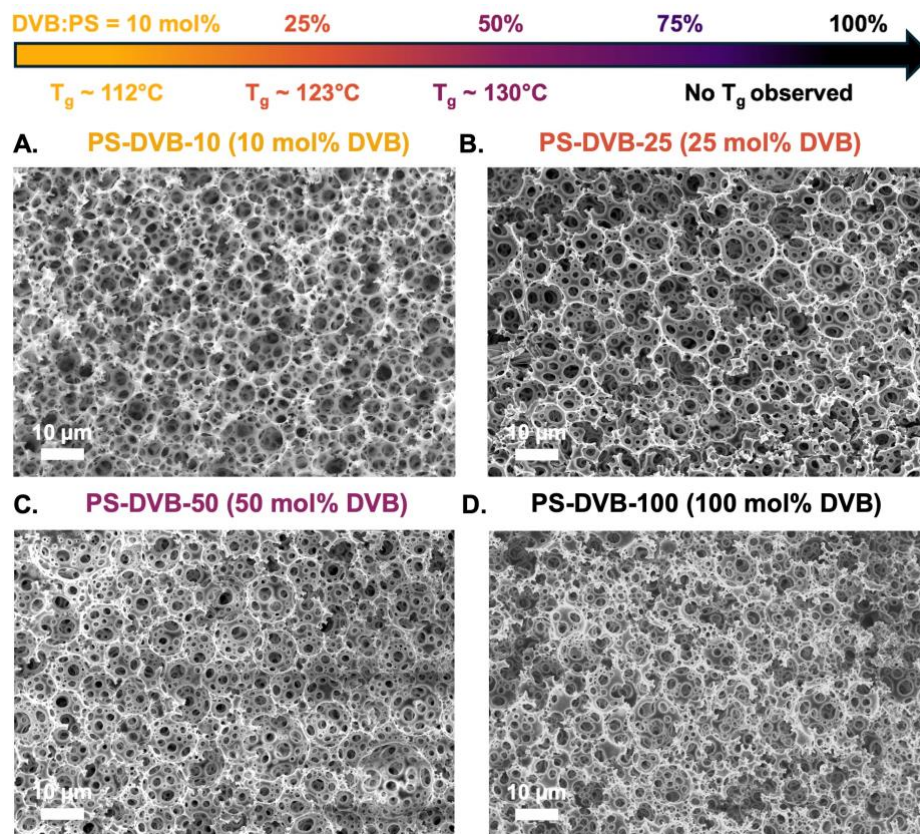
### **References (SI)**

**SI Appendix** – Automated SEM Image Analysis Code

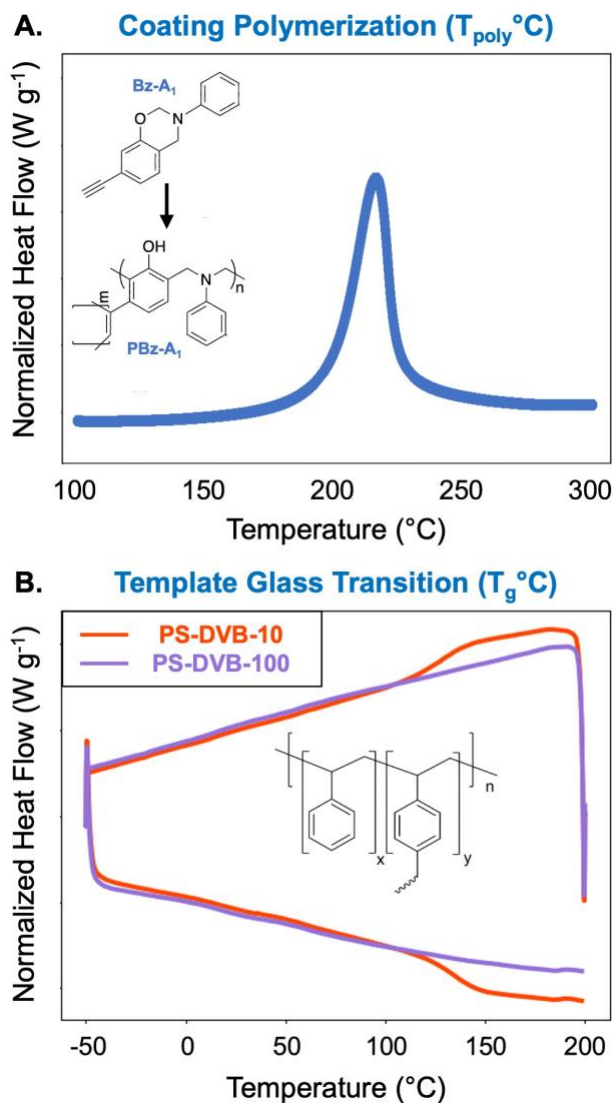




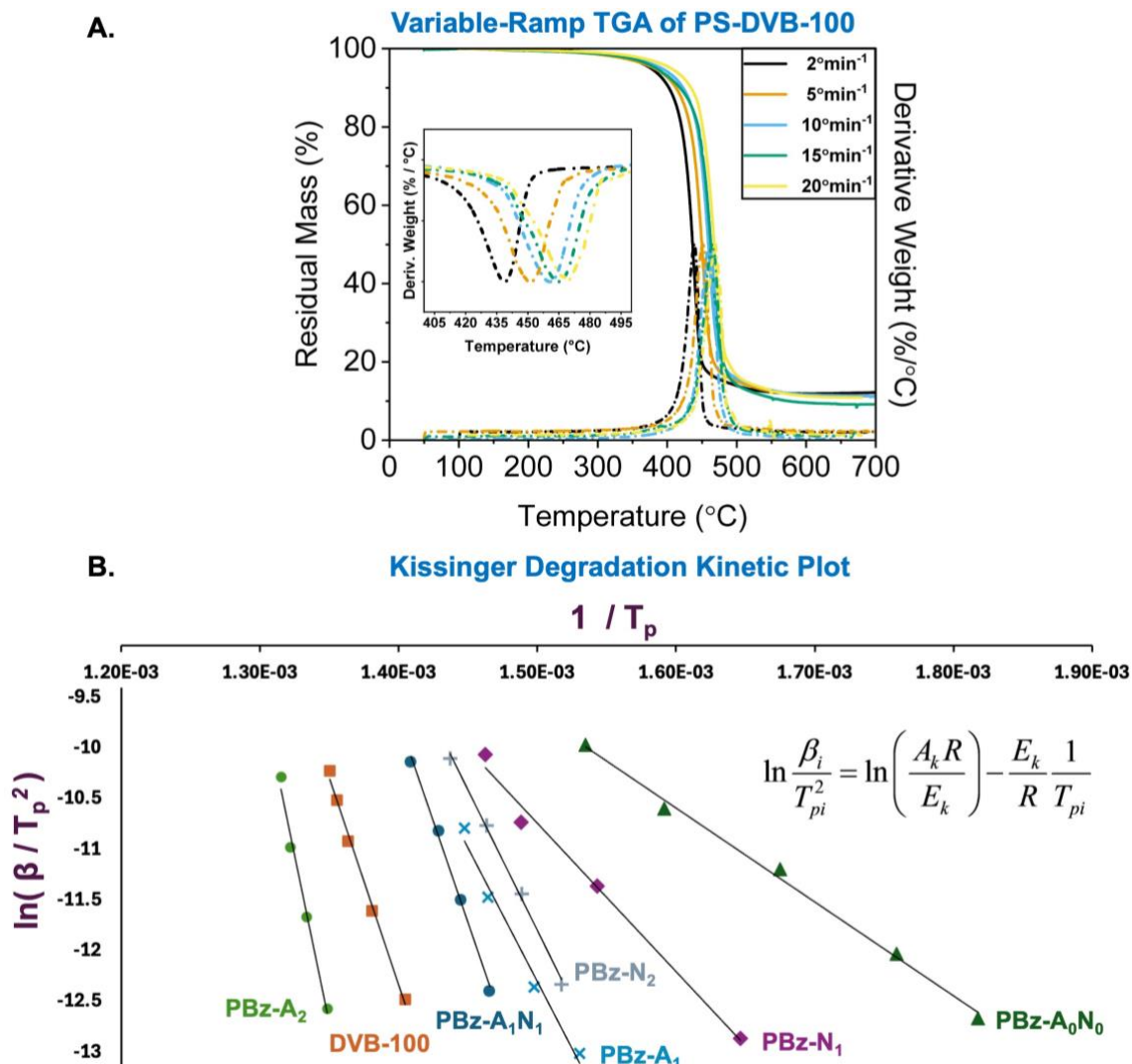
**Figure S1.** Validating synthetic compatibility of template-coating pairs. **(A)** Bare PS template. **(B)** Template infiltrated with  $[Bz-A_1] = 0.25\text{ M}$ . **(C)** Template infiltrated with  $[Bz-A_1] = 0.5\text{ M}$ . Following thermal curing at  $200\text{ }^{\circ}\text{C}$  for 24 h, both coated samples undergo catastrophic deformation due to softening of the PS template during coating polymerization. These results confirm the relevance of the synthetic compatibility criterion (i.e.,  $T_g(\text{template}) < T_{\text{poly}}(\text{coating})$ ) for successful structural inheritance.



**Figure S2.** Morphological characterization of poly(HIPE) templates synthesized with varying crosslinker content. SEM images of PS-DVB poly(HIPE)s with organic phase DVB content of (A) 10 mol%, (B) 25 mol%, (C) 50 mol%, and (D) 100 mol%. All formulations exhibit interconnected voids and hierarchical porosity, confirming successful high internal phase emulsion (HIPE) templating across the DVB composition range.

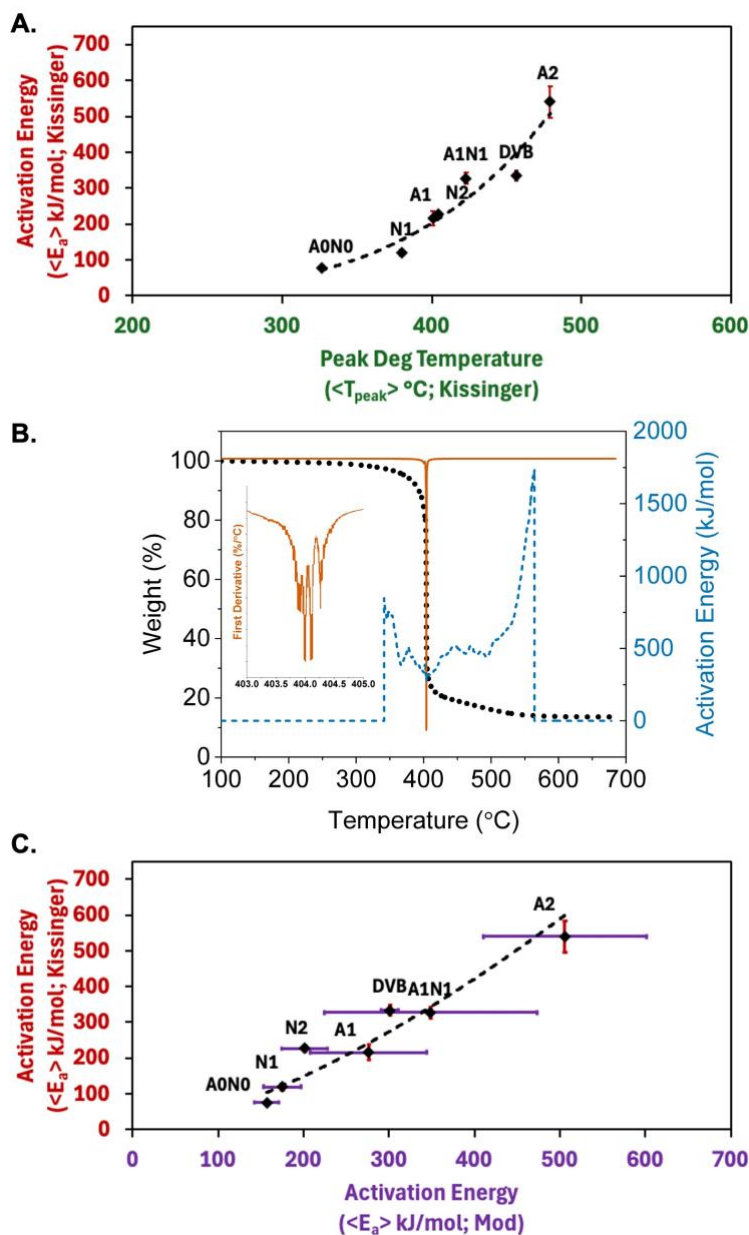


**Figure S3.** Differential scanning calorimetry (DSC) characterization at  $5\text{ }^{\circ}\text{min}^{-1}$  to verify synthetic compatibility between template and coating. **(A)** DSC profile of Bz- $A_1$  monomer during polymerization to PBz- $A_1$ , with a clear exothermic onset near  $200\text{ }^{\circ}\text{C}$  corresponding to ring-opening polymerization. **(B)** DSC traces of PS-DVB- $x$  poly(HIPE) templates with 10 mol% and 100 mol% DVB content. PS-DVB-10 exhibits a glass transition ( $T_g$ ) at  $\sim 113\text{ }^{\circ}\text{C}$ , while PS-DVB-100 shows no detectable  $T_g$  within the tested range, indicating a highly crosslinked, thermally rigid network. Together, these results validate that  $T_g(\text{PS-DVB-100}) > T_{\text{poly}}(\text{PBz-}A_1)$ .

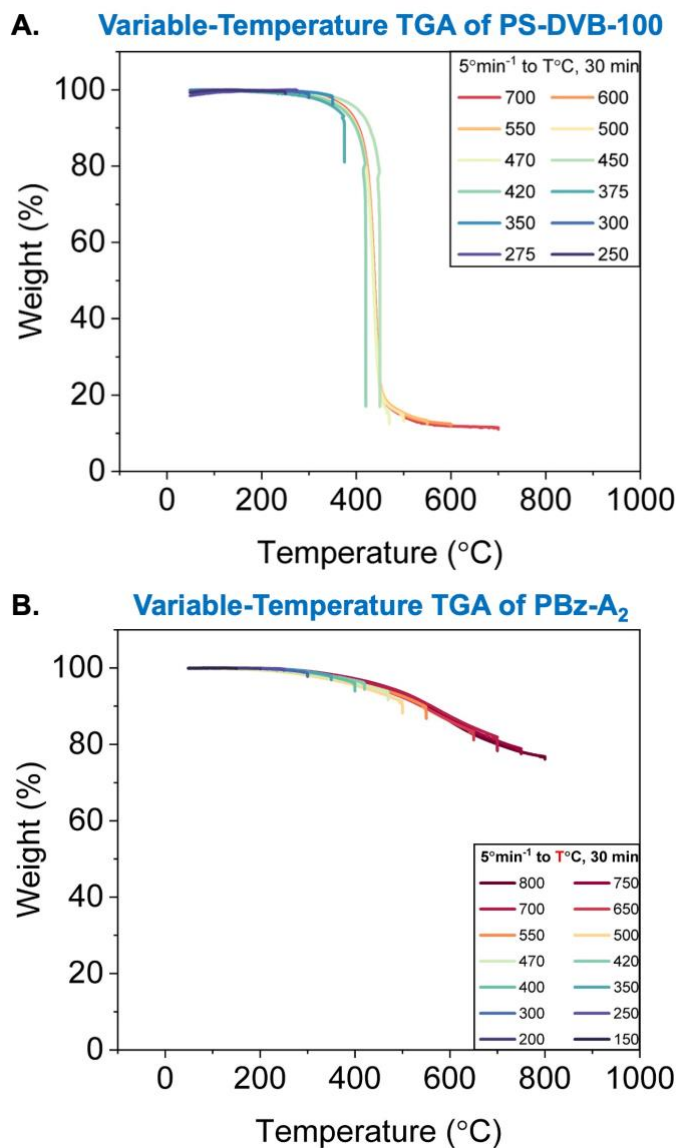


**Figure S4.** Activation energy ( $E_a$ ) determination using the Kissinger method. **(A)** Thermogravimetric analysis (TGA) of PS-DVB-100 at multiple ramp rates ( $\beta = 2, 5, 10, 15$ , and  $20\text{ }^\circ\text{min}^{-1}$ ), with corresponding derivative curves overlaid. Peak degradation temperatures ( $T_p$ ) were extracted from these derivative curves to determine degradation kinetics. **(B)** Kissinger plots of  $\ln(\beta/T_p^2)$  versus  $1/T_p$  for PS-DVB-100 and all  $p\text{PBz-A}_m\text{N}_n$  coatings. Linear fits ( $R^2 > 0.98$  for all materials) enable the calculation of activation energies from the slope ( $-E_a/R$ ), with steeper slopes indicating higher thermal stability. For instance, the orange square data points correspond to  $T_p$  values for PS-DVB-100 from panel A. This method provides a consistent framework for comparing degradation kinetics across template and coating systems. Notably, among all  $\text{PBz-A}_m\text{N}_n$ , only  $\text{PBz-A}_2$  (bearing two acetylene substituents) exhibits a higher activation energy (green circles) than PS-DVB-100, identifying it as the most thermally robust coating candidate. Please refer to the Methods section of the Supplementary Information for further experimental details.

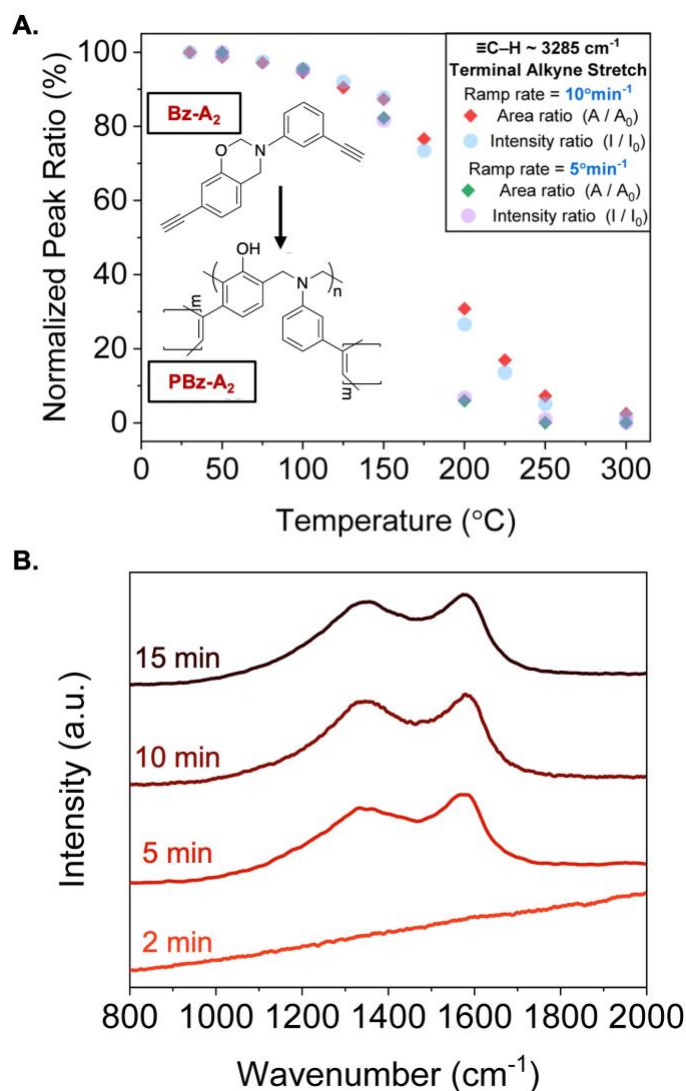




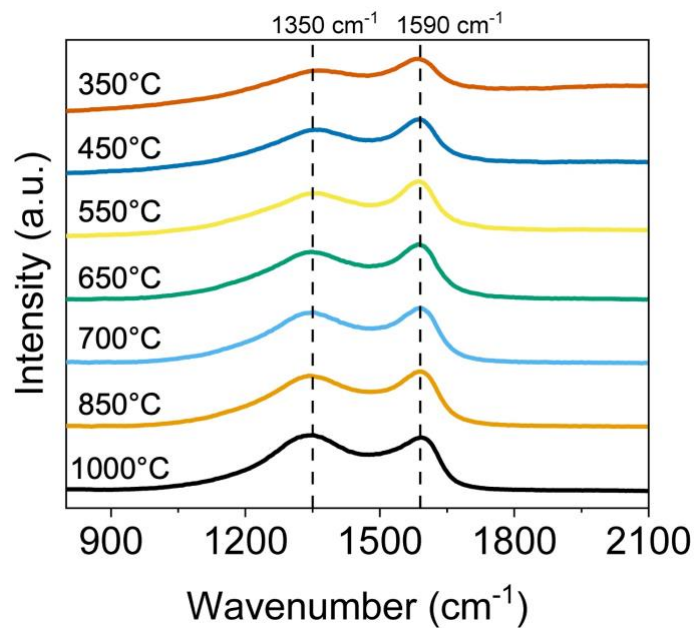
**Figure S5. (A)** Kissinger-derived activation energies plotted against the average peak degradation temperature ( $T_p$ , averaged across ramp rates). **(B)** Representative modulated TGA (MTGA) analysis of PS-DVB-100 showing the weight loss profile (black dots; left y-axis) and corresponding activation energy (blue dashes; right y-axis) as a function of temperature. The conversion-averaged activation energy ( $E_a^{Mod}$ ) was determined by averaging  $E_a$  values over the main degradation regime, defined by the peak range of the DTG curve (see inset of orange line). **(C)** Comparison of ramp-averaged activation energies from Kissinger analysis ( $E_a^{Kiss}$ ; y axis) and conversion-averaged activation energies from modulated TGA ( $E_a^{Mod}$ ; x axis). The strong correlation confirms that higher activation energies are associated with delayed decomposition, supporting the use of activation energy as a quantitative indicator of thermal stability. It also confirms consistency between the two methods for estimating the activation energy of degradation. Please refer to the Methods section of the Supplementary Information for experimental details.



**Figure S6.** *Ex-situ* pyrolysis experiments to probe thermal and structural evolution of template–coating pairs. **(A)** Thermograms of *p*PS-DVB-100 and **(B)** thermograms of *p*PBz-A<sub>2</sub> were obtained by ramping samples at 5 °C min<sup>-1</sup> to target temperatures ranging from 200 to 800 °C, followed by 30-minute isothermal holds to ensure sample equilibration. Samples were measured before and after pyrolysis to quantify mass retention, volume retention, and density evolution. These staged pyrolysis experiments enable subsequent spectroscopic (Raman, XRD) and microscopic (SEM) analyses to investigate the onset of carbonization and the evolution of architecture across the temperature range.

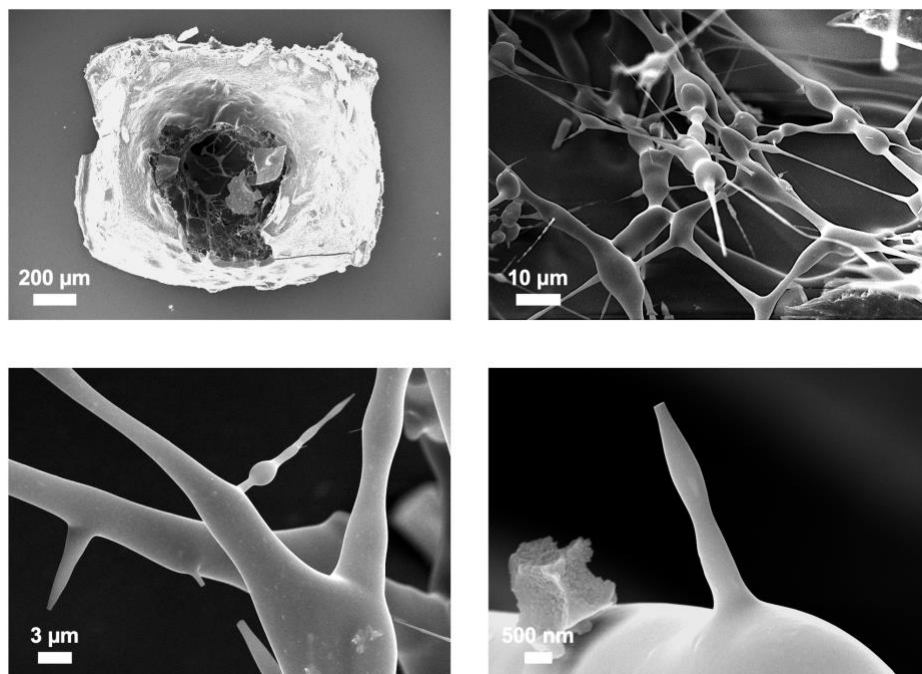


**Figure S7.** Thermal curing of Bz-A<sub>2</sub> and Raman laser-induced carbonization behavior of PBz-A<sub>2</sub>. **(A)** In-situ FTIR spectroscopy of Bz-A<sub>2</sub> during thermal curing effectively captures the ring-opening polymerization and acetylene crosslinking processes that lead to the formation of the PBz-A<sub>2</sub> network. Spectra were collected at continuous heating rates of 5 °C min<sup>-1</sup> and 10 °C min<sup>-1</sup>. The reduction in absorbance of the terminal alkyne stretching band at approximately 3285 cm<sup>-1</sup> was monitored and plotted to track acetylene consumption. The crosslinking reaction commences around ~150 °C, accelerates at ~200 °C, and concludes by ~300 °C, resulting in a highly crosslinked aromatic network (PBz-A<sub>2</sub>). **(B)** The Raman spectra of PBz-A<sub>2</sub> as a function of laser irradiation time highlight its propensity to carbonize under the Raman laser (532 nm). The spectra were collected at room temperature and show the emergence of characteristic D and G bands within 5 minutes of exposure, indicating laser-induced carbonization. This heightened sensitivity is hypothesized to arise from the highly crosslinked aromatic network formed during thermal curing, which may promote carbonization upon Raman laser irradiation.

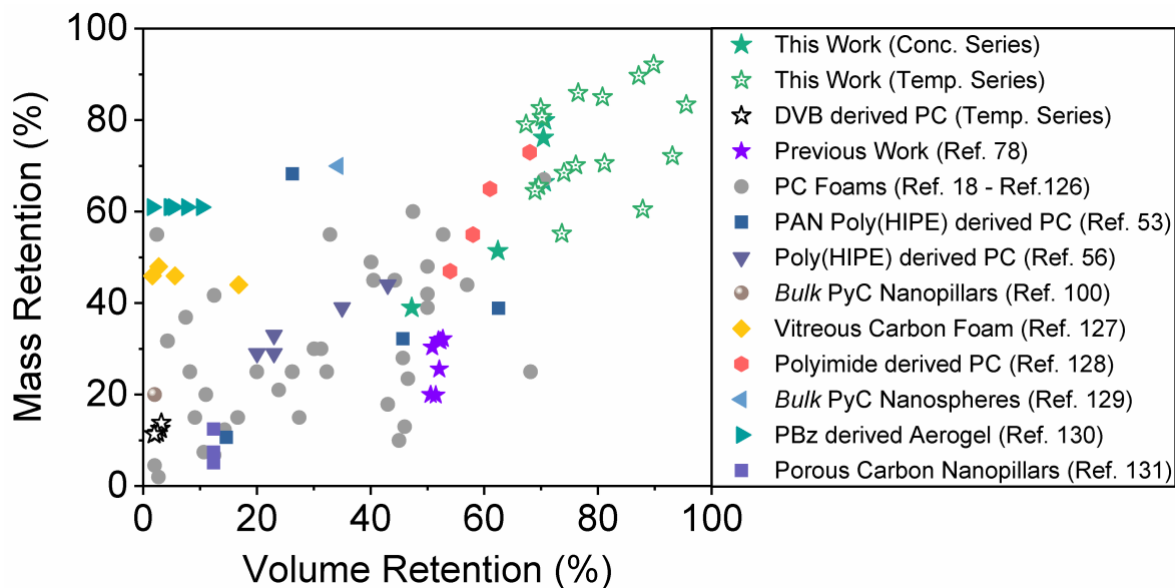


**Figure S8.** Variable-temperature Raman spectroscopy of the *p*PS-DVB/PBz-A<sub>2</sub> template-coating pair (synthesized using [Bz-A<sub>2</sub>] = 1.5 M). Raman spectra were collected at room temperature and after ex-situ pyrolysis from 350 °C (carbonization onset) to 1000 °C. Notably, the emergence and intensification of the characteristic D (~1350 cm<sup>-1</sup>) and G (~1590 cm<sup>-1</sup>) peaks signify the formation of conjugated carbon domains within an amorphous carbon matrix.





**Figure S9.** SEM images of the *p*PS-DVB-100 template after pyrolysis at 600 °C (30 min hold). The SEM images show catastrophic collapse of the internal porous architecture, with no visible interconnected voids or strut features remaining. This internal structural destruction aligns with the significant density increase observed between 400 °C and 600 °C, which is attributed to the dimensional collapse and massive volumetric shrinkage that occur upon thermal degradation.



**Figure S10.** Relationship between volume retention and mass retention in porous carbon systems derived from conventional polymer precursors (see Table S1 below). The data cluster around the  $x = y$  diagonal, indicating a strong coupling between mass and volume loss during pyrolysis. This coupling reflects the chemical and structural constraints of single-precursor systems, which lack independent control over carbon yield and architecture. In contrast, the template-coating approach enables partial decoupling of these parameters, offering access to low-density, high-retention carbon architectures (below).

| Reference #<br>(Main Text) | DOI Link                                                                                                  | Density (g cm <sup>-3</sup> ) | Volume Retention (%) |
|----------------------------|-----------------------------------------------------------------------------------------------------------|-------------------------------|----------------------|
| 78                         | <a href="https://doi.org/10.1002/adma.202206416">10.1002/adma.202206416</a>                               | 0.12                          | 50.5                 |
|                            |                                                                                                           | 0.14                          | 52.1                 |
|                            |                                                                                                           | 0.22                          | 50.8                 |
|                            |                                                                                                           | 0.27                          | 52.3                 |
|                            |                                                                                                           | 0.34                          | 51.9                 |
|                            |                                                                                                           | 0.37                          | 52.7                 |
| 132                        | <a href="https://doi.org/10.1002/adfm.202213715">10.1002/adfm.202213715</a>                               | 0.04                          | 27.5                 |
| 105                        | <a href="https://doi.org/10.1016/j.msea.2009.07.032">10.1016/j.msea.2009.07.032</a>                       | 0.48                          | 32.3                 |
| 49                         | <a href="https://doi.org/10.1002/advs.201901340">10.1002/advs.201901340</a>                               | 0.30                          | 4.3                  |
| 106                        | <a href="https://doi.org/10.1016/j.carbon.2015.09.012">10.1016/j.carbon.2015.09.012</a>                   | 0.09                          | 45.0                 |
| 107                        | <a href="https://doi.org/10.1016/j.jaap.2014.01.015">10.1016/j.jaap.2014.01.015</a>                       | 0.43                          | 7.5                  |
| 69                         | <a href="https://doi.org/10.1039/C7TA09893F">10.1039/C7TA09893F</a>                                       | 0.32                          | 11.1                 |
| 55                         | <a href="https://doi.org/10.1021/acsaelm.2c02787">10.1021/acsaelm.2c02787</a>                             | 0.31                          | 30.1                 |
| 52                         | <a href="https://doi.org/10.1002/pi.1672">10.1002/pi.1672</a>                                             | 0.25                          | 32.9                 |
| 70                         | <a href="https://doi.org/10.1016/j.carbon.2016.02.002">10.1016/j.carbon.2016.02.002</a>                   | 0.19                          | 23.8                 |
| 51                         | <a href="https://doi.org/10.1021/acs.langmuir.7b03175">10.1021/acs.langmuir.7b03175</a>                   | 0.75                          | 16.6                 |
| 108                        | <a href="https://doi.org/10.1016/j.mtcomm.2016.04.005">10.1016/j.mtcomm.2016.04.005</a>                   | 0.51                          | 68.1                 |
| 109                        | <a href="https://doi.org/10.1039/C7TA01958K">10.1039/C7TA01958K</a>                                       | 0.06                          | 46.0                 |
| 102                        | <a href="https://doi.org/10.1021/acscentsci.5b00149">10.1021/acscentsci.5b00149</a>                       | 0.47                          | 31.3                 |
| 18                         | <a href="https://doi.org/10.1016/j.reactfunctpolym.2018.07.027">10.1016/j.reactfunctpolym.2018.07.027</a> | 0.25                          | 20.0                 |
| 26                         | <a href="https://doi.org/10.1016/j.carbon.2013.05.035">10.1016/j.carbon.2013.05.035</a>                   | 1.81                          | 47.5                 |
| 103                        | <a href="https://doi.org/10.1002/cssc.201903116">10.1002/cssc.201903116</a>                               | 0.30                          | 50.0                 |
| 62                         | <a href="https://doi.org/10.1016/j.carbon.2014.03.047">10.1016/j.carbon.2014.03.047</a>                   | 0.28                          | 40.5                 |
| 110                        | <a href="https://doi.org/10.1002/adfm.201702573">10.1002/adfm.201702573</a>                               | 0.20                          | 12.5                 |
| 111                        | <a href="https://doi.org/10.1016/j.apsusc.2020.148785">10.1016/j.apsusc.2020.148785</a>                   | 0.06                          | 9.1                  |
| 112                        | <a href="https://doi.org/10.1016/j.addma.2022.103083">10.1016/j.addma.2022.103083</a>                     | 0.55                          | 45.7                 |
| 113                        | <a href="https://doi.org/10.1002/adma.201601125">10.1002/adma.201601125</a>                               | 0.06                          | 26.2                 |
| 114                        | <a href="https://doi.org/10.1002/adma.201502057">10.1002/adma.201502057</a>                               | 0.04                          | 2.7                  |
| 115                        | <a href="https://doi.org/10.1038/s41598-017-05215-1">10.1038/s41598-017-05215-1</a>                       | 0.09                          | 45.0                 |
| 116                        | <a href="https://doi.org/10.1016/j.carbon.2016.04.040">10.1016/j.carbon.2016.04.040</a>                   | 0.13                          | 8.2                  |
| 117                        | <a href="https://doi.org/10.1016/j.carbon.2016.01.030">10.1016/j.carbon.2016.01.030</a>                   | 0.72                          | 44.2                 |
| 118                        | <a href="https://doi.org/10.1016/j.carbon.2018.04.084">10.1016/j.carbon.2018.04.084</a>                   | 0.12                          | 14.3                 |
| 104                        | <a href="https://doi.org/10.1016/j.matdes.2019.107658">10.1016/j.matdes.2019.107658</a>                   | 0.19                          | 50.0                 |
| 119                        | <a href="https://doi.org/10.1016/j.carbon.2018.03.033">10.1016/j.carbon.2018.03.033</a>                   | 0.03                          | 2.0                  |
| 120                        | <a href="https://doi.org/10.1021/acsanm.3c06214">10.1021/acsanm.3c06214</a>                               | 0.40                          | 52.8                 |
| 121                        | <a href="https://doi.org/10.1021/ef501504k">10.1021/ef501504k</a>                                         | 0.30                          | 46.5                 |
| 122                        | <a href="https://doi.org/10.1021/acsanm.3c00360">10.1021/acsanm.3c00360</a>                               | 1.13                          | 2.4                  |
| 123                        | <a href="https://doi.org/10.1016/j.matchemphys.2019.121806">10.1016/j.matchemphys.2019.121806</a>         | 1.36                          | 70.5                 |
| 124                        | <a href="https://doi.org/10.1039/d5ra00110b">10.1039/d5ra00110b</a>                                       | 0.39                          | 40.1                 |
| 125                        | <a href="https://doi.org/10.1039/C3TA15065H">10.1039/C3TA15065H</a>                                       | 0.50                          | 43.0                 |
| 126                        | <a href="https://doi.org/10.1039/C0EE00277A">10.1039/C0EE00277A</a>                                       | 0.65                          | 12.5                 |
| 101                        | <a href="https://doi.org/10.1007/s10934-017-0465-3">10.1007/s10934-017-0465-3</a>                         | 0.01                          | 10.7                 |
| 92                         | <a href="https://doi.org/10.1021/acsami.5b12072">10.1021/acsami.5b12072</a>                               | 0.15                          | 57.0                 |
| 100                        | <a href="https://doi.org/10.1038/s41565-019-0486-y">10.1038/s41565-019-0486-y</a>                         | 1.40                          | 2.0                  |
| 53                         | <a href="https://doi.org/10.1016/j.polymer.2010.11.026">10.1016/j.polymer.2010.11.026</a>                 | 0.25                          | 26.2                 |
|                            |                                                                                                           | 0.12                          | 45.7                 |
|                            |                                                                                                           | 0.08                          | 62.5                 |
|                            |                                                                                                           | 0.09                          | 14.6                 |

|     |                                                                                           |       |      |
|-----|-------------------------------------------------------------------------------------------|-------|------|
| 127 | <a href="https://doi.org/10.1016/j.carbon.2017.02.020">10.1016/j.carbon.2017.02.020</a>   | 0.029 | 19.1 |
|     |                                                                                           | 0.032 | 32.9 |
|     |                                                                                           | 0.035 | 42.5 |
|     |                                                                                           | 0.050 | 42.6 |
|     |                                                                                           | 0.029 | 19.1 |
| 56  | <a href="https://doi.org/10.1016/j.polymer.2017.03.042">10.1016/j.polymer.2017.03.042</a> | 0.14  | 43.0 |
|     |                                                                                           | 0.17  | 35.0 |
|     |                                                                                           | 0.20  | 23.0 |
|     |                                                                                           | 0.18  | 20.0 |
|     |                                                                                           | 0.19  | 23.0 |
| 128 | <a href="https://doi.org/10.1016/j.carbon.2019.11.075">10.1016/j.carbon.2019.11.075</a>   | 0.08  | 68.0 |
|     |                                                                                           | 0.10  | 61.0 |
|     |                                                                                           | 0.09  | 58.0 |
|     |                                                                                           | 0.08  | 54.0 |
| 129 | <a href="https://doi.org/10.1073/pnas.2222050120">10.1073/pnas.2222050120</a>             | 1.35  | 34.3 |
|     |                                                                                           | 0.34  | 55.1 |
|     |                                                                                           | 0.38  | 72.9 |
|     |                                                                                           | 0.43  | 83.1 |
|     |                                                                                           | 0.60  | 91.3 |
| 130 | <a href="https://doi.org/10.1021/acs.chemmater.2c02797">10.1021/acs.chemmater.2c02797</a> | 0.20  | 1.6  |
|     |                                                                                           | 0.24  | 4.5  |
|     |                                                                                           | 0.26  | 4.7  |
|     |                                                                                           | 0.23  | 5.3  |
|     |                                                                                           | 0.22  | 7.6  |
|     |                                                                                           | 0.23  | 10.3 |
| 131 | <a href="https://doi.org/10.1038/s41467-024-52359-6">10.1038/s41467-024-52359-6</a>       | 0.66  | 12.4 |
|     |                                                                                           | 1.62  | 12.4 |

**Table S1.** Summary of literature-derived data points<sup>[1–46]</sup> used in Figure 5E (main text) for benchmarking the Density–Volumetric Shrinkage map.

## Experimental Materials and Methods

### Materials

Styrene (ST,  $\geq 99\%$ , with stabilizer), divinylbenzene (DVB,  $\geq 80\%$ , mixture of isomers), sorbitan monooleate (Span® 80), potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ), anhydrous calcium chloride ( $\text{CaCl}_2$ ), 3-ethynylaniline, 3-hydroxyphenylacetylene, 3-aminobenzonitrile, 3-cyanophenol, tetrahydrofuran (THF), methanol (MeOH), acetone ( $\text{C}_3\text{H}_6\text{O}$ ), chloroform ( $\text{CHCl}_3$ ), dichloromethane (DCM), hexanes ( $\text{C}_6\text{H}_{14}$ ), ethyl acetate ( $\text{C}_4\text{H}_8\text{O}_2$ ), and deuterated chloroform ( $\text{CDCl}_3$ ) were purchased from Thermo Fisher Scientific or Sigma-Aldrich and used as received unless otherwise noted. Paraformaldehyde (solid), aniline, and liquified phenol were purchased from Sigma-Aldrich. ST and DVB were passed through a basic alumina plug to remove stabilizers. All aqueous solutions were prepared using deionized water ( $\text{DI H}_2\text{O}$ ) produced in-house.

### Instrumentation

- **Thermogravimetric analysis (TGA)** characterization was conducted using a TA Instruments Discovery thermogravimetric analyzer with the high-resolution procedure (Hi-Res TGA) and default settings (ramp rate =  $2\text{--}10\text{ }^\circ\text{C min}^{-1}$  to  $T\text{ }^\circ\text{C}$ , resolution = 5), in platinum pans. The ramp rate and isothermal stage durations were varied.
- **Activation Energy Determination (TGA)** Apparent activation energies ( $E_a\text{ kJ mol}^{-1}$ ) were first estimated using the Kissinger method, which relates the thermal decomposition kinetics to the shift in peak decomposition temperature ( $T_p$ ) observed under multiple linear heating rates<sup>[47]</sup>. In this method, a series of TGA experiments is performed at different constant heating rates ( $\beta = 2, 5, 10, 15, \text{ and } 20\text{ }^\circ\text{min}^{-1}$ ), and the peak temperature ( $T_p\text{ }^\circ\text{C}$ ) of the derivative curve (DTG) is

recorded for each. The Kissinger equation (below) is used to extract  $E_a^{\text{Kiss}}$  from the slope of a plot of  $\ln(\beta/T_p^2)$  versus  $1/T_p$  (Fig. S4).

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_p}$$

This model-based approach assumes a single-step decomposition reaction and does not require prior knowledge of the reaction model (Fig. S5A). However, it yields only an average activation energy (Ramp averaged) corresponding to the peak rate of mass loss and cannot account for changes in reaction mechanism or kinetic behavior across different stages of decomposition. For complex, multistep degradation processes or systems with overlapping reactions, this simplification may limit interpretive resolution.

To address these limitations and gain a more comprehensive understanding of decomposition kinetics, modulated thermogravimetric analysis (MTGA) was employed<sup>[48]</sup>. In this approach, a sinusoidal temperature modulation is superimposed onto a conventional linear heating rate, allowing for dynamic extraction of kinetic parameters during a single experiment. Specifically, MTGA enables real-time calculation of activation energy ( $E_a^{\text{Mod}}$ ) as a function of conversion ( $\alpha$ ) by monitoring the oscillatory mass loss response under controlled thermal perturbation (Fig. S5B). The rate of mass loss ( $d\alpha/dt$ ) is modeled using the Arrhenius expression and deconvoluted to isolate the temperature-dependent kinetic component, which is independent of heating rate contributions. This technique mitigates distortions associated with multiple isothermal experiments and offers improved resolution in assessing complex decomposition behavior. The parameters used for MTGA experiments included a heating rate of  $2^\circ\text{C min}^{-1}$  from  $25^\circ\text{C}$  to  $800^\circ\text{C}$ , with a modulation amplitude of  $\pm 5^\circ\text{C}$ , a modulation period of 200 s, and a resolution of 5.

To assess the consistency between the two methods, a direct comparison was performed between the ramp-averaged activation energies obtained from Kissinger analysis ( $E_a^{\text{Kiss}}$ ) and the

conversion-averaged activation energies extracted from modulated TGA ( $E_a^{\text{Mod}}$ ) (Fig. S5C). For each sample,  $E_a^{\text{Mod}}$  was calculated by averaging the MTGA-derived activation energy values over a conversion range of  $0.1 \leq \alpha \leq 0.6$ , corresponding to the dominant mass loss regime. The resulting values showed strong agreement with  $E_a^{\text{Kiss}}$  within experimental uncertainty, confirming that both methods capture comparable energy barriers for decomposition. This correlation supports the use of MTGA as a high-resolution, model-free alternative to traditional Kissinger analysis, while also validating the fidelity of the Kissinger method for screening activation energies in thermally stable systems.

- **Differential Scanning Calorimetry (DSC)** characterization was carried out using a TA Instruments Discovery 2500 differential scanning calorimeter. Samples were prepared in aluminum hermetic pans from TA Instruments with a hole punched in the top to prevent pressure build-up. Typical test conditions involved a heat-cool-heat procedure from (30 °C, 200 °C, – 50 °C, 200 °C) with a rate of 5 °C min<sup>-1</sup>; the second heat cycle was used for analysis.
- **Raman spectroscopy** was conducted using a Horiba LabRAM HR Evolution confocal Raman microscope equipped with a 50X LWD objective lens, 10% filter, and 532 nm laser. All spectra were collected at room temperature under ambient conditions using an acquisition time of ~ 5 minutes (10 accumulations; 30 seconds each).
- **Nuclear Magnetic Resonance (NMR)** data was acquired on a 400 MHz Bruker Avance-III-HD Nanobay spectrometer equipped with a double resonance broadband (BBFO) SmartProbe.
- **Scanning Electron Microscopy (SEM)** was conducted with Carl Zeiss Merlin high-resolution Field Emission Scanning Electron Microscope (FE-SEM). The SEM was operated under the In-Lens mode with an accelerating voltage of 10 kV and a working distance of ~5-7 mm. The samples were placed on copper tape attached to stubs and sputter-coated with a thin layer (~4 nm) of Pt/Pd alloy to enhance electron

conductivity. Void sizes were analyzed using the MATLAB code (See appendix section of the SI for annotated code).

- **Tube Furnace pyrolysis** was conducted in a Thermo Scientific Lindberg/Blue M Mini-Mite TF55035C Tube Furnace equipped with 1-inch diameter quartz tubes capable of achieving up to  $\sim 1100$  °C and  $< 50$  °min<sup>-1</sup>. The tube furnace is installed with a mass flow controller set to deliver  $\sim 10$  sccm of N<sub>2</sub>. The Lindberg furnace was used for pyrolysis of small samples under direct ramp ( $5$  °min<sup>-1</sup> to 800°C, 2h isotherm) conditions. The cooling rate was set to  $2$  °min<sup>-1</sup> until 400 °C, and the furnace was left to cool naturally.

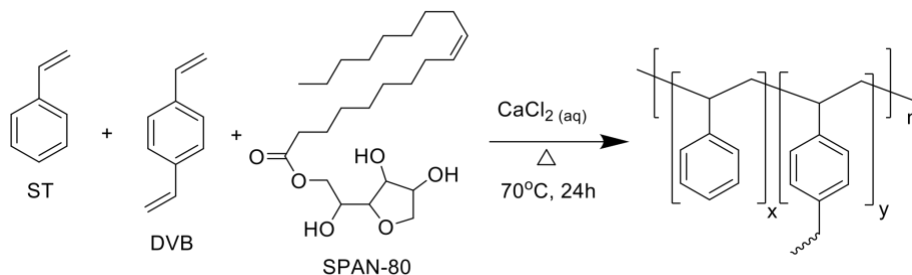
## Synthesis Methods

- **Synthesis of PS-DVB Poly(HIPE) Template Series**

Poly(HIPE) templates were synthesized by curing high internal phase emulsions (HIPEs), which are surfactant-stabilized water-in-oil emulsions with an aqueous phase volume fraction of 74% or greater. In this system, the aqueous phase ( $\sim 90$  vol%) comprised deionized water (DI H<sub>2</sub>O), calcium chloride (CaCl<sub>2</sub>) as a stabilizing salt, and potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) as a radical initiator. The organic phase ( $\sim 10$  vol%) consisted of styrene (ST, with the inhibitor removed), divinylbenzene (DVB) as a cross-linker, and sorbitan monooleate (Span 80) as the surfactant. A representative formulation for DVB-10% is outlined in Figure S11. For other PS-DVB-x compositions (where  $x = 0, 25, 50, 75, 100\%$ ), the mass ratio of ST to DVB was adjusted to achieve the desired DVB mol% while maintaining the overall volume of the organic phase constant.

To prepare the emulsion, the organic phase was first transferred into a beaker, and the aqueous phase was added dropwise at a rate of approximately  $2 \text{ mL min}^{-1}$  using a syringe pump, while stirring at a speed of around 300 rpm with an overhead stirrer. As the emulsion thickened, the stirring speed was gradually increased to about 500 rpm to ensure uniform droplet dispersion. Once the aqueous





| External/Organic Phase |             |             | Internal/Aqueous Phase   |                       |                                                  |
|------------------------|-------------|-------------|--------------------------|-----------------------|--------------------------------------------------|
| Monomer                | Crosslinker | Surfactant  | Water                    | Salt                  | Initiator                                        |
| ST (g)                 | DVB (g)     | Span80 (mL) | DI H <sub>2</sub> O (mL) | CaCl <sub>2</sub> (g) | K <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (g) |
| 1.60                   | 0.22        | 0.35        | 21.0                     | 0.218                 | 0.1                                              |

| Internal Phase      |                    | External Phase      |                    |
|---------------------|--------------------|---------------------|--------------------|
| vol% Internal Phase | wt% Internal Phase | vol% External Phase | wt% External Phase |
| 90.25               | 91.01              | 9.75                | 8.99               |

**Fig. S11** PS-DVB-10 Poly(HIPE) Template chemical reaction scheme and synthesis.

content reached 74% or more, the emulsion was classified as a high internal phase emulsion (HIPE) and transferred into 40 mL glass vials for curing. The HIPE samples were then cured in a convection oven at 70 °C for 24 hours under ambient air. The resulting PS-poly(HIPE) monoliths underwent vacuum drying for 24 hours, followed by Soxhlet extraction with water (for 24 hours) and methanol (for another 24 hours) to eliminate residual salts and unreacted organics. The final drying process under vacuum at 70 °C for an additional 24 hours produced rigid, plug-shaped monoliths, which were subsequently sectioned into approximately 0.5 cm-thick discs and further cut into ~1 cm<sup>3</sup> cuboids.

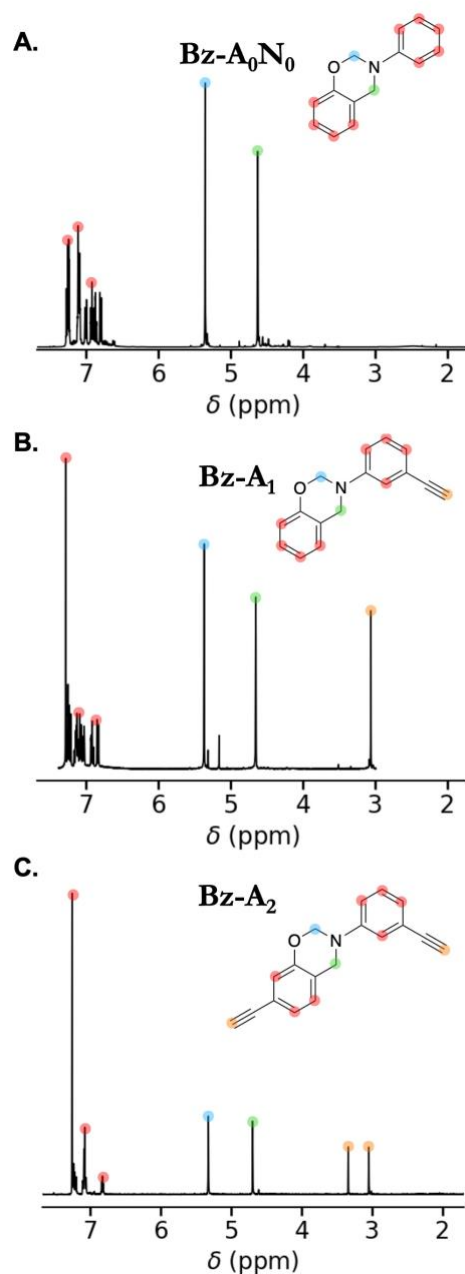
- **Synthesis of Benzoxazine Monomers and Polymers**

The synthesis of Bz-A<sub>2</sub> served as the representative procedure for all Bz-A<sub>m</sub>N<sub>n</sub> monomers. We followed the solventless synthesis procedure pioneered by Ishida and co-workers<sup>[49,50]</sup>. Bz-A<sub>2</sub> was synthesized via a solventless Minnich condensation of 3-hydroxyphenylacetylene (phenol), paraformaldehyde (aldehyde), and 3-ethynylaniline (amine). Stoichiometric quantities of each component were added to a 40 mL vial, homogenized in an ultrasonic bath for ~1 minute, and stirred at 100 °C for 30 minutes under a sealed septum with a vent needle. The crude reaction product was dissolved in chloroform and purified by liquid–liquid extraction with 3 M NaOH. After three washes, the organic layer was dried over sodium sulfate and then concentrated via rotary evaporation, followed by high-vacuum drying overnight. Further purification was carried out via column chromatography (silica gel; hexanes/ethyl acetate gradient: 4:1, 2:1, 1:1). The fractions containing the product were pooled, concentrated, and dried to yield a white, crystalline solid. All monomers were polymerized isothermally in a convection oven at 190 °C for 24 hours under ambient air to generate highly crosslinked polybenzoxazine networks through concurrent ring-opening and acetylene thermal polymerization. Structural identity and purity were confirmed by <sup>1</sup>H NMR spectroscopy (Fig. S12). Other Bz-A<sub>m</sub>N<sub>n</sub> monomers were synthesized using the same protocol, with substituted phenol and amine precursors as listed below:

| Monomer                              | Phenol                   | Amine                |
|--------------------------------------|--------------------------|----------------------|
| <b>Bz-A<sub>0</sub>N<sub>0</sub></b> | Liquid phenol            | Aniline              |
| <b>Bz-A<sub>1</sub></b>              | Liquid phenol            | 3-Ethynylaniline     |
| <b>Bz-N<sub>1</sub></b>              | Liquid phenol            | 3-Amino-benzonitrile |
| <b>Bz-A<sub>2</sub></b>              | 3-Hydroxyphenylacetylene | 3-Ethynylaniline     |
| <b>Bz-N<sub>2</sub></b>              | 3-Cyanophenol            | 3-Amino-Benzonitrile |

- **Synthesis of Poly(HIPE)-Polybenzoxazine Template-Coating Pairs**

To generate template-coating pairs, Poly(HIPE) monoliths were immersed in chloroform solutions of PBz-A<sub>m</sub>N<sub>n</sub> at various concentrations. Samples were subjected to vacuum infiltration for 24 hours to ensure complete monomer permeation into the tortuous, interconnected porous architecture. Chloroform was chosen for its favorable compatibility with the poly(HIPE) matrix and ability to facilitate thorough permeation. After infiltration, samples were thermally cured at 200 °C for 24 hours in air under isothermal conditions. This initiated in situ ring-opening polymerization of the benzoxazine monomer (Fig. S7A), forming a conformal polybenzoxazine coating throughout the poly(HIPE) framework. Polymerization was evident by the darkening and increased rigidity of the monoliths. Following curing, the coated samples were sequentially Soxhlet-extracted with methanol and water to remove unreacted monomer and byproducts. Final drying was performed under vacuum at 70 °C, and the resulting template-coating pairs were subjected to structural and thermal characterization.



**Fig. S12** Representative  $^1\text{H}$  NMR spectra confirming the successful synthesis of acetylene-functional benzoxazine monomers. **A)** PBz-A<sub>0</sub>N<sub>0</sub> (unsubstituted), **B)** PBz-A<sub>1</sub> (mono-acetylene substituted), and **C)** PBz-A<sub>2</sub> (di-acetylene substituted). Proton signals in the aromatic region ( $\sim 7$  ppm), labeled with red markers, confirm the presence of aryl rings derived from the phenol and amine precursors. Peaks at  $\sim 5.2$  ppm (blue marker) and  $\sim 4.8$  ppm (green marker) correspond to protons on the oxazine ring, with the blue marker indicating the two protons situated between the nitrogen and oxygen atoms. In PBz-A<sub>1</sub> and PBz-A<sub>2</sub>, additional peaks near  $\sim 3.2$  ppm, labeled with orange markers, correspond to terminal acetylene protons, confirming successful acetylene substitution. The progressive intensity of these acetylene signals from panels A to C reflects an increasing degree of acetylene substitution.

## References – Supporting Information

- [1] M. Jalalian, Q. Jiang, A. Coulon, M. Storb, R. Woodward, A. Bismarck, *Materials & Design* **2019**, *168*, 107658.
- [2] M. Inagaki, N. Ohta, Y. Hishiyama, *Carbon* **2013**, *61*, 1.
- [3] H. Steldinger, A. Esposito, K. Brunnengräber, J. Gläsel, B. J. M. Etzold, *Adv. Sci.* **2019**, *6*, 1901340.
- [4] W. Hu, F. Xie, Y. Li, Z. Wu, K. Tian, M. Wang, L. Pan, L. Li, *Langmuir* **2017**, *33*, 13364.
- [5] D. Wang, N. L. Smith, P. M. Budd, *Polymer International* **2005**, *54*, 297.
- [6] N. Cohen, M. S. Silverstein, *Polymer* **2011**, *52*, 282.
- [7] S. Kovačič, B. Schafzahl, N. B. Matsko, K. Gruber, M. Schmuck, S. Koller, S. A. Freunberger, C. Slugovc, *ACS Appl. Energy Mater.* **2022**, acsaem.2c02787.
- [8] R. T. Woodward, A. Jobbe-Duval, S. Marchesini, D. B. Anthony, C. Petit, A. Bismarck, *Polymer* **2017**, *115*, 146.
- [9] A. Szczurek, V. Fierro, A. Pizzi, A. Celzard, *Carbon* **2014**, *74*, 352.
- [10] R. T. Woodward, F. Markoulidis, F. De Luca, D. B. Anthony, D. Malko, T. O. McDonald, M. S. P. Shaffer, A. Bismarck, *J. Mater. Chem. A* **2018**, *6*, 1840.
- [11] R. T. Woodward, D. W. H. Fam, D. B. Anthony, J. Hong, T. O. McDonald, C. Petit, M. S. P. Shaffer, A. Bismarck, *Carbon* **2016**, *101*, 253.
- [12] A. Suresh, S. J. Rowan, C. Liu, *Advanced Materials* **2023**, *35*, 2206416.
- [13] L. Zhang, M. Liu, S. Roy, E. K. Chu, K. Y. See, X. Hu, *ACS Appl. Mater. Interfaces* **2016**, *8*, 7422.
- [14] X. Zhang, L. Zhong, A. Mateos, A. Kudo, A. Vyatskikh, H. Gao, J. R. Greer, X. Li, *Nat. Nanotechnol.* **2019**, *14*, 762.
- [15] S. Yu, Z. Chen, Y. Wang, R. Luo, Y. Pan, *J Porous Mater* **2018**, *25*, 527.

- [16] J. W. F. To, Z. Chen, H. Yao, J. He, K. Kim, H.-H. Chou, L. Pan, J. Wilcox, Y. Cui, Z. Bao, *ACS Cent. Sci.* **2015**, *1*, 68.
- [17] M. Mazaj, M. Bjelica, E. Žagar, N. Z. Logar, S. Kovačič, *ChemSusChem* **2020**, *13*, 2089.
- [18] M. Jalalian, Q. Jiang, M. Birot, H. Deleuze, R. T. Woodward, A. Bismarck, *Reactive and Functional Polymers* **2018**, *132*, 145.
- [19] P. Lorjai, S. Wongkasemjit, T. Chaisuwan, *Materials Science and Engineering: A* **2009**, *527*, 77.
- [20] C. J. Zúñiga Ruiz, A. Szczurek, A. Martínez De Yuso Arisa, J. C. Ronda, V. Cádiz, V. Fierro, A. Celzard, *Carbon* **2015**, *95*, 919.
- [21] Q. Lin, S. Dong, L. Qu, C. Fang, K. Luo, *Journal of Analytical and Applied Pyrolysis* **2014**, *106*, 164.
- [22] A. Foulet, M. Birot, R. Backov, G. Sonnemann, H. Deleuze, *Materials Today Communications* **2016**, *7*, 108.
- [23] K. Kapilov-Buchman, L. Portal, Y. Zhang, N. Fechler, M. Antonietti, M. S. Silverstein, *J. Mater. Chem. A* **2017**, *5*, 16376.
- [24] M. Xiang, H. Wu, H. Liu, J. Huang, Y. Zheng, L. Yang, P. Jing, Y. Zhang, S. Dou, H. Liu, *Adv Funct Materials* **2017**, *27*, 1702573.
- [25] M. A. Aslam, W. Ding, S. Ur Rehman, A. Hassan, Y. Bian, Q. Liu, Z. Sheng, *Applied Surface Science* **2021**, *543*, 148785.
- [26] R. Llamas-Unzueta, J. A. Menéndez, M. Suárez, A. Fernández, M. A. Montes-Morán, *Additive Manufacturing* **2022**, *59*, 103083.
- [27] K. Xiao, L. Ding, G. Liu, H. Chen, S. Wang, H. Wang, *Advanced Materials* **2016**, *28*, 5997.
- [28] Q. Liang, Z. Li, X. Yu, Z. Huang, F. Kang, Q. Yang, *Advanced Materials* **2015**, *27*, 4634.
- [29] T. N. Pham, T. Sharifi, R. Sandström, W. Siljebo, A. Shchukarev, K. Kordas, T. Wågberg, J.-P. Mikkola, *Sci Rep* **2017**, *7*, 6112.

- [30] S. Wang, N. Xiao, Y. Zhou, Z. Ling, M. Li, J. Qiu, *Carbon* **2016**, *105*, 224.
- [31] Y. Li, B. Shen, X. Pei, Y. Zhang, D. Yi, W. Zhai, L. Zhang, X. Wei, W. Zheng, *Carbon* **2016**, *100*, 375.
- [32] Y. Sun, S. Luo, H. Sun, W. Zeng, C. Ling, D. Chen, V. Chan, K. Liao, *Carbon* **2018**, *136*, 299.
- [33] M. Islam, J. Flach, R. Martinez-Duarte, *Carbon* **2018**, *133*, 140.
- [34] J. Men, J. Feng, Y. Jiang, L. Li, Y. Hu, J. Feng, *ACS Appl. Nano Mater.* **2024**, *7*, 7132.
- [35] Q. X. Huang, R. P. Wang, W. J. Li, Y. J. Tang, Y. Chi, J. H. Yan, *Energy Fuels* **2014**, *28*, 6398.
- [36] J. Kemppainen, I. Gallegos, A. S. Krieg, J. R. Gissinger, K. E. Wise, M. Kowalik, J. A. King, S. Gowtham, A. Van Duin, G. M. Odegard, *ACS Appl. Eng. Mater.* **2023**, *1*, 2555.
- [37] S. Zhang, Q. Ran, Q. Fu, Y. Gu, *Materials Chemistry and Physics* **2019**, *236*, 121806.
- [38] J. E. Mosquera, L. Delevingne, F. Delbecq, E. Daouk, A. Drelich, K. Saleh, R. Gautier, M. Leturia, *RSC Adv.* **2025**, *15*, 6783.
- [39] S. Wang, W.-C. Li, L. Zhang, Z.-Y. Jin, A.-H. Lu, *J. Mater. Chem. A* **2014**, *2*, 4406.
- [40] F. Su, C. K. Poh, J. S. Chen, G. Xu, D. Wang, Q. Li, J. Lin, X. W. Lou, *Energy Environ. Sci.* **2011**, *4*, 717.
- [41] M. Letellier, C. Delgado-Sanchez, M. Khelifa, V. Fierro, A. Celzard, *Carbon* **2017**, *116*, 562.
- [42] J. Li, Y. Ding, N. Yu, Q. Gao, X. Fan, X. Wei, G. Zhang, Z. Ma, X. He, *Carbon* **2020**, *158*, 45.
- [43] J. Kim, D. Lee, C. Kim, H. Lee, S. Baek, J. H. Moon, *Proc. Natl. Acad. Sci. U.S.A.* **2023**, *120*, e2222050120.
- [44] V. A. Edlabadkar, S. Gorla, R. U. Soni, A. B. M. S. U. Doulah, J. Gloriod, S. Hackett, N. Leventis, C. Sotiriou-Leventis, *Chem. Mater.* **2023**, *35*, 432.
- [45] Z. Li, A. Bhardwaj, J. He, W. Zhang, T. T. Tran, Y. Li, A. McClung, S. Nuguri, J. J. Watkins, S.-W. Lee, *Nat Commun* **2024**, *15*.

- [46] S. Scott, J. Chew, J. Barnard, A. Burrows, M. Smith, S. Tennison, S. Perera, *Adv Funct Materials* **2023**, *33*, 2213715.
- [47] F. Yao, Q. Wu, Y. Lei, W. Guo, Y. Xu, *Polymer Degradation and Stability* **2008**, *93*, 90.
- [48] R. L. Blaine, B. K. Hahn, *Journal of Thermal Analysis and Calorimetry* **1998**, *54*, 695.
- [49] H. J. Kim, Z. Brunovska, H. Ishida, *Polymer* **1999**, *40*, 6565.
- [50] H. Jin Kim, Z. Brunovska, H. Ishida, *Polymer* **1999**, *40*, 1815.

## **Appendix – Supporting Information**

To quantify void sizes in poly(HIPE) SEM images, we developed an image analysis pipeline using Python (script below). Each image was cropped to retain the top 93% to eliminate artifacts, such as scale bars. The cropped images were then converted to grayscale and denoised through Gaussian blurring. Edge features were extracted using Canny edge detection and further enhanced via morphological dilation. Contours were identified in the processed images and filtered based on circularity and size to isolate approximately spherical voids. For each valid contour, the minimum enclosing circle was computed, and its diameter was converted from pixels to micrometers using the known scale bar. Only voids within a specified diameter range were retained for analysis. The resulting diameters were utilized to compute the mean, standard deviation, and log-normal distribution statistics. A standard correction factor of  $4/\pi$  was applied to the void diameter dataset to account for the statistical bias that causes spherical pores intersected by a 2D imaging plane to appear smaller unless sectioned through their centers; integrating over all sectioning positions results in an average measured radius of  $R \cdot \pi/4$ . By applying this correction, we estimated the true void diameters from the 2D SEM image projections. The void diameters were subsequently appended to a global DataFrame to facilitate batch processing across multiple images. To investigate trends, the average void diameter was plotted as a function of pyrolysis temperature, complete with standard deviation error bars (Fig. 4E of the main text).

```
from google.colab import drive

# Mount Google Drive
drive.mount('/content/drive')

import cv2
```



```

import numpy as np
import matplotlib.pyplot as plt
import pandas as pd

global_df = pd.DataFrame(columns=['label', 'temp',
'void_diameter_micrometers'])

def find_voids(image, show_all_steps=False,
circularity_thresh=0.3, image_width_micrometers=100,
min_void_diameter_micrometers=3,
max_void_diameter_micrometers=15, add_to_df=False, label=0,
temp=0): # ----- LOWER circularity_thresh TO ALLOW FOR
LESS CIRCULAR VOIDS
    # Parameters (you can modify these values)
    image_pixel_width = image.shape[1] # The width of the image
in pixels
    image_pixel_height = image.shape[0] # The height of the
image in pixels

    # Convert the diameter range from micrometers to pixels
    min_void_diameter_pixels = (min_void_diameter_micrometers /
image_width_micrometers) * image_pixel_width
    max_void_diameter_pixels = (max_void_diameter_micrometers /
image_width_micrometers) * image_pixel_width

    # Calculate the new height to keep the top 93% of the image
    keep_percentage = 0.93 # 93%
    new_height = int(image_pixel_height * keep_percentage)

    # Crop the image to keep the top 93%
    cropped_image = image[:new_height, :]

    if show_all_steps:
        # Show the cropped image
        plt.figure(figsize=(10, 10))
        plt.imshow(cv2.cvtColor(cropped_image,
cv2.COLOR_BGR2RGB))
        plt.title("Cropped Image (Top 93%)")
        plt.axis('off')
        plt.show()

    # Convert to grayscale
    gray_image = cv2.cvtColor(cropped_image, cv2.COLOR_BGR2GRAY)

    if show_all_steps:
        # Show the grayscale image
        plt.figure(figsize=(10, 10))

```

```

plt.imshow(gray_image, cmap='gray')
plt.title("Grayscale Image")
plt.axis('off')
plt.show()

# Apply Gaussian blur to reduce noise and enhance edges
blurred_image = cv2.GaussianBlur(gray_image, (5, 5), 0)

if show_all_steps:
    # Show the blurred image
    plt.figure(figsize=(10, 10))
    plt.imshow(blurred_image, cmap='gray')
    plt.title("Blurred Image")
    plt.axis('off')
    plt.show()

# Apply Canny edge detection to detect edges of the bright
outlines
edges = cv2.Canny(blurred_image, 50, 150)

if show_all_steps:
    # Show the edges detected by Canny
    plt.figure(figsize=(10, 10))
    plt.imshow(edges, cmap='gray')
    plt.title("Canny Edge Detection")
    plt.axis('off')
    plt.show()

# Dilate the edges to make the outlines more pronounced
kernel = np.ones((3, 3), np.uint8)
dilated_edges = cv2.dilate(edges, kernel, iterations=1)

if show_all_steps:
    # Show the dilated edges
    plt.figure(figsize=(10, 10))
    plt.imshow(dilated_edges, cmap='gray')
    plt.title("Dilated Edges")
    plt.axis('off')
    plt.show()

# Invert the dilated image so that voids are solid shapes
inverted_image = cv2.bitwise_not(dilated_edges)

if show_all_steps:
    # Show the inverted image
    plt.figure(figsize=(10, 10))
    plt.imshow(inverted_image, cmap='gray')

```

```

plt.title("Inverted Dilated Edges")
plt.axis('off')
plt.show()

# Find contours in the inverted image
contours, _ = cv2.findContours(inverted_image,
cv2.RETR_EXTERNAL, cv2.CHAIN_APPROX_SIMPLE)

# Collect void diameters
void_diameters = []

# Draw circles around each detected void within the
specified diameter range
output_image = cv2.cvtColor(gray_image, cv2.COLOR_GRAY2BGR)
# Convert back to color for drawing

for contour in contours:
    if len(contour) < 5:
        continue

    # Get the convex hull of the contour
    hull = cv2.convexHull(contour)
    hull_area = cv2.contourArea(hull)

    # Calculate the perimeter of the convex hull
    hull_perimeter = cv2.arcLength(hull, True)

    # Calculate circularity:  $4\pi * \text{area} / \text{perimeter}^2$ 
    circularity = 4 * np.pi * (hull_area / (hull_perimeter *
hull_perimeter))

    if circularity > circularity_thresh: # Allow for rough
circularity
        (x, y), radius = cv2.minEnclosingCircle(hull)
        diameter = 2 * radius
        if min_void_diameter_pixels <= diameter <=
max_void_diameter_pixels:
            void_diameters.append(diameter)
            center = (int(x), int(y))
            radius = int(radius)
            cv2.circle(output_image, center, radius, (0,
255, 0), 2) # Draw the circle in green

    if add_to_df:
        # Convert each void diameter from pixels to micrometers
and append to the global DataFrame
        global global_df

```

```

        for diameter_pixels in void_diameters:
            diameter_micrometers = (diameter_pixels *
image_width_micrometers) / image_pixel_width
            new_row = {'label': label, 'temp': temp,
'void_diameter_micrometers': diameter_micrometers}
            global_df = pd.concat([global_df,
pd.DataFrame([new_row])], ignore_index=True)

    # Calculate statistics
    if void_diameters:
        avg_diameter_pixels = np.mean(void_diameters)
        std_diameter_pixels = np.std(void_diameters)
    else:
        avg_diameter_pixels = 0
        std_diameter_pixels = 0

    # Convert the average diameter and std dev from pixels to
micrometers
    avg_diameter_micrometers = (avg_diameter_pixels *
image_width_micrometers) / image_pixel_width
    std_diameter_micrometers = (std_diameter_pixels *
image_width_micrometers) / image_pixel_width

    print("Average Diameter: " + str(avg_diameter_micrometers))
    print("Std Dev of Diameter: " +
str(std_diameter_micrometers))

    # Display the result with detected voids circled
    plt.figure(figsize=(10, 10))
    plt.imshow(cv2.cvtColor(output_image, cv2.COLOR_BGR2RGB))
    plt.title("Voids Detected and Circled within Diameter Range
(Top 93% of Image)")
    plt.axis('off')
    plt.show()

    return avg_diameter_micrometers, std_diameter_micrometers

# Prepare to collect data
temperatures = []
average_diameters = []
std_devs = []

# Process each image in the folder
for filename in os.listdir(image_folder_path):
    # Check if there's a '0' before the last underscore
    if re.search(r'0_[^_]*$', filename):

```

```

        # Extract temperature from the filename (number before
first '_')
        temp_match = re.match(r'(\d+)_', filename)
        if temp_match:
            temperature = int(temp_match.group(1))
        else:
            print(f"Skipping file {filename}: temperature not
found")
            continue

        print(f"Processing file: {filename} with temperature
{temperature}°C") # Debug: Check which files are being
processed

        # Load the image
        image_path = os.path.join(image_folder_path, filename)
        image = cv2.imread(image_path, cv2.IMREAD_UNCHANGED)

        if image is None:
            print(f"Skipping file {filename}: image not loaded")
            continue

        avg_diameter, std_diameter = find_voids(image,
circularity_thresh=0.3, image_width_micrometers=100,
min_void_diameter_micrometers=3,
max_void_diameter_micrometers=12, add_to_df=True, label=0,
temp=temperature)

        # Store the results
        temperatures.append(temperature)
        average_diameters.append(avg_diameter)
        std_devs.append(std_diameter)

# Add a 'label' column with 0 for the first dataset
labels_0 = [0] * len(temperatures)

# Create a DataFrame for label 0
data_0 = {
    'label': labels_0,
    'temp': temperatures,
    'avg_diameter': average_diameters,
    'std_diameter': std_devs
}
df_0 = pd.DataFrame(data_0)

# Sort the data by temperature
sorted_indices = np.argsort(temperatures)

```

```

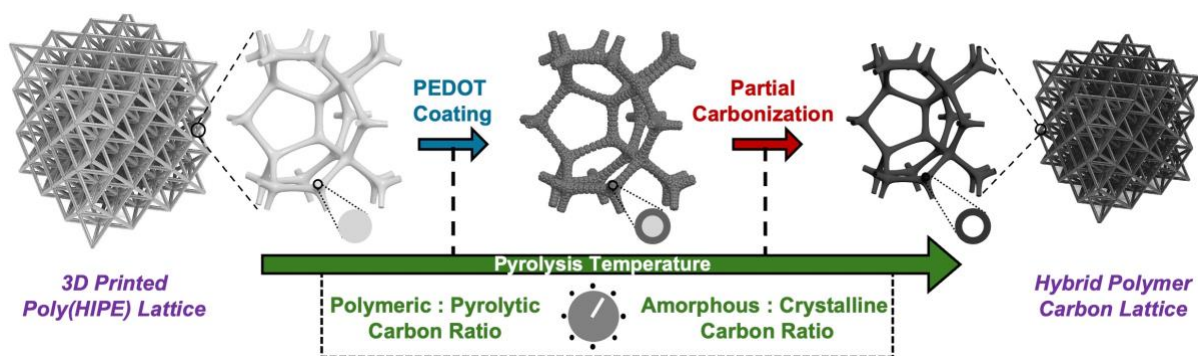
temperatures = np.array(temperatures)[sorted_indices]
average_diameters_micrometers =
np.array(average_diameters)[sorted_indices]
std_devs_micrometers = np.array(std_devs)[sorted_indices]

# Plot the average void diameter with error bars in micrometers
plt.figure(figsize=(12, 6))
plt.errorbar(temperatures, average_diameters_micrometers,
yerr=std_devs_micrometers, fmt='o', capsize=5)
plt.plot(temperatures, average_diameters_micrometers,
linestyle='-', color='blue') # Connect only consecutive points
plt.xlabel('Temperature (°C)')
plt.ylabel('Average Void Diameter (micrometers)')
plt.title('Average Void Diameter vs Temperature')
plt.grid(True)
plt.show()

```

## CHAPTER 4

Balancing strength, toughness, and shrinkage in 3D porous carbon architectures through partial carbonization of template-coating pairs



## **4.1 Abstract**

Balancing strength, toughness, and shrinkage remains a central challenge in the fabrication of 3D pyrolytic carbon architectures. This study presents a scalable strategy that challenges these longstanding trade-offs by partially carbonizing 3D-printed template–coating pairs. Polymerized high internal phase emulsions (poly(HIPE)s) are first 3D printed into geometrically complex lattices with hierarchical porosity spanning multiple length scales. A conformal layer of poly(3,4-ethylenedioxythiophene) (PEDOT) is then applied to form a thermally robust template–coating pair that preserves structural and dimensional integrity during pyrolysis. Partial carbonization is subsequently employed to tune the evolving carbon microstructure—specifically, the polymeric-to-pyrolytic carbon and amorphous-to-crystalline carbon ratios—while suppressing shrinkage. The resulting hybrid polymer-carbon lattices exhibit specific strengths of up to  $\sim 128 \text{ MPa g}^{-1} \text{ cm}^3$ , specific toughnesses of up to  $\sim 32 \text{ J g}^{-1}$ , and exceptional dimension retention of up to 80%—a combination not previously achieved in macroscale 3D porous carbon systems. When benchmarked against monolithic and fully carbonized counterparts, these lattices occupy a previously inaccessible region of the toughness–shrinkage design space. This platform enables the macroscale fabrication of lightweight, damage-tolerant 3D porous carbon architectures with tunable mechanical properties, making them suitable for real-world deployment in structural applications that demand simultaneous load-bearing and energy absorption capabilities.

**Keywords:** Porous carbon, 3D Printing, Template-Coating, Partial Carbonization, Energy absorption



## **4.2 Introduction**

Precisely controlling the three-dimensional architecture of materials—from macroscale geometry to microscale features—is central to unlocking their full mechanical potential. Architected materials, defined by deliberate structural designs across multiple length scales<sup>[1]</sup>, provide an approach to circumvent traditional processing limitations such as brittleness, limited formability, and high melting points inherent to ceramics, glasses, metals, and carbons<sup>[2]</sup>. To overcome these challenges, additive manufacturing (AM) of polymeric precursors<sup>[3–6]</sup>, followed by thermal treatments such as pyrolysis or sintering, has emerged as an effective route to realize complex, hierarchical architectures from otherwise intractable materials<sup>[7,8]</sup>. Decoupling the printing process from the final material formation provides unparalleled flexibility in designing architected materials with remarkable mechanical properties<sup>[9–15]</sup>(Fig. 1A). Noteworthy examples include ultralight, ultrastiff ceramics derived from 3D-printed preceramic polymers<sup>[16–21]</sup>, optical-grade glass fabricated from organic-inorganic polymer resins<sup>[22]</sup>, and metal–ceramic interpenetrating phase composites with exceptional strength and energy absorption<sup>[23,24]</sup>.

In porous carbon-based systems, the 3D printing and pyrolysis strategy has enabled the creation of complex pyrolytic carbon architectures with outstanding mechanical properties by exploiting size effects that emerge at the nanoscale<sup>[25–28]</sup>. In these approaches, substantial volumetric shrinkage—often exceeding 98%—is intentionally used to miniaturize initially polymeric microlattices into pyrolytic carbon nanolattices exhibiting remarkably high strength to density ratios, among the highest ever reported<sup>[29–35]</sup>(Fig. 1B). However, these impressive properties are directly linked to their nanoscale dimensions, making it challenging to scale these structures without incurring significant mechanical performance losses due to increased sensitivity to defects—posing practical limitations for structural applications at macroscopic length scales.

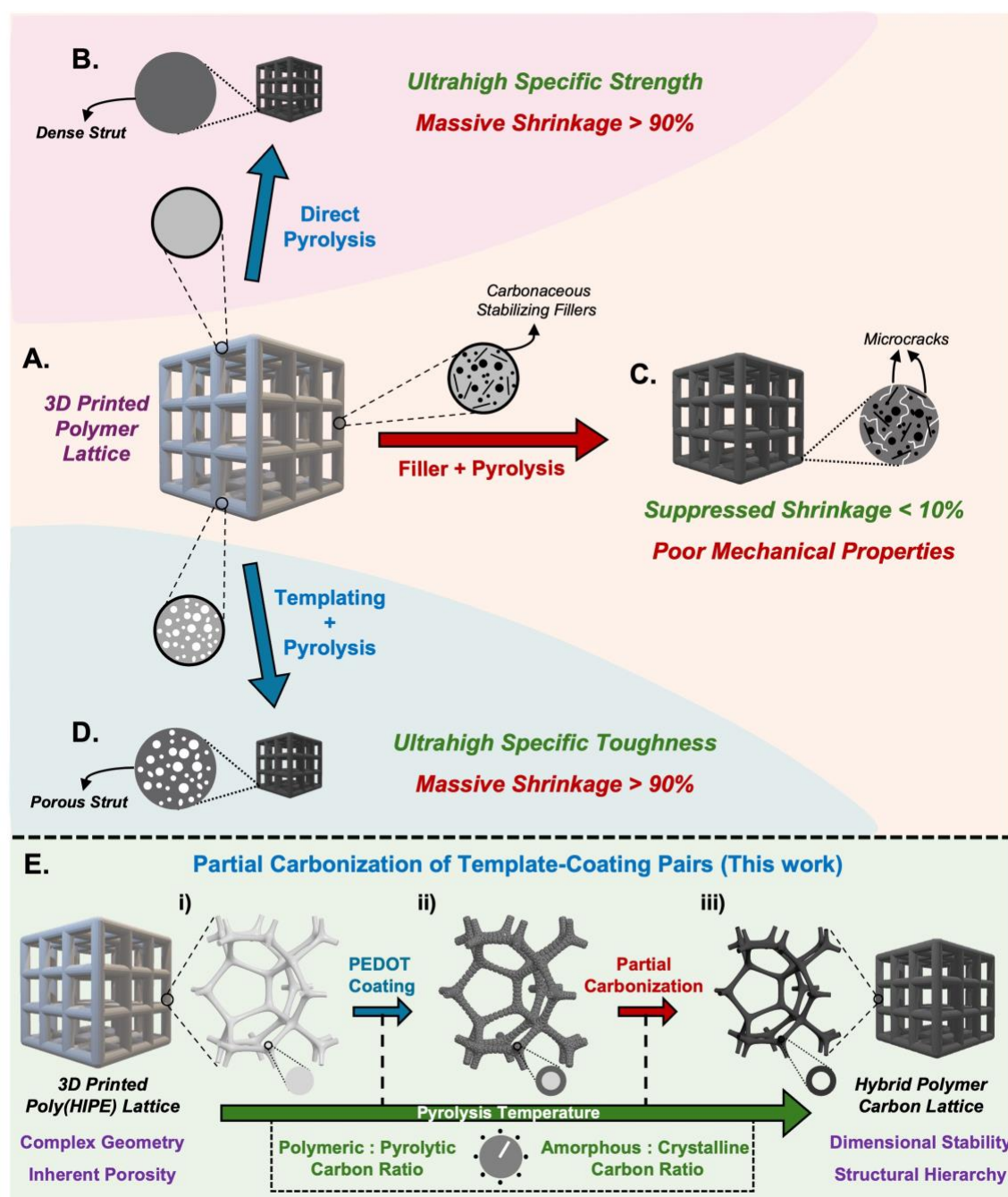
To address these shrinkage-related challenges, strategies such as modular assembly, in which individual pyrolytic carbon microlattice units are joined through designed interfaces, enable the creation of relatively large-scale structures that retain their mechanical advantages<sup>[36–38]</sup>. Notably, the strength and stiffness of such assemblies have even been shown to increase with the number of building blocks; however, this comes at the cost of significant processing complexity and fabrication overhead. Other strategies to achieve shrinkage suppression involve stabilizing the 3D printed polymer precursor through crosslinking<sup>[39–43]</sup>, infiltration with acrylonitrile<sup>[44]</sup>, or incorporation of stabilizing carbonaceous fillers, such as chopped carbon fibers and carbon nanotubes<sup>[45–50]</sup>. While some of these methods have yielded complex pyrolytic carbon architectures with impressively low shrinkage (>90% dimensional retention), they often introduce new challenges: filler agglomeration and interfacial cracking can disrupt pore architecture, ultimately degrading mechanical performance (Fig. 1C).

Considering these challenges, templating strategies present a promising alternative. By directly encoding hierarchical porosity into the precursor through methods such as phase separation or emulsion templating, these methods not only reduce density but also enhance mechanical properties<sup>[51–55]</sup>. For instance, nanostructured carbon pillars fabricated via nanoimprint lithography and etchable bottlebrush block copolymer templates demonstrate remarkable combinations of low density ( $\sim 0.66\text{--}0.82\text{ g cm}^{-3}$ ), ultrahigh strength, and energy absorption capability<sup>[56]</sup>. However, the challenge of significant shrinkage persists due to the inherently fragile nature of porous templates (Fig. 1D).

To address this persistent trade-off between shrinkage and mechanical resilience, partial carbonization emerges as a promising approach. By arresting pyrolysis at intermediate temperatures and carefully controlling the degree of carbonization, it becomes possible to fine-tune the balance between strength and toughness while mitigating excessive shrinkage—a combination that is rarely achieved at the macroscale due to their inherent mutual exclusivity<sup>[57]</sup>. For example, partially

carbonized millimeter-scale polymer-carbon hybrid lattices retain ~50% of their original dimensions and exhibit impressive specific strength of  $\sim 100 \text{ MPa g}^{-1} \text{ cm}^3$  and specific toughness of up to  $\sim 50 \text{ J g}^{-1}$ <sup>[58]</sup>. Nevertheless, these systems reflect a fundamental trade-off: the strength-to-toughness ratio remains highly dependent on the degree of shrinkage, limiting independent control over mechanical properties without incurring shrinkage.

This work introduces a fabrication strategy that directly addresses the longstanding trade-offs between strength, toughness, and shrinkage in 3D porous carbon architectures. Emulsion-templated polymers (poly(HIPE)s) are 3D printed into lattices with tunable macroscale geometry and microscale porosity (Fig. 1E i). To circumvent drastic shrinkage inevitable during direct carbonization<sup>[59]</sup>, a conformal, high-char-yield PEDOT coating is applied to reinforce the template, thereby preserving both architecture and dimensions during pyrolysis (Fig. 1E ii). This template-coating approach, previously demonstrated in porous poly(HIPE) foams, is here extended to complex 3D-printed poly(HIPE) lattices for the first time, enabling the fabrication of hierarchically porous and dimensionally stable 3D carbon architectures (Fig. 1E iii). Partial carbonization is then employed to tune the polymeric-to-pyrolytic carbon and amorphous-to-crystalline carbon ratios, enabling access to a broad spectrum of mechanical properties while maintaining minimal shrinkage. By varying pyrolysis temperature, the resulting carbon lattices achieve compressive strengths of  $\sim 5$  to  $25 \text{ MPa}$  and toughness values of  $\sim 3$  to  $6 \text{ J cm}^{-3}$ . At optimal conditions, the lattices combine low density ( $\sim 0.19 \text{ g cm}^{-3}$ ), high specific strength ( $\sim 115 \text{ MPa g cm}^{-3}$ ), specific stiffness exceeding  $500 \text{ MPa g cm}^{-3}$ , high energy absorption capacity of  $\sim 32 \text{ J g}^{-1}$ , and exceptional dimensional retention (up to 80%)—a combination not previously demonstrated in macroscopic 3D porous carbons. This platform lays the groundwork for macroscale fabrication of customizable 3D carbon lattices with tunable mechanical performance for load-bearing applications at practical length scales.



**Figure 1.** Pyrolytic conversion strategies and trade-offs in the fabrication of 3D porous carbon lattices. **A)** 3D printed polymer lattice with tunable macroscale geometry. Each arrow originating from the precursor lattice in panel (A) represents a distinct pyrolytic pathway leading to the 3D pyrolytic carbon architectures shown in panels (B–D). **B)** Direct pyrolysis yields ultrahigh-strength carbon microlattices but causes massive shrinkage. **C)** The addition of high-char-yield fillers (e.g., carbon nanotubes) significantly suppresses pyrolytic shrinkage but can compromise mechanical performance due to filler agglomeration and interfacial cracking. **D)** Pyrolysis of emulsion-templated porous polymers (e.g., PolyHIPEs) creates hierarchical porosity but leads to pronounced shrinkage and deformation. **E)** Template–coating pair design strategy introduced in this work: the 3D printed Poly(HIPE) lattice serves as the structural blueprint, while the conformal PEDOT coating acts as the primary carbon source, transcribing the template architecture into pyrolytic carbon and preserving both structural and dimensional integrity.

## **4.3 Results and Discussion**

### **4.3.1 Partial Carbonization of Template-Coating Pairs**

The mechanical properties of pyrolytic carbon architectures are fundamentally governed by the degree of carbonization and the resulting carbon microstructure. At low pyrolysis temperatures, residual polymer networks retain ductility but lack the stiffness and strength of fully carbonized frameworks. At the other extreme, complete carbonization produces highly rigid but brittle structures, where high compressive strength comes at the cost of limited energy absorption. Partial carbonization offers a tunable middle ground: by arresting pyrolysis at intermediate temperatures, it is possible to retain sufficient polymer content to enhance ductility and damage tolerance, while progressively introducing pyrolytic carbon domains that contribute to stiffness and load-bearing capacity. Theoretically, this partial carbonization regime presents an opportunity to achieve high strength and toughness-to-weight ratios simultaneously.

To test this hypothesis, a series of variable-temperature experiments was conducted on cylindrical 3D-printed poly(HIPE) plug specimens, composed of elastomer 2-ethylhexyl acrylate (EHA) and monomer isobornyl acrylate (IBOA). These monolithic samples were fabricated using a previously developed, commercial vat photopolymerization (or stereolithography) setup (Fig. S1)[60,61]. Three types of plug variants were prepared: 1) an inherently porous poly(HIPE) plug (denoted 3DP), 2) a coated porous plug (denoted 3DP-PEDOT- $x$ , where  $x = [\text{EDOT}] = 2.5\text{M}$  or  $4.0\text{M}$ ), where the 3DP template was coated with a poly(3,4-ethylenedioxythiophene) (PEDOT) layer of tunable coating thickness depending on EDOT concentration used, and 3) a dense, non-porous plug (3DP-NP), composed of the same formulation as the 3DP sample but lacking any porosity. The 3DP-NP plug is completely dense and serves as a control to isolate the role of inherent porosity on structural and dimensional preservation during pyrolysis (Fig. S2). To prepare the coated variants, 3DP

samples (Fig. 2A i) were first soaked in an iron(III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) solution in tetrahydrofuran (THF) at room temperature under house vacuum to ensure complete infiltration (Fig. 2A ii). Following initiator saturation, the plugs were immersed in a 3,4-Ethylenedioxythiophene (EDOT) solution (in THF) at 70 °C to polymerize and form a conformal PEDOT coating (Fig. 2A iii), yielding 3DP-PEDOT-x samples.

All samples were then subjected to gravimetric (Section 2.2), spectroscopic (Section 2.3), and mechanical (Section 2.4) characterization to assess temperature-resolved pyrolytic transformation and identify the optimal partial carbonization window (Fig. 2A iv). These plug experiments primarily served as a screening platform for evaluating how pyrolysis temperature influences the evolving carbon microstructure—specifically the polymeric-to-pyrolytic and amorphous-to-crystalline carbon ratios—and their impact on mechanical performance. The pyrolysis conditions that yield the best balance between specific strength and toughness, collectively defining the partial carbonization regime, are then applied in more complex lattice architectures, as detailed in section 2.5.

All samples were then subjected to gravimetric (Section 2.2), spectroscopic (Section 2.3), and mechanical (Section 2.4) characterization to assess temperature-resolved pyrolytic transformation and identify the optimal partial carbonization window. These plug experiments primarily served as a screening platform for evaluating how pyrolysis temperature influences the evolving carbon microstructure—specifically the polymeric-to-pyrolytic and amorphous-to-crystalline carbon ratios—and their impact on mechanical performance. The pyrolysis conditions that yield the best balance between specific strength and toughness, collectively defining the partial carbonization regime, are then applied in more complex lattice architectures, as detailed in Section 2.5.

### **4.3.2 Gravimetric and Dimensional Evolution**

Variable-temperature thermogravimetric analysis (TGA) was conducted to evaluate the degradation behavior and char yield (Fig. S3). All samples were ramped at  $5^{\circ}\text{C min}^{-1}$  to target pyrolysis temperatures ranging from  $200^{\circ}\text{C}$  to  $1000^{\circ}\text{C}$  and then held isothermally for 30 minutes to ensure thermal equilibration (Fig. S4). As illustrated in Figure 2A, the bare template (3DP) exhibits rapid decomposition, with mass loss initiating around  $300^{\circ}\text{C}$  and nearly complete degradation by  $450^{\circ}\text{C}$ , indicating its low char yield and poor thermal stability. In contrast, the PEDOT-coated samples (3DP-PEDOT-2.5 and 3DP-PEDOT-4.0) exhibit significantly improved thermal stability, retaining considerably more mass at elevated temperatures. At  $1000^{\circ}\text{C}$ , 3DP-PEDOT-2.5 retains  $\sim 18$  wt% of its original mass, while 3DP-PEDOT-4.0 retains  $\sim 35$  wt%, demonstrating a concentration-dependent increase in char yield on account of the PEDOT coating (Fig. S5).

To quantify macroscopic shrinkage behavior across the temperature range, macroscopic size retention was assessed by tracking dimensional retention ( $L/L_0$ ) and volumetric retention ( $V/V_0$ ) as a function of pyrolysis temperature (Fig. 2B). The uncoated 3DP plugs shrink dramatically with increasing temperature, retaining only  $\sim 25\%$  of their original length and  $\sim 1.5\%$  of their original volume by  $1000^{\circ}\text{C}$ . In contrast, both PEDOT-coated plug variants—3DP-PEDOT-2.5 and 3DP-PEDOT-4.0—show remarkable preservation of bulk geometry, with dimensional retention of  $\sim 80\%$  and corresponding volume retention of  $\sim 50\%$  at  $1000^{\circ}\text{C}$ . Notably, the improvement in shrinkage resistance appeared largely independent of PEDOT concentration, suggesting that the presence of a carbonizable PEDOT coating, rather than its precise mass loading, is sufficient to mitigate collapse.

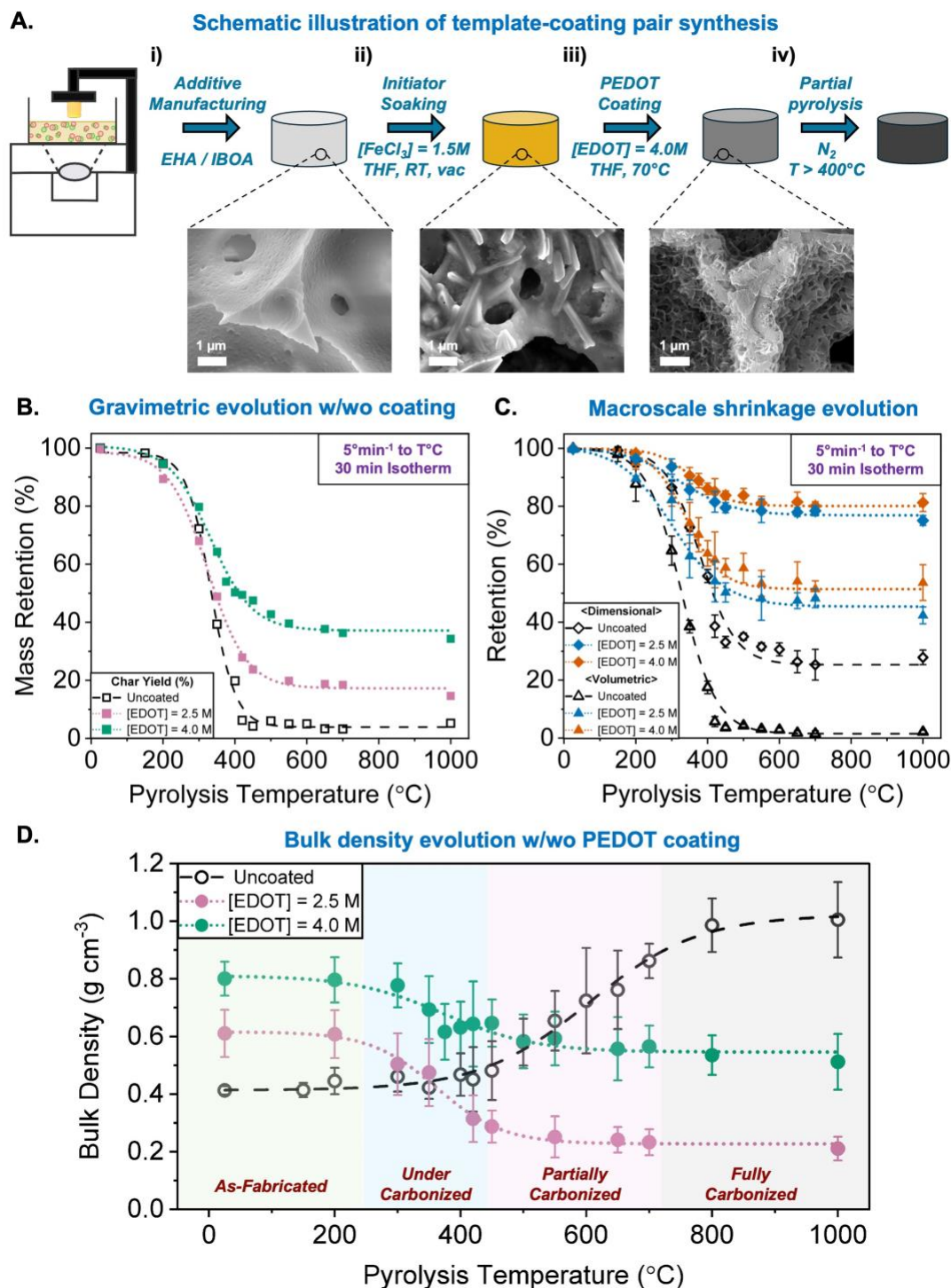
To further quantify structural evolution, bulk density was calculated for the 3DP, 3DP-NP, and 3DP-PEDOT-x (for  $x = 2.5$  and  $4.0$ ) samples across the pyrolysis temperature range (Fig. 2C). For 3DP, the initial bulk density of approximately  $0.4\text{ g cm}^{-3}$  remains relatively stable up to  $325^{\circ}\text{C}$ , and

increases beyond 400°C—coinciding with the onset of degradation and carbonization—to reach a final plateau value of  $\sim 1.0 \text{ g cm}^{-3}$  at 1000°C. This dramatic rise reflects an extensive volume loss that exceeds mass loss, leading to densification of the carbon residue.

The 3DP-NP plug, which lacks internal porosity, begins at a significantly higher density of  $\sim 1.1 \text{ g cm}^{-3}$  (Fig. S6). Its density decreases sharply to  $\sim 0.5 \text{ g cm}^{-3}$  by 500 °C due to substantial mass loss during decomposition. However, this is followed by massive shrinkage beyond 600 °C, which results in a re-densification of the material, ultimately reaching  $\sim 1.2 \text{ g cm}^{-3}$  by 1000 °C. This biphasic trend—initial densification loss due to degradation, followed by densification gain from shrinkage—highlights the inability of dense systems to dissipate internal stresses during pyrolysis, resulting in structural distortion.

In contrast, both coated samples exhibit decreasing density trends with increasing pyrolysis temperature. The 3DP-PEDOT-2.5 sample begins at  $\sim 0.6 \text{ g cm}^{-3}$  and decreases to  $\sim 0.2 \text{ g cm}^{-3}$  by 1000 °C, while the 3DP-PEDOT-4.0 sample begins at  $\sim 0.8 \text{ g cm}^{-3}$  and decreases to  $\sim 0.5 \text{ g cm}^{-3}$ . These trends are consistent with the enhanced dimensional retention of the 3DP-PEDOT-x samples. Although mass is lost through polymer degradation, volume is largely retained, resulting in lower final bulk densities compared to the bare 3DP template. These trends highlight the PEDOT coating's ability to preserve volume while shedding mass, allowing for the formation of lightweight, pyrolytic carbon architectures with enhanced dimensional stability and lower bulk density.





**Figure 2.** Gravimetric and dimensional evolution as a function of pyrolysis temperature. **A)** Mass retention profiles reveal the low char yield and rapid degradation of 3DP, in contrast to the enhanced thermal stability of 3DP-PEDOT-2.5 and 3DP-PEDOT-4.0. **B)** Dimensional and volumetric retention shows extensive shrinkage in 3DP and substantial dimensional stability in 3DP-PEDOT-x samples. **C)** Bulk density evolution highlights densification in 3DP due to massive volumetric collapse, whereas 3DP-PEDOT-x samples exhibit decreasing densities consistent with preserved volume and progressive mass loss.

### **4.3.3 Structural Evolution**

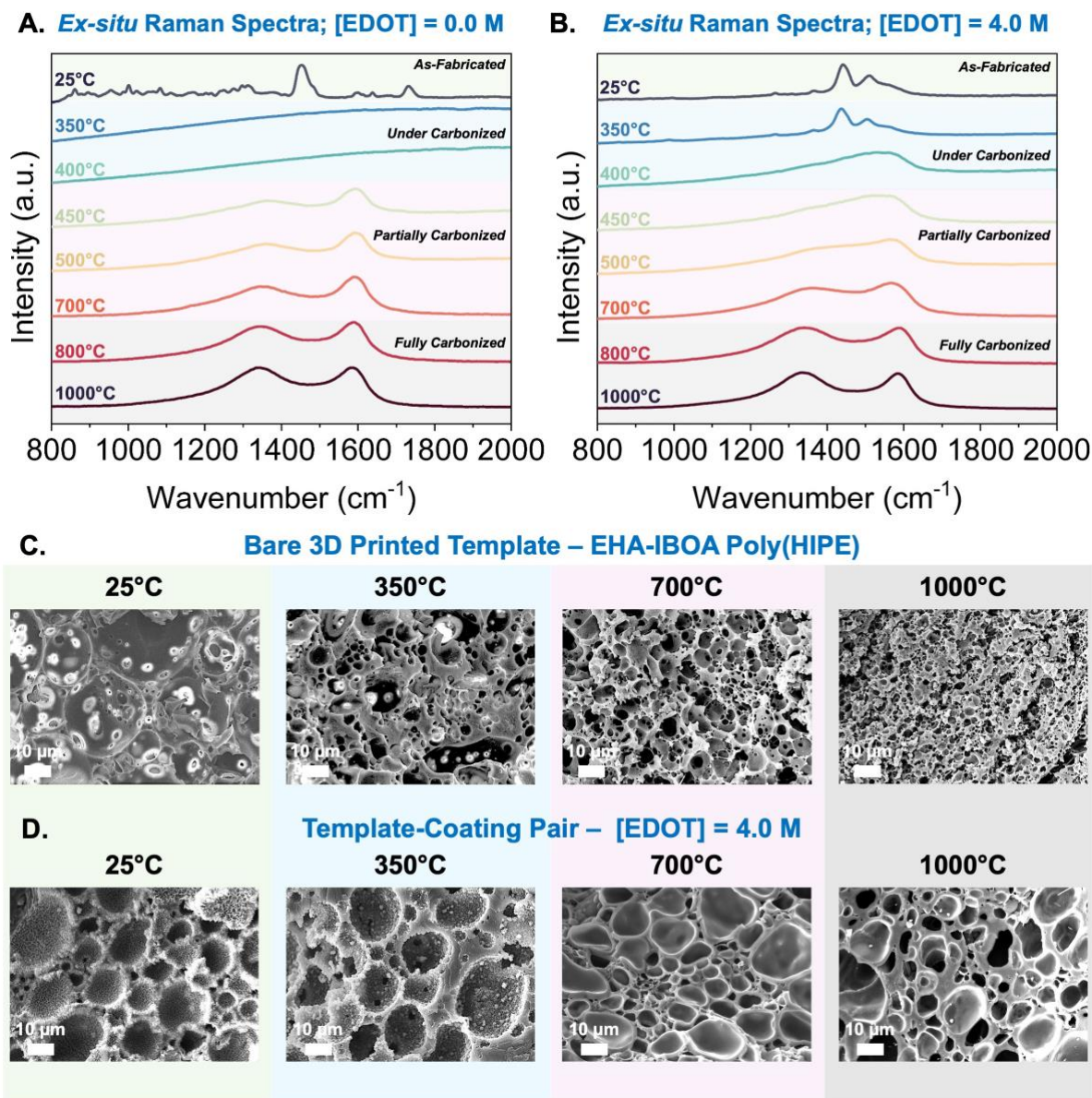
To evaluate the development of carbon microstructure during pyrolysis, variable-temperature Raman spectroscopy was used to monitor the carbonization progression of 3DP and 3DP-PEDOT-4.0M plugs by tracking the evolution of the D ( $\sim 1350\text{ cm}^{-1}$ ) and G ( $\sim 1580\text{ cm}^{-1}$ ) bands. In the uncoated 3DP plugs, polymeric peaks disappear between  $25^{\circ}\text{C}$  and  $350^{\circ}\text{C}$ , aligning with the onset of degradation at  $300^{\circ}\text{C}$  (Fig. 3A). At  $400^{\circ}\text{C}$ , the char yield is approximately 36 wt%, but it drops sharply to approximately 5 wt% by  $450^{\circ}\text{C}$ . This steep reduction indicates that most of the polymer has decomposed by  $450^{\circ}\text{C}$ , and the small amount of residue remaining rapidly converts to pyrolytic carbon, consistent with the appearance of D and G bands.

In contrast, the 3DP-PEDOT-4.0M plugs exhibit an earlier onset of carbonization at approximately  $400^{\circ}\text{C}$ , accompanied by a slower and more gradual spectral evolution (Fig. 3B). This behavior correlates with only a modest decrease in char yield—from  $\sim 50\%$  at  $400^{\circ}\text{C}$  to  $\sim 47\%$  at  $450^{\circ}\text{C}$ —indicating that a significantly larger carbon mass remains to be progressively carbonized. Consequently, the development of the D and G bands is more gradual and less resolved at intermediate temperatures ( $\sim 450^{\circ}\text{C}$ – $700^{\circ}\text{C}$ ) compared to 3DP, suggesting more gradual structural ordering. By  $1000^{\circ}\text{C}$ , however, both 3DP and 3DP-PEDOT-4.0M exhibit comparable spectra, indicating that carbonization has gone to completion in both systems by this stage.

To visualize the corresponding morphological evolution of the uncoated 3DP and coated 3DP-PEDOT-4.0 architectures across the pyrolysis temperature range, scanning electron microscopy (SEM) was performed at representative stages:  $25^{\circ}\text{C}$ ,  $350^{\circ}\text{C}$ ,  $700^{\circ}\text{C}$ , and  $1000^{\circ}\text{C}$ . In the uncoated 3DP samples, significant structural changes were observed as early as  $350^{\circ}\text{C}$ , also consistent with the onset of degradation (Fig. 3C). The porous architecture progressively collapsed with increasing temperature, and by  $1000^{\circ}\text{C}$ , extensive shrinkage of the pores was evident, indicating substantial volumetric loss

and densification of the carbon residue. In contrast, the 3DP-PEDOT-4.0 samples showed markedly enhanced structural retention across the same temperature range (Fig. 3D). At 25 °C, the PEDOT coating was visible on the poly(HIPE) pore surfaces, and no noticeable morphological changes were observed even at 350°C. By 700°C, 3DP-PEDOT-4.0 exhibited surface features consistent with the onset of carbonization; the morphology appeared notably smoother, suggesting the progressive formation of pyrolytic carbon. At 1000°C, the 3DP-PEDOT-4.0 sample appeared fully carbonized, with only modest shrinkage apparent.

Taken together, these variable-temperature experiments demonstrate how the PEDOT coating alters the carbonization pathway, suppressing early degradation and extending the evolution of the carbon microstructure across a broader temperature range. These observations reflect the gradual transformation of polymeric to pyrolytic carbon, as well as the concurrent ordering of amorphous to graphitic carbon domains—two key ratios that critically govern mechanical performance and are directly tunable through pyrolysis temperature.



**Figure 3.** Structural evolution of 3D-printed plugs during pyrolysis. Variable-temperature Raman spectra of **A)** 3DP and **B)** 3DP-PEDOT-4.0 showing the development of D ( $\sim 1350\text{ cm}^{-1}$ ) and G ( $\sim 1580\text{ cm}^{-1}$ ) bands. 3DP exhibits a sharp onset of carbonization around  $450\text{ }^{\circ}\text{C}$ , whereas 3DP-PEDOT-4.0 displays a more gradual spectral evolution, beginning near  $400\text{ }^{\circ}\text{C}$ . Variable-temperature SEM images of **C)** 3DP and **D)** 3DP-PEDOT-4.0 collected at four representative temperatures ( $25^{\circ}\text{C}$ ,  $350^{\circ}\text{C}$ ,  $700^{\circ}\text{C}$ , and  $1000^{\circ}\text{C}$ ). 3DP undergoes extensive collapse and densification, whereas 3DP-PEDOT-4.0 retains its porous architecture, underscoring the critical role of the coating in preserving structural and dimensional fidelity during pyrolysis.

#### **4.3.4 Mechanical Property Evolution of Template-Coating Pairs**

The mechanical properties of the 3DP and 3DP-PEDOT-x samples undergo significant evolution with increasing pyrolysis temperature, reflecting the macro- and microscale structural transformations described above. To evaluate how mechanical performance evolves with pyrolysis temperature, representative engineering stress–strain curves for 3DP and 3DL-PEDOT-4.0 are shown in Figure S7 of the Supporting Information. As pyrolysis progresses, the interplay between residual polymer content, emerging pyrolytic carbon domains, and evolving carbon microstructure is most clearly reflected in the trends in specific strength, specific modulus, and specific toughness as a function of pyrolysis temperature (Figure 4).

The specific strength ( $\text{MPa g}^{-1} \text{cm}^3$ ) of the uncoated 3DP samples (Fig. 4A; blue circles),  $\sim 1.5 \text{ MPa g}^{-1} \text{cm}^3$  at room temperature, increases to  $\sim 6 \text{ MPa g}^{-1} \text{cm}^3$  by  $450^\circ\text{C}$ , coinciding with the onset of carbonization, as indicated by Raman data (Fig. 3A). By  $500^\circ\text{C}$ , poly(HIPE) decomposition is complete as indicated by the stable char yield ( $\sim 5 \text{ wt}\%$ ) (Fig. 2A; black squares), and the specific strength reaches a value of  $\sim 12 \text{ MPa g}^{-1} \text{cm}^3$ . From  $700^\circ\text{C}$  to  $1000^\circ\text{C}$ , the pyrolytic carbon framework stabilizes, as indicated by a plateau in specific strength of  $\sim 11 \text{ MPa g}^{-1} \text{cm}^3$  that persists up to  $1000^\circ\text{C}$ . This trend aligns with the steep mass loss and the appearance of D and G bands in Raman spectra at  $450^\circ\text{C}$ , indicating that carbonization proceeds rapidly between  $400^\circ\text{C}$  and  $450^\circ\text{C}$ .

In contrast, the specific strength of the 3DP-PEDOT-4.0 samples (Fig. 4A; green squares) increases gradually, starting near  $400^\circ\text{C}$  and continues to increase steadily to a value of  $\sim 40 \text{ MPa g}^{-1} \text{cm}^3$  by  $700^\circ\text{C}$  and  $\sim 50 \text{ MPa g}^{-1} \text{cm}^3$  by  $800^\circ\text{C}$ , ultimately plateauing at  $\sim 55 \text{ MPa g}^{-1} \text{cm}^3$  by  $1000^\circ\text{C}$ . This progressive increase reflects the slower and more extended carbonization process facilitated by the PEDOT coating. As indicated by the Raman spectra (Fig. 3B), the D and G bands emerge

gradually between 400 °C and 700 °C, indicating the steady, rather than abrupt, development of pyrolytic carbon networks in 3DP-PEDOT-4.0.

Notably, between 500°C and 1000°C—the range in which char yield has stabilized for both systems—the coated 3DP-PEDOT-4.0 samples are consistently lighter ( $\sim 0.6 - 0.5 \text{ g cm}^{-3}$ ) and mechanically stronger ( $\sim 16 - 28 \text{ MPa}$ ) than their uncoated 3DP counterparts, which are denser ( $\sim 0.6 - 1 \text{ g cm}^{-3}$ ) yet weaker ( $\sim 7 - 10 \text{ MPa}$ ). This can be attributed to the fundamental difference in how bare templates and template-coating pairs undergo pyrolysis. In 3DP, rapid decomposition and extensive shrinkage lead to the collapse of the porous architecture, resulting in a denser and structurally compromised carbon framework (Fig. 3C). In contrast, 3DP-PEDOT-4.0, featuring exceptional dimensional stability, preserves the hierarchical pore architecture, enabling more uniform load distribution and nearly six times the load-bearing capacity under compressive stress. These results highlight that mechanical performance is governed not only by material density but also by the ability to maintain structural hierarchy across length scales.

The evolution of specific modulus ( $\text{MPa g}^{-1} \text{ cm}^3$ ) broadly mirrors the trends observed in specific strength. For the 3DP samples, the specific modulus increases sharply from  $\sim 2.5 \text{ MPa g}^{-1} \text{ cm}^3$  at 400 °C to  $\sim 25 \text{ MPa g}^{-1} \text{ cm}^3$  at 500 °C (Fig. 4B; black circles). Beyond this point, it stabilizes at  $\sim 29 \text{ MPa g}^{-1} \text{ cm}^3$  by 1000 °C, consistent with the plateauing behavior observed in specific strength. The 3DP-PEDOT-4.0 samples follow a similar trend but reach much higher values overall, with a gradual increase starting near  $\sim 11 \text{ MPa g}^{-1} \text{ cm}^3$  at 400 °C, reaching  $\sim 150 \text{ MPa g}^{-1} \text{ cm}^3$  by 800°C, and plateauing at  $\sim 164 \text{ MPa g}^{-1} \text{ cm}^3$  at 1000 °C (Fig. 4B; orange squares). This steady rise and elevated final modulus again reflect the role of the PEDOT coating in promoting gradual microstructural development and maintaining architectural stability throughout the pyrolysis process.

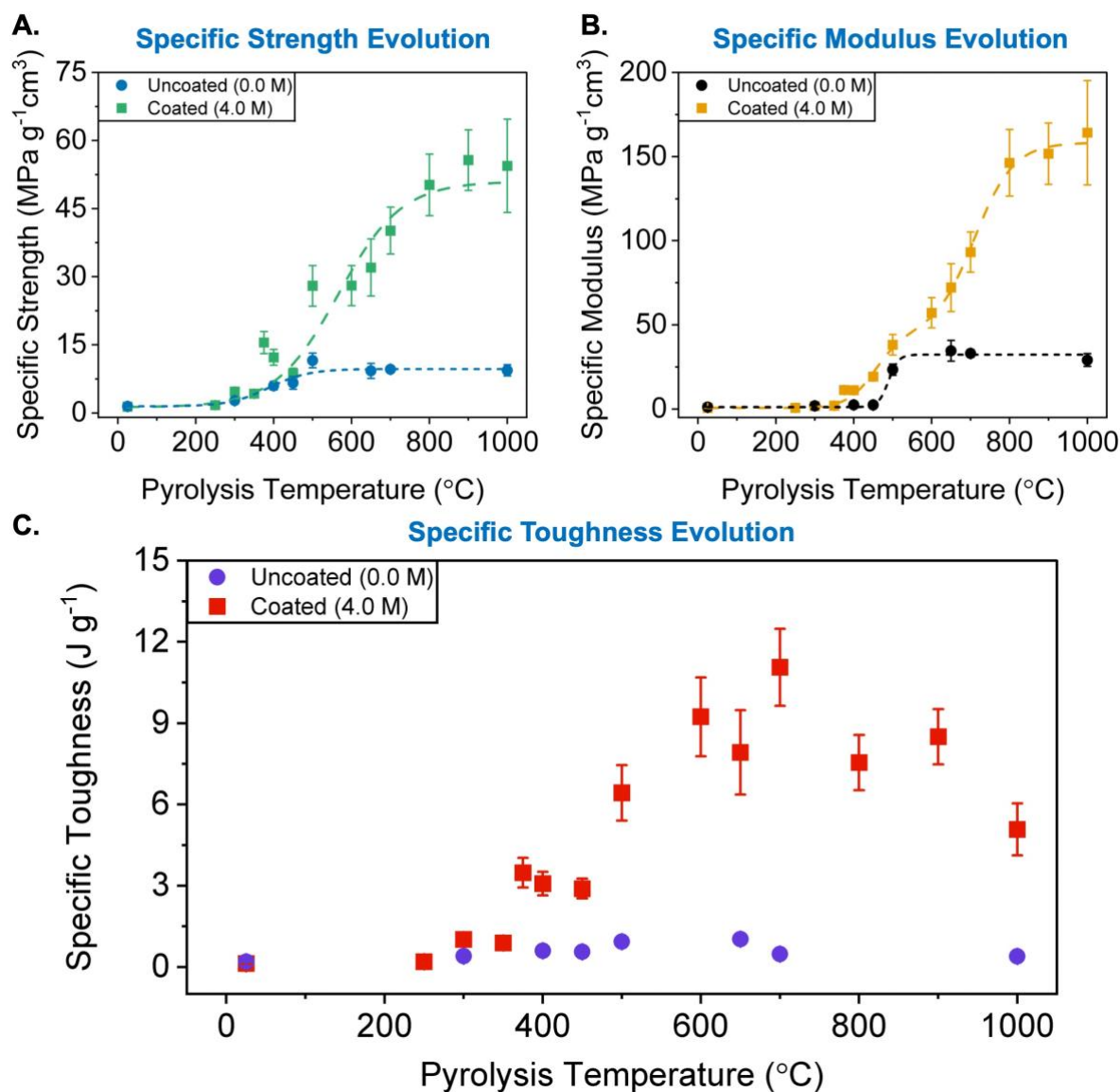
As illustrated in Figure 4C, the specific toughness ( $\text{J g}^{-1}$ ) of both 3DP and 3DP-PEDOT-4.0 samples exhibits distinct temperature-dependent behavior. For the 3DP samples, specific toughness remains relatively flat, showing only a modest increase from  $\sim 0.2 \text{ J g}^{-1}$  at room temperature to  $\sim 1.0 \text{ J g}^{-1}$  at  $500^\circ\text{C}$  before gradually declining to  $\sim 0.5 \text{ J g}^{-1}$  at  $700^\circ\text{C}$  and ultimately  $\sim 0.3 \text{ J g}^{-1}$  at  $1000^\circ\text{C}$ . This consistently low, nearly flat toughness profile aligns with the rapid carbonization and structural densification that leads quickly to brittleness. In contrast, the 3DP-PEDOT-4.0 samples display a pronounced non-monotonic specific toughness profile, with significantly higher overall values. Starting at  $\sim 0.4 \text{ J g}^{-1}$  at  $25^\circ\text{C}$ , the specific toughness gradually increases to  $\sim 6.4 \text{ J g}^{-1}$  by  $500^\circ\text{C}$ , then rises further to a distinct peak of  $\sim 11.1 \text{ J g}^{-1}$  at  $700^\circ\text{C}$  before progressively declining to  $\sim 5.1 \text{ J g}^{-1}$  by  $1000^\circ\text{C}$ . Compared to uncoated 3DP, this represents an approximately  $22\times$  increase in specific toughness at  $700^\circ\text{C}$  ( $11.1$  vs.  $0.5 \text{ J g}^{-1}$ ) and a  $17\times$  increase at  $1000^\circ\text{C}$  ( $5.1$  vs.  $0.3 \text{ J g}^{-1}$ ).

The distinct peak in specific toughness observed at  $700^\circ\text{C}$  in the 3DP-PEDOT-4.0 samples, compared to the relatively flat toughness profile of the uncoated 3DP samples, highlights the significant influence of compositional differences on carbonization dynamics. The uncoated 3DP samples, comprised entirely of poly(HIPE), undergo rapid mass loss and structural collapse between  $300\text{--}450^\circ\text{C}$ , accompanied by the abrupt emergence of D and G bands in Raman spectra (Fig. 3A), signaling swift conversion to a predominantly pyrolytic structure. Consequently, the beneficial polymer-carbon hybrid regime responsible for toughness enhancement is short-lived, leading to rapid embrittlement soon after pyrolytic carbon formation. In contrast, the 3DP-PEDOT-4.0 samples, which initially comprise  $\sim 86 \text{ wt\%}$  PEDOT and  $\sim 14 \text{ wt\%}$  poly(HIPE), exhibit carbonization dynamics dominated by the coating component, characterized by a higher carbonization temperature, slower carbonization rate, and enhanced char yield ( $\sim 40 \text{ wt\%}$  at  $1000^\circ\text{C}$ ) compared to poly(HIPE) ( $\sim 4 \text{ wt\%}$  at  $1000^\circ\text{C}$ ). Consequently, the carbonization of 3DP-PEDOT-4.0 occurs more gradually, allowing polymeric and pyrolytic domains to coexist over an extended temperature range (Fig. 3B). This

prolonged hybrid regime, coupled with a greater residual carbon content, delays the onset of embrittlement, results in a pronounced toughness peak at 700 °C, and significantly enhances energy absorption prior to structural failure.

Overall, these findings show that by tuning the pyrolysis temperature, it is possible to access a regime in which both strength and toughness are simultaneously enhanced—two properties that are typically mutually exclusive in pyrolytic carbon systems. In the case of 3DP-PEDOT-4.0, this regime is centered around 700 °C, where the carbonized architecture achieves a peak strength-to-toughness ratio ( $\sim 22$  MPa and  $\sim 6$  MJ m<sup>-3</sup>), coupled with excellent dimensional retention ( $\sim 80\%$ ) and low density ( $\sim 0.55$  g cm<sup>-3</sup>). The ability to systematically modulate mechanical performance through controlled thermal processing of a structurally stabilized template underscores the effectiveness of the template-coating design and confirms that partial carbonization offers a robust and tunable route to achieving mechanically robust porous carbon architectures at macroscopic length scales.





**Figure 4.** Mechanical property evolution of 3D-printed plugs as a function of pyrolysis temperature. **A)** Specific strength for 3DP and 3DP-PEDOT-4.0 samples, showing a rapid increase and early plateau in 3DP, versus a gradual increase and higher final strength in 3DP-PEDOT-4.0. **B)** Specific modulus trends follow similar behavior, with 3DP-PEDOT-4.0 exhibiting enhanced stiffness and a more progressive increase with temperature. **C)** Specific toughness exhibits a non-monotonic trend in both uncoated and coated samples, with 3DP-PEDOT-4.0 achieving a delayed and significantly higher peak ( $\sim 11 \text{ J g}^{-1}$  at  $700^\circ\text{C}$ ), compared to the early and modest peak ( $\sim 1 \text{ J g}^{-1}$  at  $500^\circ\text{C}$ ) observed in 3DP.

#### **4.3.5 Demonstration of Simultaneous Strength and Toughness in Lattice Architectures**

The next step was to explore if the simultaneous enhancement of strength and toughness achieved through the partial carbonization of template–coating pairs can be extended from simple plug geometries to complex, macroscale lattice architectures. Lattices, with their high structural efficiency and design versatility, provide an ideal platform for unraveling how lattice architecture can be leveraged to access unique combinations of otherwise mutually exclusive mechanical properties<sup>[62]</sup>.

Among these, the cubic vertex centroid lattice architecture was selected as the model system due to its geometric regularity and compatibility with high-resolution 3D printing. It consists of a cubic unit cell where struts connect each of the eight vertices directly to the centroid, forming a symmetric open framework. Each cell contains nine nodes (eight corners and one center) and eight cylindrical struts. Applying Maxwell's stability criterion ( $M = s - 3j + 6$ ) with  $s = 8$  and  $j = 9$  yields  $M = -13$ , confirming a bending-dominated architecture. In this configuration, struts primarily undergo flexural deformation, while the vertex nodes act as hinges, allowing for progressive and stable buckling. This promotes distributed collapse and energy absorption, characteristics desirable for energy absorption and damage tolerance applications.

In addition to its geometric advantages, this lattice architecture exhibits a high degree of structural hierarchy, as the lattice struts are composed of inherently porous poly(HIPE) material, resulting in hierarchical porosity across multiple scales. Feature sizes span from centimeter-scale lattice geometry to  $\sim 1\ \mu\text{m}$  pores within the struts, covering nearly four orders of magnitude. This multiscale architecture reduces density while enhancing performance, enabling (i) higher specific strength via size-dependent strengthening and (ii) improved toughness through macroscopic strut collapse and microscale pore collapse. Together, these features form a robust foundation for macroscopic, low-density, high-strength, and damage-tolerant lattices.

Building on this lattice design, a template–coating fabrication strategy was employed to test whether the combined benefits of hierarchical porosity and partial carbonization could be realized at the macroscale. To do so, three types of lattices were 3D printed: a dense, non-porous lattice (3DL-NP; Fig. 5A i), an inherently porous poly(HIPE) lattice (3DL; Fig. 5A ii), and a coated porous lattice (3DL-PEDOT-4.0; Fig. 5A iii), where the 3DL structure was coated with a PEDOT layer ([EDOT] = 4.0 M). Although 3DL-NP shares the same composition as the poly(HIPE)-based 3DL, it features solid struts without internal porosity and was used to isolate the role of inherent porosity on structural and dimensional preservation during pyrolysis. Upon pyrolysis at 1000 °C, the 3DL-NP lattice exhibited significant warpage due to its inability to accommodate the internal stresses induced by massive (ca. 95%) volumetric shrinkage. Meanwhile, the 3DL lattice, owing to its inherent voids, tolerated these stresses more effectively, avoiding warpage while exhibiting comparable volumetric shrinkage of ~96% (Fig. S8). Most notably, the 3DL-PEDOT-4.0 lattice demonstrated the highest dimensional stability, retaining approximately 77% of its original dimensions. This result underscores the effectiveness of the PEDOT coating in preserving the lattice architecture and minimizing shrinkage during pyrolysis, even in geometrically complex macroscale structures.

In the subsequent phase, the coated lattices (3DL-PEDOT-4.0) were subjected to pyrolysis at a series of temperatures: 500 °C, 600 °C, 650 °C, 700 °C, and 1000 °C. This temperature range was chosen based on findings discussed above, where the char yield was observed to plateau, indicating the complete volatilization of degradable polymeric domains and the formation of a stable hybrid carbon framework. To evaluate how mechanical performance evolves with pyrolysis temperature, representative engineering stress–strain curves for 3DL-PEDOT-4.0 are shown in Figure 5B. As expected, the lattice pyrolyzed at 500 °C exhibited the highest strain before failure, collapsing at approximately 60% strain, while the lattice pyrolyzed at 1000 °C failed at a much lower strain of ~23%.

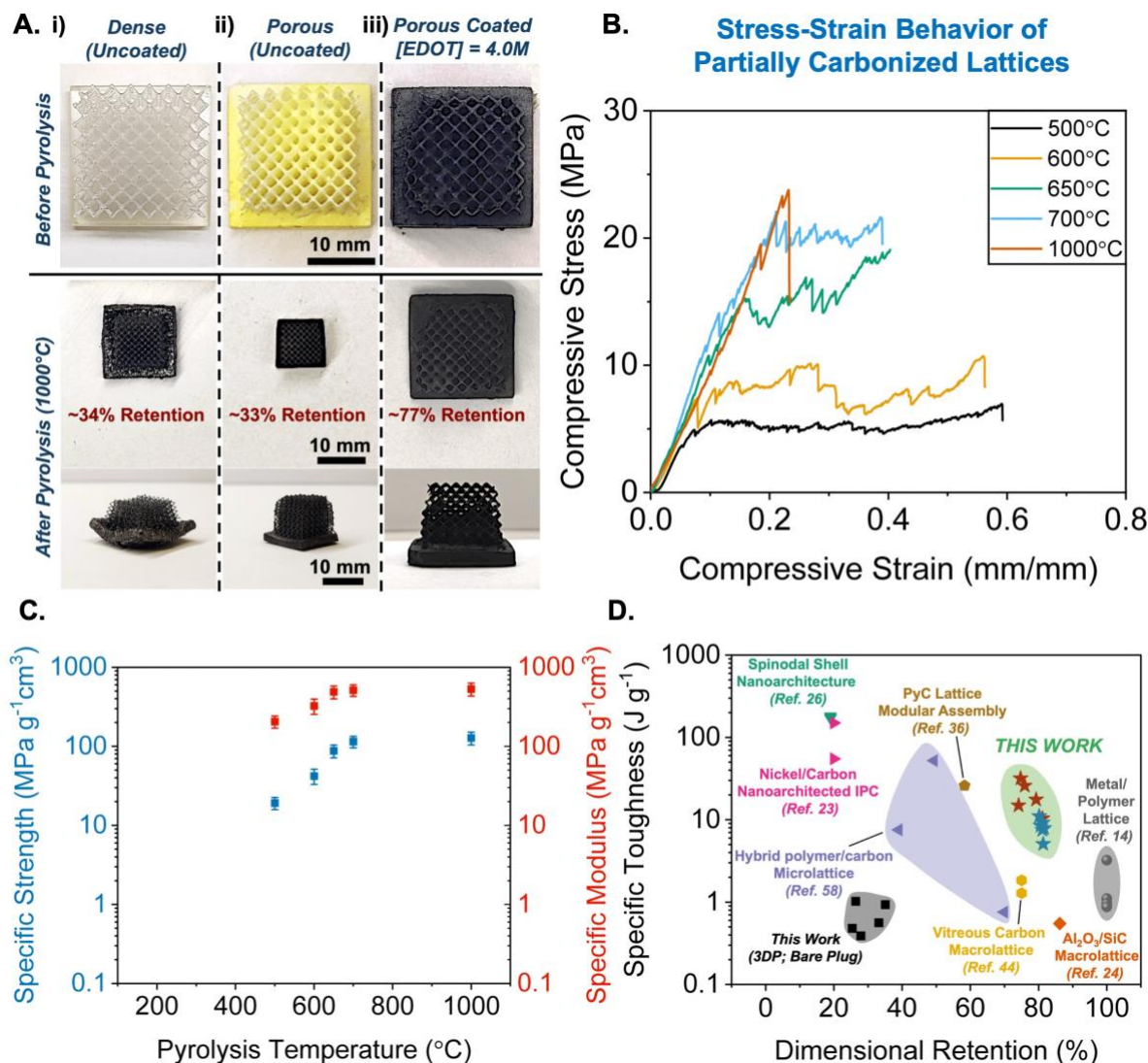
The intermediate cases (600–700 °C) showed a steady reduction in densification strain—from 55% to 40%—reflecting progressive stiffening and embrittlement of the material.

This evolution in stress–strain behavior is closely linked to the underlying carbon chemistry, as revealed by Raman spectra collected for 3DL and 3DL-PEDOT-x samples at representative temperatures across the carbonization range (Fig. S9). At 25 °C, both the as-fabricated 3DL (Fig. S9A; black) and 3DL-PEDOT-4.0 (Fig. S9A; green) samples display fully polymeric spectra with no detectable carbon features. By 325 °C, the 3DL samples undergo substantial decomposition and exhibit no characteristic peaks, whereas the 3DL-PEDOT-4.0 samples remain largely unchanged, indicating minimal degradation at this stage (Fig. S9B). At 500 °C, the 3DL samples exhibit a sudden emergence of the D and G bands, marking the onset of carbonization (Fig. S9C). In contrast, the 3DL-PEDOT-4.0 samples exhibit a more gradual transition, with the initial appearance of carbon peaks indicating the onset of partial carbonization. In this regime, 3DL-PEDOT-4.0 retains a significant fraction of polymeric domains, which impart ductility and allow for large deformation before collapse. By 1000 °C, these polymeric regions have converted mainly to pyrolytic carbon, consistent with a fully carbonized structure (Fig. S9D). This transition from a soft, polymer-rich matrix to a rigid carbon network leads to increased stiffness and reduced strain at failure. Additionally, the evolution from amorphous to more ordered carbon domains likely contributes to the increased brittleness observed at elevated temperatures. From stress–strain curves of 3DL-PEDOT-4.0, the strength, modulus, and toughness were extracted, providing a quantitative basis for comparing mechanical performance across the pyrolysis temperature range.

A quantitative analysis of the stress–strain data reveals a distinct trend of increasing specific strength with increasing pyrolysis temperatures (Fig. 5C; green). At 500°C, the lattice exhibits a bulk density of  $\sim 0.29 \text{ g cm}^{-3}$  and a peak stress of  $\sim 5.5 \text{ MPa}$ , yielding a specific strength of  $\sim 19 \text{ MPa g}^{-1} \text{ cm}^3$ .

<sup>3</sup>. At 600 °C, the density decreases to  $\sim 0.24 \text{ g cm}^{-3}$  and the peak stress increases to  $\sim 10.0 \text{ MPa}$ , yielding a specific strength of  $\sim 42 \text{ MPa g}^{-1} \text{ cm}^3$ —more than double that at 500 °C. At 650 °C, the density further decreases to  $\sim 0.22 \text{ g cm}^{-3}$ , while the peak stress increases to  $\sim 19 \text{ MPa}$ , resulting in a specific strength of  $\sim 88 \text{ MPa g}^{-1} \text{ cm}^3$ , a  $2.1\times$  increase compared to the previous step. At 700 °C, the lattice achieves a density of  $\sim 0.19 \text{ g cm}^{-3}$  and a peak stress of  $\sim 22 \text{ MPa}$ , culminating in a specific strength of around  $\sim 115 \text{ MPa g}^{-1} \text{ cm}^3$ . Beyond this temperature, the trend begins to plateau at 1000 °C, with the strength modestly rising to  $\sim 24 \text{ MPa}$ , while the specific strength reaches  $\sim 128 \text{ MPa g}^{-1} \text{ cm}^3$ . The relative increases in specific strength from 650 to 700 °C and from 700 to 1000 °C are only about  $1.3\times$  and  $1.1\times$ , respectively, highlighting a plateau regime of diminishing returns despite ongoing microstructural evolution.

The evolution of specific modulus with pyrolysis temperature closely mirrors that of specific strength, highlighting the increasing stiffness of the carbon framework as polymeric domains transition into pyrolytic and graphitic carbon. At 500 °C, the lattice demonstrates a Young's modulus of 59 MPa, which corresponds to a specific modulus of approximately  $206 \text{ MPa g}^{-1} \text{ cm}^3$ . The specific modulus rises sharply to about  $325 \text{ MPa g}^{-1} \text{ cm}^3$  at 600 °C and continues to increase to roughly  $489 \text{ MPa g}^{-1} \text{ cm}^3$  by 650 °C, reflecting enhancements of  $1.6\times$  and  $1.5\times$ , respectively. At 700 °C, the specific modulus increases to approximately  $514 \text{ MPa g}^{-1} \text{ cm}^3$ , representing a modest  $1.1\times$  increase from 650 °C. By 1000 °C, the modulus stabilizes at  $\sim 99 \text{ MPa}$ , with the specific modulus reaching a plateau at  $\sim 532 \text{ MPa g}^{-1} \text{ cm}^3$ . These findings confirm that most gains in stiffness occur up to 700 °C, beyond which further pyrolysis yields minimal improvements in stiffness.



**Figure 5.** Macroscale fabrication and mechanical evolution of cubic vertex centroid lattice architectures. **A)** Photographs of three cubic vertex centroid lattice variants before pyrolysis (top row) and after pyrolysis at 1000  $^{\circ}\text{C}$  (middle and bottom rows). The middle row shows a top-down view, while the bottom row shows a side view of each lattice type: **(i)** dense, non-porous 3DL-NP, **(ii)** inherently porous 3DL, and **(iii)** coated porous 3DL-PEDOT-4.0, illustrating the enhanced dimensional stability provided by the PEDOT coating. **B)** Representative compressive stress–strain curves of 3DL-PEDOT-4.0 lattices pyrolyzed at 500, 600, 650, 700, and 1000  $^{\circ}\text{C}$ , showing the relationship between pyrolysis temperature and mechanical behavior. **C)** Trends in specific strength and specific modulus as a function of pyrolysis temperature. **D)** A specific toughness versus dimensional retention map, positioning the 3DP-PEDOT-4.0 monoliths and 3DL-PEDOT-4.0 lattices in a unique region combining high toughness with minimal shrinkage ( $\sim 80\%$  dimensional retention) compared to other literature-reported architectures<sup>[14,23,24,26,36,44,56,58]</sup>.

The evolution of specific toughness with pyrolysis temperature exhibits a non-monotonic trend, in contrast to the plateauing behavior of strength and modulus. At 500 °C, the lattice displays a toughness of  $\sim 3 \text{ MJ m}^{-3}$ , corresponding to a specific toughness of  $\sim 10 \text{ J g}^{-1}$ . As the pyrolysis temperature increases, the toughness improves steadily, reaching  $\sim 18 \text{ J g}^{-1}$  at 600°C and  $26 \text{ J g}^{-1}$  at 650°C, reflecting enhancements of  $1.7\times$  and  $1.5\times$ , respectively. The specific toughness reaches a pronounced peak of  $\sim 32 \text{ J g}^{-1}$  at 700°C, representing a more modest  $1.2\times$  increase. This upward trend reflects the underlying evolution of the carbon composition and microstructure: between 500 °C and 700°C, polymeric domains are progressively converted to pyrolytic domains, resulting in a hybrid microstructure composed of ductile polymer chains, which impart toughness, and stiff carbon networks, which impart strength. The clear peak in toughness at 700 °C corresponds to the point where this hybrid phase reaches an optimal balance: enough carbonization has occurred to support compressive load, yet sufficient polymeric material remains to absorb and redistribute stress through plastic deformation, enabling relatively large strains before failure and subsequent densification. Continued pyrolysis drives further dehydrogenation and ordering of the carbon framework, as evidenced by the increasing peak resolution of Raman D and G bands (Fig. S9). This transition toward a fully carbonized structure is accompanied by a loss of polymeric ductility and an increase in graphitic order, resulting in a more brittle mechanical response. By 1000 °C, the specific toughness falls sharply to  $\sim 15 \text{ J g}^{-1}$  ( $\sim 2.8 \text{ MJ m}^{-3}$ ), reflecting the limited damage-tolerance capacity of the now fracture-prone, fully carbonized network.

The trends observed in 3DL-PEDOT-4.0 lattices closely track those of 3DP-PEDOT-4.0 plugs, validating the use of plug specimens for screening optimal pyrolysis conditions. However, a direct comparison at matched temperatures reveals that the lattice architecture substantially amplifies mechanical performance across all regimes of carbonization. At 500°C, where both systems are primarily polymeric, the lattice exhibits moderate improvements in specific toughness ( $1.6\times$ ) and

stiffness (5.4 $\times$ ), while strength remains comparable (0.7 $\times$ )—reflecting the early-stage dominance of ductile polymeric domains. By 650°C, as both systems transition into a hybrid state, the benefits of the lattice architecture become pronounced: specific strength, modulus, and toughness improve by 2.7 $\times$ , 6.8 $\times$ , and 3.3 $\times$ , respectively, over the plug. These advantages persist through higher carbonization levels. At 700°C, the lattice exhibits enhancements of  $\sim$ 2.9 $\times$  in toughness, 2.9 $\times$  in strength, and 5.5 $\times$  in modulus relative to the plug. At 1000°C, these enhancements remain substantial, with values of  $\sim$ 2.9 $\times$  for toughness, 2.4 $\times$  for strength, and 3.2 $\times$  for modulus, lattice versus plug. The bending-dominated, hierarchical design of the lattice enables more uniform stress distribution, delayed failure, and enhanced stiffness without compromising density. When integrated with partial carbonization and template-coating strategies, this approach allows for a regime of lightweight, damage-tolerant performance that is inaccessible among monolithic or plug-based carbon architectures.

To contextualize the role of dimensional stability in the design of lightweight, energy-absorbing pyrolytic carbon architectures, the specific toughness of various systems<sup>[14,23,24,26,36,44,56,58]</sup> is plotted against their characteristic dimension retention (Fig. 5D), an indicator of dimensional stability assuming linear isotropic shrinkage of pyrolytic precursors. 3D carbon architectures in the upper-left region of the energy absorption-shrinkage landscape—such as spinodal shell nanoarchitectures<sup>[26]</sup> or nanoarchitected metal/ceramic interpenetrating phase composites<sup>[23]</sup>—demonstrate extremely high energy absorption but suffer from severe dimensional loss (<25% linear retention, <2% volume retention), which limits their scalability. Another prominent example from the literature is that of partially carbonized polymer-carbon hybrid lattices, which retain  $\sim$ 50% of their original dimensions and achieve remarkably high toughness values, approaching  $\sim$ 50 J g<sup>-1</sup><sup>[58]</sup>. These systems utilize the energy absorption of residual polymer and the load-bearing capacity of pyrolytic carbon, representing a significant step toward addressing the trade-off between shrinkage and mechanical performance.



The 3DL-PEDOT-4.0 lattices introduced in this work extend the landscape by achieving high specific toughness ( $\sim 30 \text{ J g}^{-1}$ ) alongside exceptional dimensional retention ( $\sim 75\text{-}81\%$ ), positioning them in the upper-right quadrant of the plot. As such, this platform advances beyond the traditional strength–toughness–shrinkage trade-off and enables the macroscale fabrication of high-performance 3D carbon lattices.

#### **4.4 Conclusion**

This work introduces a scalable fabrication strategy that addresses the longstanding trade-offs between strength, toughness, and shrinkage in 3D porous carbon architectures. The approach begins by 3D printing emulsion-templated poly(HIPE)s into geometrically complex lattices with hierarchical porosity spanning nearly four orders of magnitude in length scale. A conformal, high-char-yield PEDOT coating is then applied to form a thermally robust template–coating pair that preserves structural and dimensional integrity during pyrolysis. By arresting pyrolysis at intermediate temperatures, partial carbonization is employed to tune the evolving carbon microstructure—specifically the polymeric-to-pyrolytic carbon and amorphous-to-crystalline carbon ratios—while suppressing shrinkage.

This strategy enables access to a wide range of tunable mechanical responses: across the 500–1000 °C carbonization window, specific strength varies from  $\sim 19$  to  $128 \text{ MPa g}^{-1} \text{ cm}^3$ , specific modulus from  $\sim 206$  to  $532 \text{ MPa g}^{-1} \text{ cm}^3$ , and specific toughness from  $\sim 10$  to  $32 \text{ J g}^{-1}$ . Notably, an optimal pyrolysis temperature of  $\sim 700 \text{ °C}$  yields the most favorable balance between stiffness, strength, and energy absorption, marking the point at which the hybrid polymer–carbon network reaches peak mechanical synergy. Comparative analysis with monolithic counterparts lacking a designed architecture confirms that these enhancements arise not only from compositional control. They also stem from the bending-dominated nature of the cubic vertex centroid lattice geometry,

which redistributes stress, promotes stable strut buckling, and enables greater energy dissipation prior to failure. When benchmarked against prior pyrolytic carbon systems, these hierarchically porous, dimensionally stable carbon lattices occupy a previously inaccessible region of the toughness–shrinkage design space. This work opens new opportunities for fabricating lightweight, damage-tolerant 3D carbon architectures for load-bearing and energy-absorbing applications at practical, macroscopic scales.

#### **4.5 Acknowledgments**

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## 4.6 References

- [1] J. U. Surjadi, C. M. Portela, *Nat. Mater.* **2025**, *24*, 493.
- [2] M. Bechthold, J. C. Weaver, *Nat Rev Mater* **2017**, *2*, 17082.
- [3] G. Lipkowitz, M. A. Saccone, M. A. Panzer, I. A. Coates, K. Hsiao, D. Ilyn, J. M. Kronenfeld, J. R. Tumbleston, E. S. G. Shaqfeh, J. M. DeSimone, *Proc. Natl. Acad. Sci. U.S.A.* **2024**, *121*, e2303648121.
- [4] M. A. S. R. Saadi, A. Maguire, N. T. Pottackal, M. S. H. Thakur, M. Md. Ikram, A. J. Hart, P. M. Ajayan, M. M. Rahman, *Advanced Materials* **2022**, *34*, 2108855.
- [5] W. P. Moestopo, A. J. Mateos, R. M. Fuller, J. R. Greer, C. M. Portela, *Adv. Sci.* **2020**, *7*, 2001271.
- [6] R. L. Truby, J. A. Lewis, *Nature* **2016**, *540*, 371.
- [7] P. R. Onffroy, S. Chiovoloni, H. L. Kuo, M. A. Saccone, J. Q. Lu, J. M. DeSimone, *JACS Au* **2024**, *4*, 3706.
- [8] Y. M. Eggeler, K. C. Chan, Q. Sun, A. D. Lantada, D. Mager, R. Schwaiger, P. Gumbsch, R. Schröder, W. Wenzel, J. G. Korvink, M. Islam, *Adv Funct Materials* **2024**, *34*, 2302068.
- [9] J. U. Surjadi, B. F. G. Aymon, M. Carton, C. M. Portela, *Nat. Mater.* **2025**, DOI 10.1038/s41563-025-02219-5.
- [10] M. Kagias, J. R. Greer, **2023**, DOI 10.21203/rs.3.rs-3536097/v2.
- [11] A. Kudo, K. Kanamaru, J. Han, R. Tang, K. Kisu, T. Yoshii, S. Orimo, H. Nishihara, M. Chen, *Small* **2023**, *19*, DOI 10.1002/sml.202301525.
- [12] J. R. Greer, J. Park, *Nano Lett.* **2018**, *18*, 2187.
- [13] L. Fan, T. Yang, Y. Zhao, J. Luan, G. Zhou, H. Wang, Z. Jiao, C.-T. Liu, *Nat Commun* **2020**, *11*, 6240.

- [14] M. Mieszala, M. Hasegawa, G. Guillonéau, J. Bauer, R. Raghavan, C. Frantz, O. Kraft, S. Mischler, J. Michler, L. Philippe, *Small* **2017**, *13*, 1602514.
- [15] X. Zheng, H. Lee, T. H. Weisgraber, M. Shusteff, J. DeOtte, E. B. Duoss, J. D. Kuntz, M. M. Biener, Q. Ge, J. A. Jackson, S. O. Kucheyev, N. X. Fang, C. M. Spadaccini, *Science* **2014**, *344*, 1373.
- [16] A. Dutto, E. Bianda, J. G. Melo, Z. Saraw, E. Tervoort, A. R. Studart, *Adv Materials Technologies* **2025**, *10*, 2401104.
- [17] J. Bauer, C. Crook, A. Guell Izard, Z. C. Eckel, N. Ruvalcaba, T. A. Schaedler, L. Valdevit, *Matter* **2019**, *1*, 1547.
- [18] Z. C. Eckel, C. Zhou, J. H. Martin, A. J. Jacobsen, W. B. Carter, T. A. Schaedler, *Science* **2016**, *351*, 58.
- [19] J. Bauer, S. Hengsbach, I. Tesari, R. Schwaiger, O. Kraft, *Proceedings of the National Academy of Sciences* **2014**, *111*, 2453.
- [20] L. R. Meza, S. Das, J. R. Greer, *Science* **2014**, *345*, 1322.
- [21] P. Colombo, G. Mera, R. Riedel, G. D. Sorarù, *Journal of the American Ceramic Society* **2010**, *93*, 1805.
- [22] J. Bauer, C. Crook, T. Baldacchini, *Science* **2023**, *380*, 960.
- [23] J. Bauer, M. Sala-Casanovas, M. Amiri, L. Valdevit, *Sci. Adv.* **2022**, *8*, eabo3080.
- [24] H. Mei, R. Zhao, Y. Xia, J. Du, X. Wang, L. Cheng, *Journal of Alloys and Compounds* **2019**, 797, 786.
- [25] J. Bauer, J. A. Kraus, C. Crook, J. J. Rimoli, L. Valdevit, *Advanced Materials* **2021**, *33*, 2005647.
- [26] A. Guell Izard, J. Bauer, C. Crook, V. Turlo, L. Valdevit, *Small* **2019**, *15*, 1903834.
- [27] J. Bauer, L. R. Meza, T. A. Schaedler, R. Schwaiger, X. Zheng, L. Valdevit, *Adv. Mater.* **2017**, *29*, 1701850.

- [28] O. Kraft, P. A. Gruber, R. Mönig, D. Weygand, *Annu. Rev. Mater. Res.* **2010**, *40*, 293.
- [29] P. Serles, J. Yeo, M. Haché, P. G. Demingos, J. Kong, P. Kiefer, S. Dhulipala, B. Kumral, K. Jia, S. Yang, T. Feng, C. Jia, P. M. Ajayan, C. M. Portela, M. Wegener, J. Howe, C. V. Singh, Y. Zou, S. Ryu, T. Filleter, *Advanced Materials* **2025**, *37*, 2410651.
- [30] T. Mori, H. Wang, W. Zhang, C. C. Ser, D. Arora, C.-F. Pan, H. Li, J. Niu, M. A. Rahman, T. Mori, H. Koishi, J. K. W. Yang, *Nat Commun* **2023**, *14*, DOI 10.1038/s41467-023-41535-9.
- [31] C. M. Portela, B. W. Edwards, D. Veyssset, Y. Sun, K. A. Nelson, D. M. Kochmann, J. R. Greer, *Nat. Mater.* **2021**, *20*, 1491.
- [32] C. Crook, J. Bauer, A. Guell Izard, C. Santos de Oliveira, J. Martins de Souza e Silva, J. B. Berger, L. Valdevit, *Nat Commun* **2020**, *11*, 1579.
- [33] X. Zhang, L. Zhong, A. Mateos, A. Kudo, A. Vyatskikh, H. Gao, J. R. Greer, X. Li, *Nat. Nanotechnol.* **2019**, *14*, 762.
- [34] X. Zhang, A. Vyatskikh, H. Gao, J. R. Greer, X. Li, *Proc Natl Acad Sci USA* **2019**, *116*, 6665.
- [35] J. Bauer, A. Schroer, R. Schwaiger, O. Kraft, *Nature Mater* **2016**, *15*, 438.
- [36] A. Naderi, W. Lin, A. Tarafdar, T. Zhang, Y. Wang, *Commun Mater* **2025**, *6*, 13.
- [37] Q. Sun, C. Dolle, C. Kurpiers, K. Kraft, M. Islam, R. Schwaiger, P. Gumbsch, Y. M. Eggeler, *Adv Funct Materials* **2024**, *34*, 2302358.
- [38] V. Hahn, P. Kiefer, T. Frenzel, J. Qu, E. Blasco, C. Barner-Kowollik, M. Wegener, *Adv Funct Materials* **2020**, *30*, 1907795.
- [39] Y. Lu, J. Hu, K. W. J. Ng, X. Hu, *Additive Manufacturing* **2024**, *83*, 104053.
- [40] M. Usselman, J. Bansmann, A. J. C. Kuehne, *Advanced Materials* **2023**, *35*, DOI 10.1002/adma.202208484.
- [41] D.-Y. Kang, C. Kim, G. Park, J. H. Moon, *Sci Rep* **2015**, *5*, 18185.

- [42] J. W. F. To, Z. Chen, H. Yao, J. He, K. Kim, H.-H. Chou, L. Pan, J. Wilcox, Y. Cui, Z. Bao, *ACS Cent. Sci.* **2015**, *1*, 68.
- [43] H. Steldinger, A. Esposito, K. Brunnengräber, J. Gläsel, B. J. M. Etzold, *Adv. Sci.* **2019**, *6*, 1901340.
- [44] A. J. Jacobsen, S. Mahoney, W. B. Carter, S. Nutt, *Carbon* **2011**, *49*, 1025.
- [45] S. Gupta, T. Sohail, M. Checa, M. D. Toomey, L. T. Kearney, R. Chahal, S. S. Rohewal, N. Kanbargi, S. Ghosh, L. Collins, D. McConnell, I. N. Ivanov, A. K. Naskar, C. C. Bowland, *Adv. Funct. Materials* **2025**, *35*, 2502972.
- [46] S. Park, B. Shi, M. M. Islam, J. He, D. H. Sung, C. Zhang, Z. Cao, Y. Shang, L. Liu, K. Fu, *Adv. Funct. Materials* **2024**, *34*, DOI 10.1002/adfm.202410164.
- [47] P. Smith, A. G. Obando, A. Griffin, M. Robertson, E. Bounds, Z. Qiang, *Advanced Materials* **2023**, *35*, 2208029.
- [48] P. Smith, J. Hu, A. Griffin, M. Robertson, A. Güillen Obando, E. Bounds, C. B. Dunn, C. Ye, L. Liu, Z. Qiang, *Nat Commun* **2024**, *15*, 838.
- [49] C. Zhang, B. Shi, J. He, L. Zhou, S. Park, S. Doshi, Y. Shang, K. Deng, M. Giordano, X. Qi, S. Cui, L. Liu, C. Ni, K. K. Fu, *Advanced Materials* **2023**, *35*, DOI 10.1002/adma.202208230.
- [50] S. Park, Z. Cao, D. H. Sung, K. K. Fu, *Advanced Energy Materials* **2023**, *13*, 2301704.
- [51] V. A. Bobrin, H. G. Hackbarth, Y. Yao, D. Kundu, N. M. Bedford, R. P. Kuchel, J. Zhang, N. Corrigan, C. Boyer, *Small Science* **2024**, *4*, DOI 10.1002/smssc.202300275.
- [52] V. A. Bobrin, Y. Yao, X. Shi, Y. Xiu, J. Zhang, N. Corrigan, C. Boyer, *Nat Commun* **2022**, *13*, 3577.
- [53] Z. Dong, H. Cui, H. Zhang, F. Wang, X. Zhan, F. Mayer, B. Nestler, M. Wegener, P. A. Levkin, *Nat Commun* **2021**, *12*, 247.

- [54] F. Mayer, D. Ryklin, I. Wacker, R. Curticean, M. Čalkovský, A. Niemeyer, Z. Dong, P. A. Levkin, D. Gerthsen, R. R. Schröder, M. Wegener, *Advanced Materials* **2020**, *32*, 2002044.
- [55] M. G. M. Marascio, J. Antons, D. P. Pioletti, P. Bourban, *Adv Materials Technologies* **2017**, *2*, 1700145.
- [56] Z. Li, A. Bhardwaj, J. He, W. Zhang, T. T. Tran, Y. Li, A. McClung, S. Nuguri, J. J. Watkins, S.-W. Lee, *Nat Commun* **2024**, *15*, DOI 10.1038/s41467-024-52359-6.
- [57] R. O. Ritchie, *Nature Mater* **2011**, *10*, 817.
- [58] J. U. Surjadi, Y. Zhou, S. Huang, L. Wang, M. Li, S. Fan, X. Li, J. Zhou, R. H. W. Lam, Z. Wang, Y. Lu, *Matter* **2022**, *5*, 4029.
- [59] N. Sengokmen-Ozsoz, R. Boston, J. S. Dean, C. Rodenburg, F. Claeysens, *Carbon* **2025**, *234*, 119933.
- [60] N. Sengokmen-Ozsoz, F. Claeysens, *Current Opinion in Colloid & Interface Science* **2025**, *77*, 101921.
- [61] N. Sengokmen-Ozsoz, M. Aleemardani, M. Palanca, A. Hann, G. C. Reilly, E. Dall'Ara, F. Claeysens, *Biofabrication* **2025**, *17*, 015012.
- [62] L. R. Meza, G. P. Phlipot, C. M. Portela, A. Maggi, L. C. Montemayor, A. Comella, D. M. Kochmann, J. R. Greer, *Acta Materialia* **2017**, *140*, 424.

## **CHAPTER 4 – SUPPORTING INFORMATION**

### **List of Figures**

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**Figure S2** – Plug geometry before and after pyrolysis with SEM insets

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**Figure S5** – SEM of 3DP-PEDOT-x showing cell wall thickening with [EDOT]

**Figure S6** – Density evolution of 3DP and 3DP-NP during pyrolysis

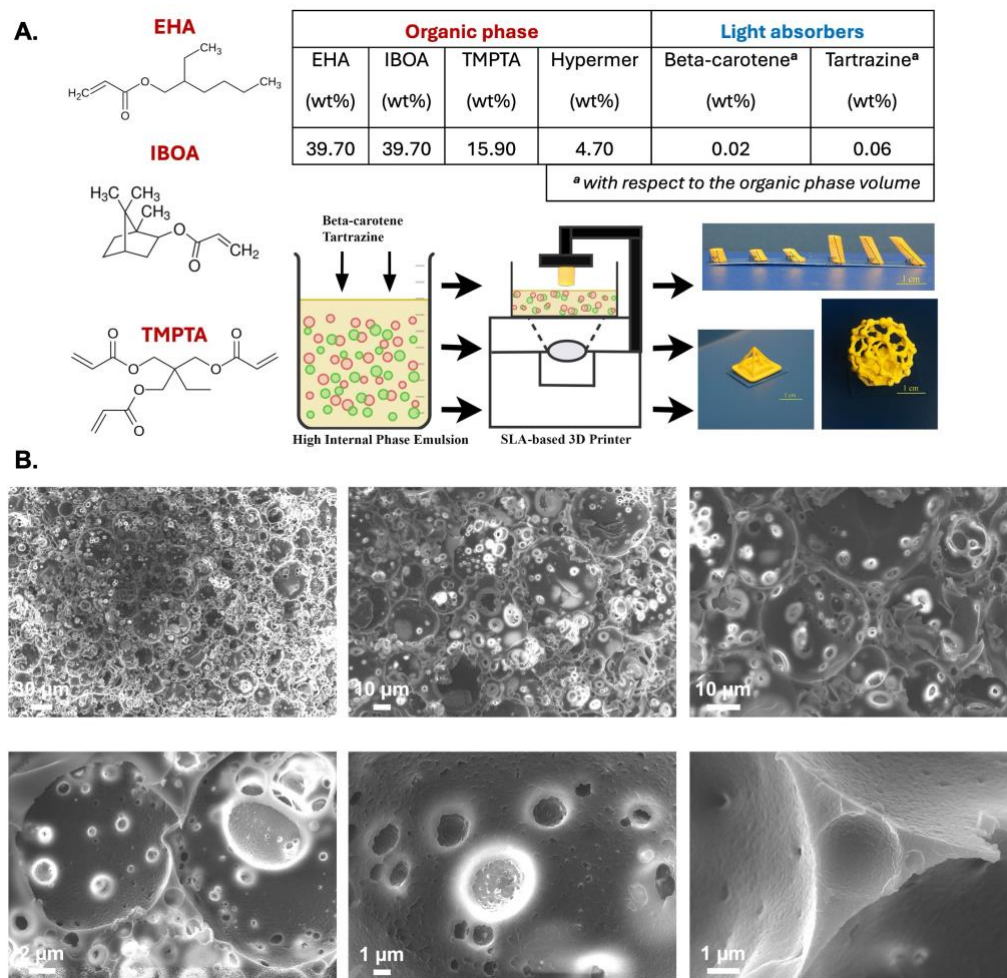
**Figure S7** – Stress–strain curves for 3DP and 3DP-PEDOT-4.0 plugs

**Figure S8** – SEM images of fully carbonized 3DL-PEDOT-4.0 lattices

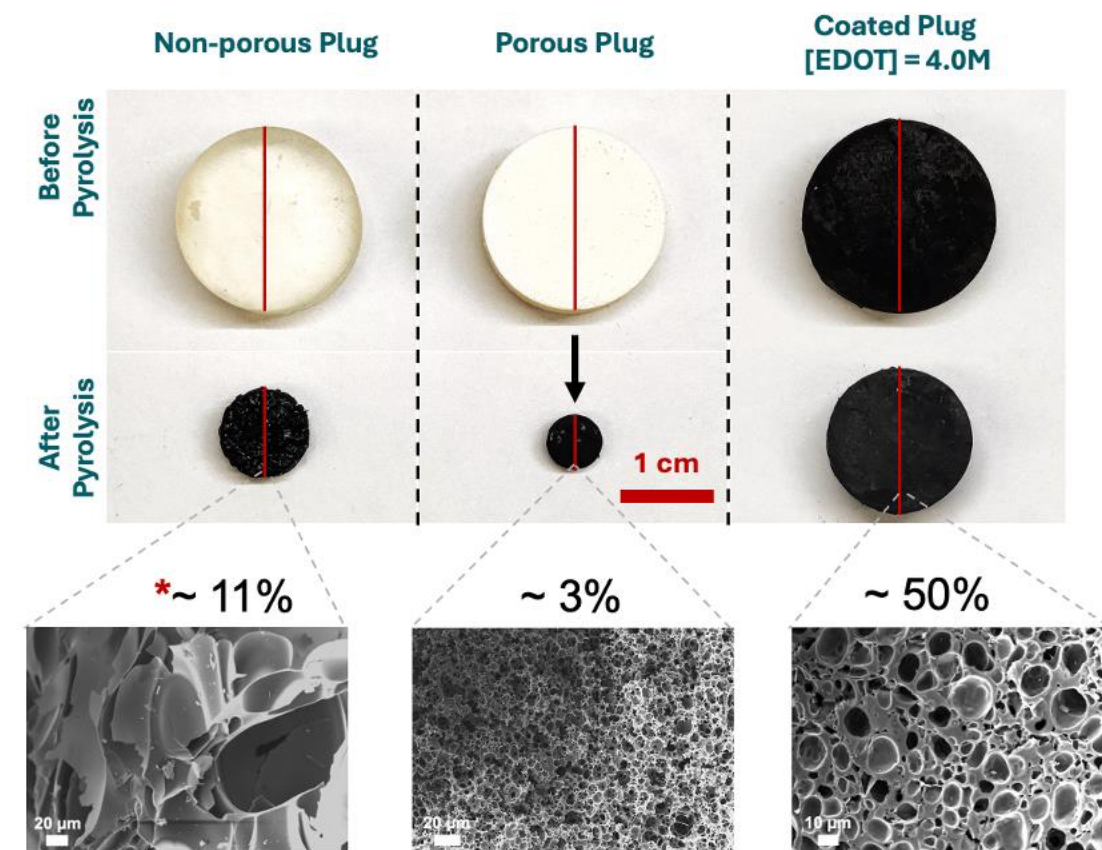
**Figure S9** – Variable temperature TGA profiles of 3DL and 3DL-PEDOT-x lattices

### **Materials and Methods**

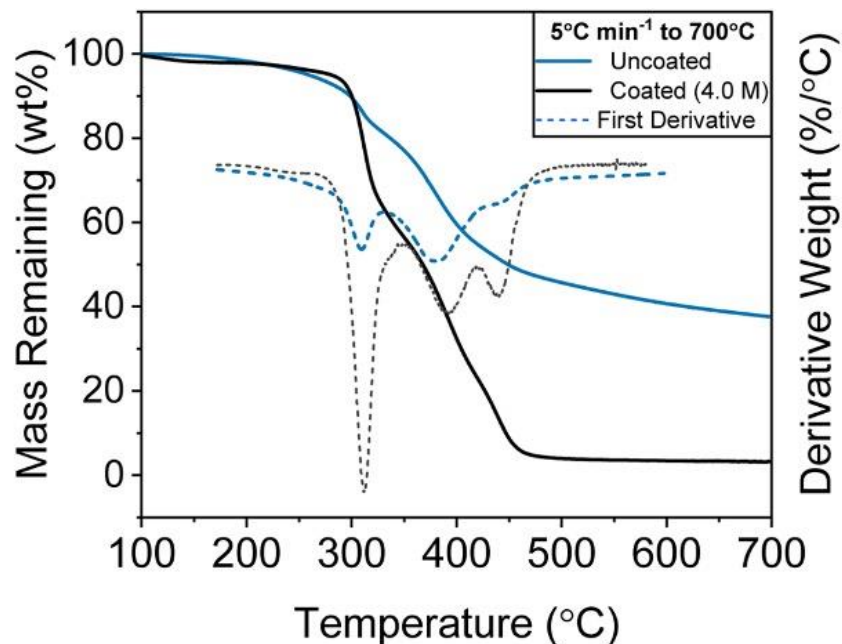




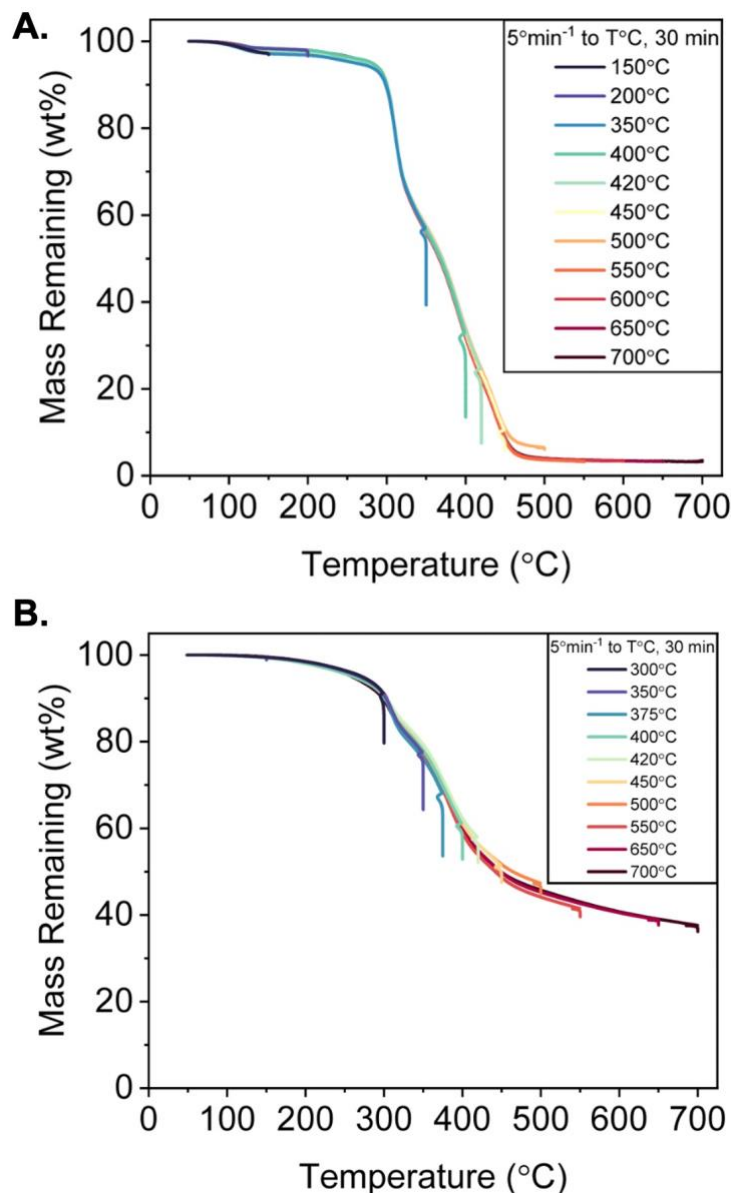
**Figure S1. A)** Schematic illustrating the formulation and stereolithographic 3D printing of poly(HIPE) structures. A high internal phase emulsion (HIPE) composed of acrylate monomers, crosslinker, surfactants, and photoinitiators is prepared and printed using a DLP-based vat photopolymerization process to produce cylindrical plugs and cubic centroid lattices. **B)** Scanning electron microscopy (SEM) images of 3D-printed poly(HIPE) structures shown in increasing order of magnification.



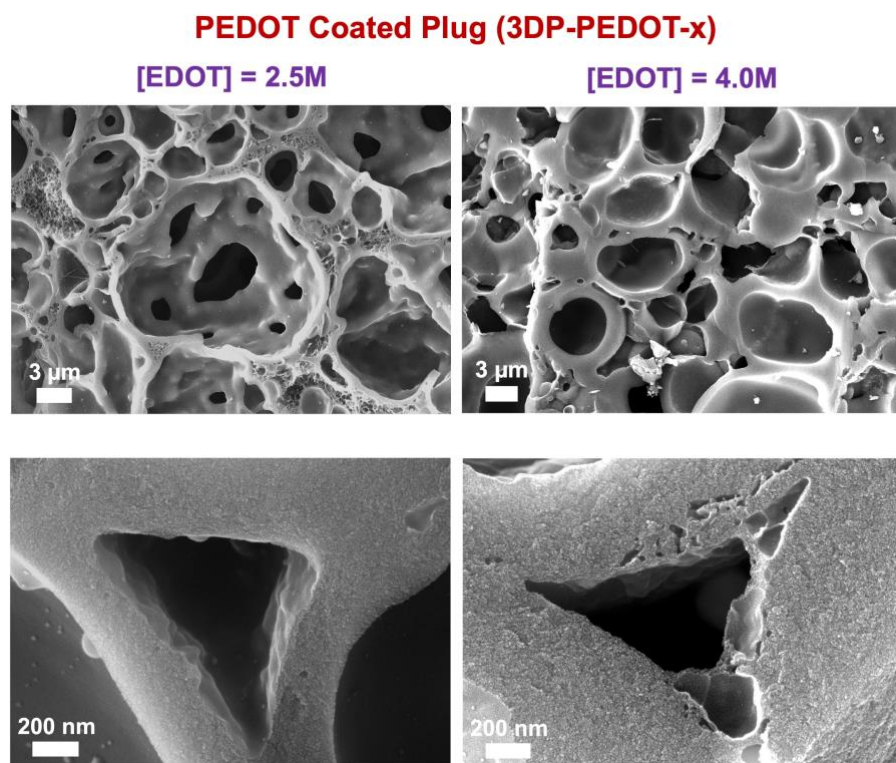
**Figure S2.** Diagram of the three plug types before and after pyrolysis, alongside SEM views of the corresponding carbon architectures. Top row: As-printed geometries of the non-porous plug (3DP-NP, left), porous plug (3DP, center), and coated plug (3DP-PEDOT-4.0, right). Middle row: Carbonized plugs following pyrolysis at 1000 °C, showing distinct differences in volume retention—approximately 11% for 3DP-NP, 3% for 3DP, and 50% for 3DP-PEDOT-4.0. Bottom row: Scanning electron microscopy (SEM) images of the carbonized plugs, highlighting the microstructural consequences of collapse, densification, or retention.



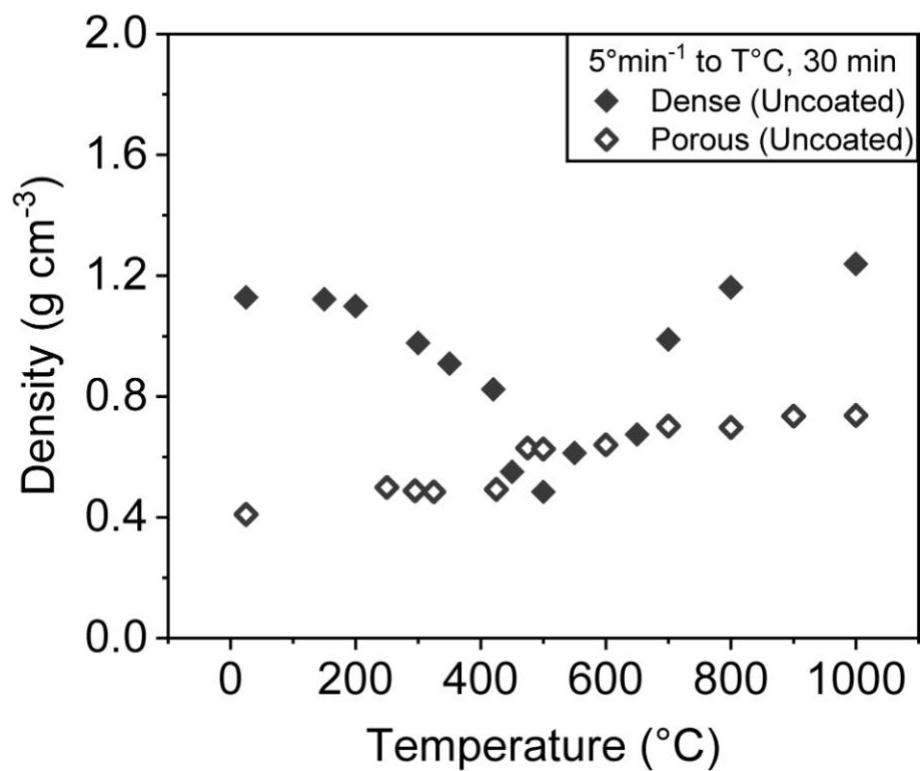
**Figure S3.** Thermogravimetric analysis (TGA) of 3DP and 3DP-PEDOT-4.0 samples was performed under nitrogen with a 5 °C min<sup>-1</sup> ramp to 700 °C. The primary thermograms (left y-axis) reveal significantly higher char yield for the coated sample relative to the uncoated 3DP plug, consistent with enhanced thermal stability conferred by the PEDOT layer. Derivative weight loss curves (right y-axis) indicate key degradation events at approximately 310°C, 395°C, and 450°C, corresponding to the template degradation.



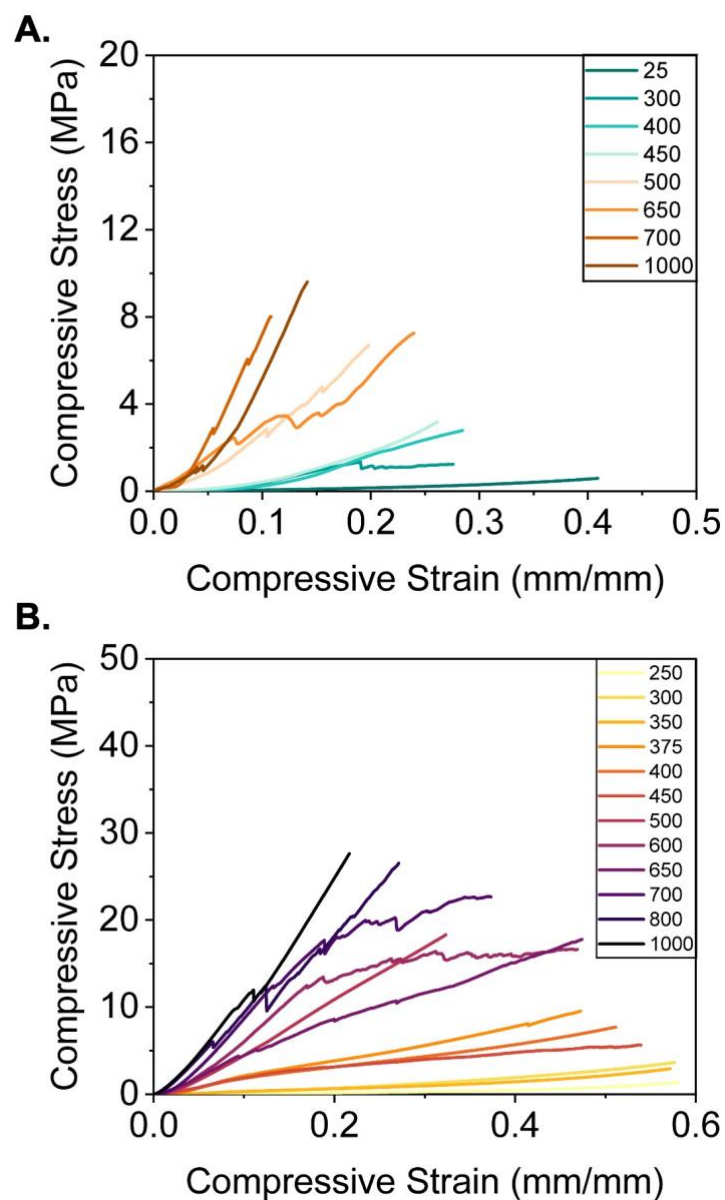
**Figure S4.** Variable temperature TGA spectra of 3DP and 3DP-PEDOT-4.0 samples under nitrogen atmosphere. **A)** 3DP plug heated from room temperature to various target temperatures (25–700 °C) at  $5^{\circ}\text{C min}^{-1}$  and held isothermally for 30 minutes. **B)** 3DP-PEDOT-4.0 plug subjected to the same thermal protocol. The staged weight loss observed in both samples reveals temperature-dependent degradation behavior, with 3DP undergoing more rapid and extensive mass loss compared to the coated sample. The PEDOT coating significantly moderates the decomposition profile, resulting in improved mass retention and more gradual transitions across the temperature range.



**Figure S5.** SEM images of carbonized 3DP-PEDOT-x plugs pyrolyzed at 1000 °C, showing increased cell wall thickness with higher EDOT concentrations.

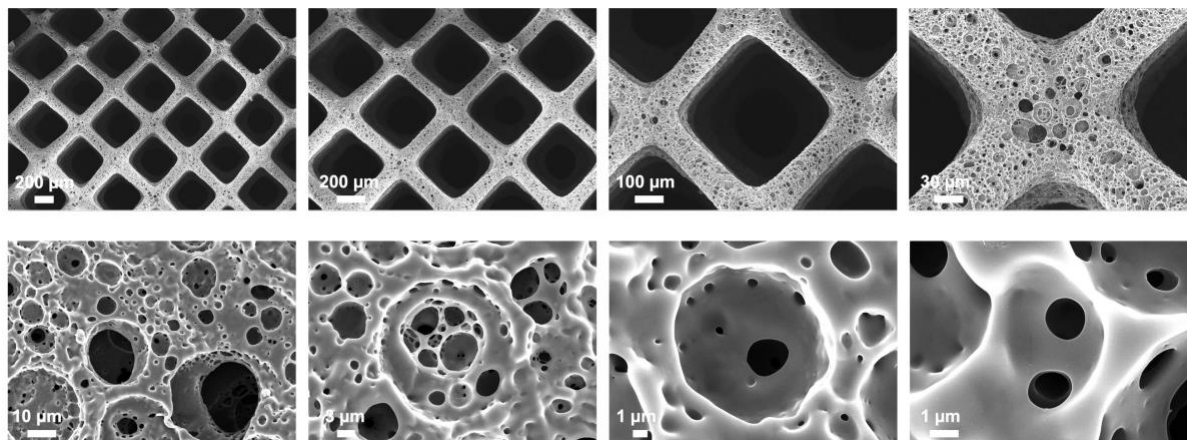


**Figure S6.** Density evolution of 3DP and 3DP-NP plugs during pyrolysis. 3DP-NP shows an initial drop followed by re-densification from shrinkage, while 3DP exhibits continuous densification due to coupled mass loss and volume reduction.



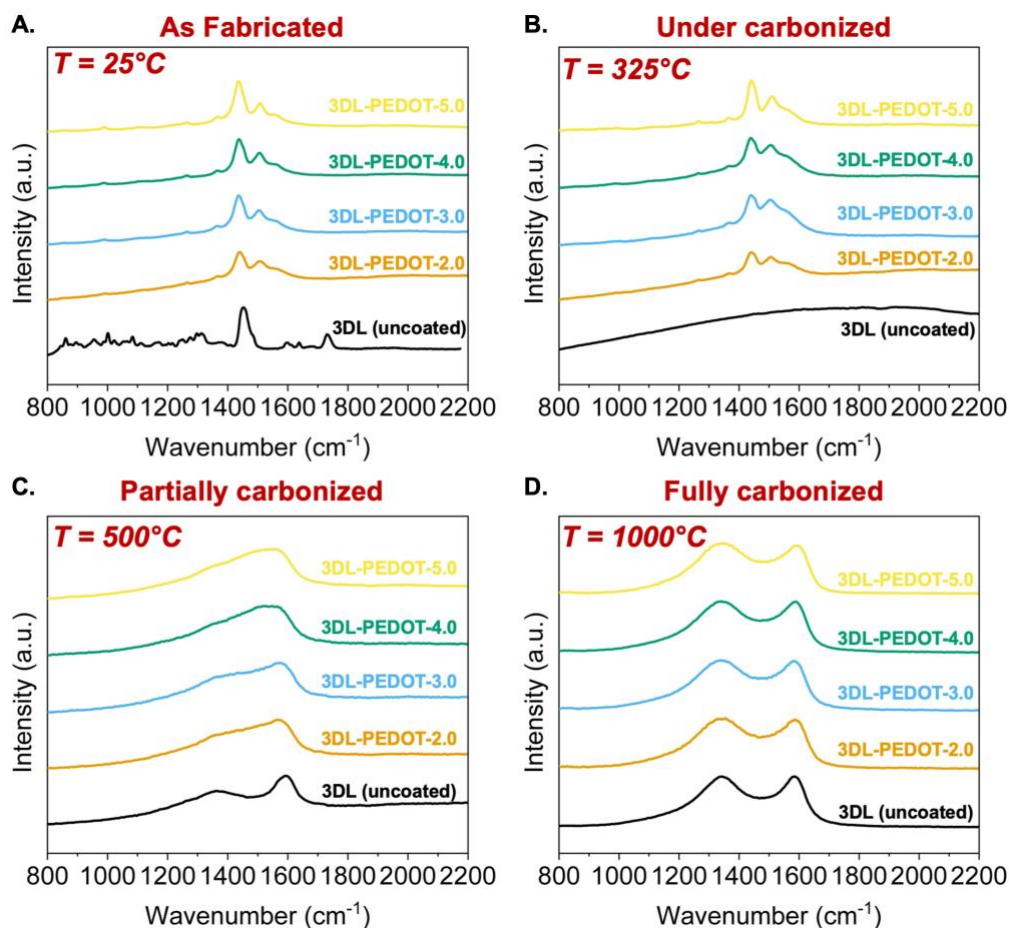
**Figure S7.** Representative stress–strain curves of **A)** 3DP and **B)** 3DP-PEDOT-4.0 across the pyrolysis temperature range.





**Figure S8.** SEM images of fully carbonized 3DP-PEDOT-4.0 lattices (3DL) shown in increasing order of magnification. Images reveal well-preserved architecture and intact porous features following pyrolysis at 1000 °C.





**Figure S9.** Figure S9. Raman spectra collected from 3DL and 3DL-PEDOT- $x$  lattices at representative pyrolysis temperatures of A)  $25^{\circ}\text{C}$  (As fabricated), B)  $325^{\circ}\text{C}$  (Under carbonized), C)  $500^{\circ}\text{C}$  (Partially carbonized), and D)  $1000^{\circ}\text{C}$  (Fully carbonized). Each panel includes spectra for 3DL (black) and 3DL-PEDOT- $x$  with increasing coating weight fraction: 3DP-PEDOT-2.0 (orange), 3DP-PEDOT-3.0 (blue), 3DP-PEDOT-4.0 (green), and 3DP-PEDOT-5.0 (yellow).

## Experimental Materials and Methods

### Materials

All chemicals were used as received unless otherwise noted. The photopolymerizable emulsion ink used to fabricate both plugs and lattice templates was synthesized by collaborators at the University of Sheffield and comprised 2-ethylhexyl acrylate (EHA, Sigma-Aldrich), isobornyl acrylate (IBOA, Sigma-Aldrich), and trimethylolpropane triacrylate (TMPTA, Sigma-Aldrich) as monomers, stabilized with Hypermer B246-SO-M (Croda). A dual photoinitiator system—2-hydroxy-2-methylpropiophenone (Darocur 1173, Sigma-Aldrich) and diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO, Sigma-Aldrich)—was employed to facilitate UV curing under 405 nm light. Beta-carotene and tartrazine were included as hydrophobic and hydrophilic light absorbers, respectively, to suppress overcuring during printing. Deionized water served as the dispersed phase for high internal phase emulsion (HIPE) formulation. Additional materials for post-processing and coating included 3,4-ethylenedioxythiophene (EDOT, AstaTech), iron(III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , Thermo Fisher), and tetrahydrofuran (THF, Thermo Fisher).

### Instrumentation

- **Thermogravimetric analysis (TGA)** characterization was conducted using a TA Instruments Discovery thermogravimetric analyzer with the high-resolution procedure (Hi-Res TGA) and default settings (ramp rate =  $2\text{--}10\text{ }^\circ\text{C min}^{-1}$  to  $T\text{ }^\circ\text{C}$ , resolution = 5), in platinum pans. The ramp rate and isothermal stage durations were varied.
- **Raman spectroscopy** was conducted using a Horiba LabRAM HR Evolution confocal Raman microscope equipped with a 50X LWD objective lens, 10% filter, and 532 nm laser. All spectra were collected at room temperature under ambient conditions using an acquisition time of  $\sim 5$  minutes (10 accumulations; 30 seconds each).

- **Scanning Electron Microscopy (SEM)** was conducted with Carl Zeiss Merlin high-resolution Field Emission Scanning Electron Microscope (FE-SEM). The SEM was operated under the In-Lens mode with an accelerating voltage of 10 kV and a working distance of  $\sim 5\text{--}7$  mm. The samples were placed on copper tape attached to stubs and sputter-coated with a thin layer ( $\sim 4$  nm) of Pt/Pd alloy to enhance electron conductivity. Void sizes were analyzed using the MATLAB code (See appendix section of the SI for annotated code).
- **Furnace pyrolysis** was conducted in a Thermo Scientific Lindberg/Blue M Mini-Mite TF55035C Tube Furnace equipped with 1-inch diameter quartz tubes capable of achieving up to  $\sim 1100$  °C and  $< 50$  °min<sup>-1</sup>. The tube furnace is installed with a mass flow controller set to deliver  $\sim 10$  sccm of N<sub>2</sub>. The Lindberg furnace was used for pyrolysis of small samples under direct ramp (5 °min<sup>-1</sup> to 800°C, 2h isotherm) conditions. The cooling rate was set to 2 °min<sup>-1</sup> until 400 °C, and the furnace was left to cool naturally.

## Methods

- **3D Printing of Poly(HIPEs)**

The 3D printing of both the cylindrical plugs and open-cell lattices was carried out using a HIPE-based emulsion ink optimized for stereolithography. The organic phase was formulated by mixing 37.3 wt% EHA, 37.3 wt% IBOA, 16.4 wt% TMPTA, and 9.0 wt% Hypermer B246-SO-M. This solution was heated to  $\sim 50$  °C under stirring to dissolve the surfactant. Light absorbers—beta-carotene (0.4 wt%) and tartrazine (0.1 wt%)—were added to the continuous phase before the photoinitiators to reduce overcuring and enable high-resolution fabrication. A dual-photoinitiator system consisting of 2.5 wt% TPO and 2.5 wt% Darocur 1173 was then added and dissolved under mild heating. Following preparation of the continuous phase, 80 vol% deionized water was gradually added under constant stirring at 300 rpm to form a stable high internal phase emulsion (HIPE). The final emulsion was viscous and stable for up to 7 days under ambient conditions. All structures were printed using a Kudo 3D Titan 2 HR stereolithography printer equipped with a 405 nm LED digital light projection (DLP) system. CAD models for the cylindrical plugs (5 mm diameter  $\times$  5 mm height) and cubic centroid lattices (unit cell size: 1.5 mm, comprising  $3 \times 3 \times 3$  cells) were prepared in SolidWorks and sliced using Creation Workshop (version 1.0.0.75) with a layer thickness

of 30  $\mu\text{m}$ . For the plugs, the print files included approximately 233 layers. Exposure parameters were optimized for each geometry: base layers were cured for 20 seconds, while normal layers received 6–8 seconds of exposure depending on resin opacity. The z-stage lift speed was 1.5 mm/s, with a 5 mm lift distance and a 2-second rest time between layers. Support structures were used to ensure platform adhesion during the printing process. Due to the strong light-scattering nature of HIPEs, unmodified resins often suffer from overcuring, distortion, and surface skin formation. The use of beta-carotene and tartrazine allowed for improved resolution, better shape retention, and open-surface porosity by minimizing internal overexposure and skin effects. After printing, structures were rinsed thoroughly in acetone to remove residual unpolymerized emulsion and then air-dried under ambient conditions for at least 12 hours. Printed plugs and lattices were stored in a desiccator until further pyrolysis and characterization.

- **Fabrication of Template-Coating Pairs (PEDOT coating protocol)**

As-printed and acetone-rinsed 3DP plugs were first dried under vacuum at 70 °C for at least 6 hours to remove residual solvent and moisture. Dried samples were then immersed in a 1.5 M solution of iron(III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) in tetrahydrofuran (THF) for 24 hours at room temperature. This step allowed the oxidizing agent to infiltrate the interconnected pore network and adsorb onto internal surfaces. Samples were gently agitated or rotated during this period to promote uniform diffusion. Following infiltration, the plugs were removed from the solution, briefly air-dried, and then vacuum-dried for 15 minutes to remove excess surface THF and minimize dilution of the subsequent monomer phase. Immediately afterward, the oxidant-loaded plugs were submerged in preheated EDOT/THF solutions at 70 °C for 24 hours to initiate polymerization. The EDOT monomer was freshly dissolved in anhydrous THF at concentrations of 2.5 M or 4.0 M, depending on the desired coating thickness. The solutions were then sparged with nitrogen to minimize premature oxidation. Plugs were maintained in sealed glass containers at 70 °C during the coating reaction. Polymerization of EDOT proceeded spontaneously upon contact with the pre-adsorbed  $\text{FeCl}_3$ , yielding a thin, adherent layer of PEDOT along the internal surfaces of the porous matrix. Samples were then rinsed thoroughly with fresh THF and transferred to a Soxhlet extractor for exhaustive washing in methanol for 24 hours to remove unreacted oxidant and residual

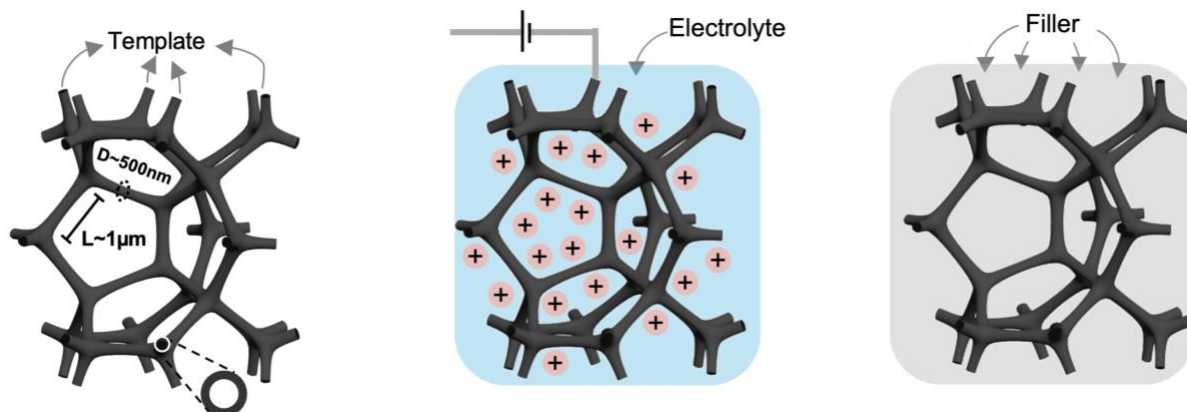
oligomers. After Soxhlet cleaning, the coated samples were vacuum-dried at 70 °C for 12 hours and stored in a desiccator until further use. PEDOT-coated samples are denoted as 3DP-PEDOT-x, where x refers to the EDOT monomer concentration (in M) used during polymerization. Final coatings were visibly darker and more rigid than uncoated samples, and no macroscale swelling or deformation was observed during the coating process.

- **Measurement of Mechanical Properties**

Mechanical properties were derived from the stress–strain curves obtained during quasi-static compression testing of cylindrical plugs. Force and displacement data were continuously recorded and converted to engineering stress and strain based on the original cross-sectional area and height of each plug. All measurements were performed at room temperature. Compressive strength was defined as the maximum engineering stress reached during the test, which corresponded to the peak of the stress–strain curve. For both uncoated and coated samples, this point typically preceded catastrophic fracture. No smoothing or filtering was applied before determining the peak value. Elastic modulus was extracted from the initial linear region of the stress–strain curve. For most samples, this corresponded to the strain range between 0.5% and 3%, although the exact window was adjusted in individual cases to exclude toe regions. A linear regression was applied to this segment to determine the best-fit slope, which was reported as the modulus. Toughness was calculated as the strain energy absorbed before densification. To define the upper integration limit objectively, the second derivative of each stress–strain curve was computed numerically, and the onset of densification was identified as the strain corresponding to the minimum in the second derivative—the point where the curve transitioned from a strain-hardening regime into densification. The area under the stress–strain curve up to this point was then integrated using the trapezoidal rule, and the result was reported as the toughness. This method ensured consistent and reproducible quantification of energy absorption, excluding artifacts introduced by post-collapse compression.

## CHAPTER 5

### Beyond the Template: Conclusions and Outlook\*



\*Note: portions of this chapter were taken from a first-authored manuscript published (as of December 2020) to *Molecular Systems Design & Engineering* (<https://doi.org/10.1039/D0ME00090F>)

## **5.1 Summary and Key Contributions**

The fabrication of porous carbon materials that are simultaneously lightweight, mechanically robust, and dimensionally stable remains a central challenge in materials science. Across conventional approaches, efforts to improve one performance dimension—such as strength or dimensional retention—often come at the expense of another. In pyrolytic systems, primarily, nanoscale strengthening effects are typically accessed through extreme shrinkage, which limits scalability and degrades structural integrity. Conversely, attempts to suppress shrinkage result in compromised mechanical performance. These persistent trade-offs have defined the boundaries of what is possible in architected carbon systems.

This thesis introduces a design strategy that fundamentally reconfigures those boundaries. By decoupling the structural and carbon-supplying roles within the pyrolytic precursor and exploiting thermal mismatches between them, the template-coating framework enables orthogonal control over the critical parameters of shrinkage, density, and mechanical response. The coating transforms into carbon before the template degrades, preserving the architecture while determining the final carbon content. This approach converts the shrinkage process—once considered a liability—into a design tool, allowing the material’s form and function to be tuned independently. The result is a system that escapes the conventional one-dimensional trade-off axis and instead opens a multidimensional design space, where structural retention, stiffness, and toughness can each be controlled with intent.

This strategy is developed and validated across three distinct materials platforms, each targeting a different long-standing trade-off. In Chapter 2, the template-coating framework is applied to PEDOT-coated poly(HIPE) foams to confront the trade-off between shrinkage and mechanical strength. While pyrolysis of polymer foams typically results in catastrophic volume loss (>98%) and compromised mechanical integrity, this system achieves ~80% dimension retention and ~50% volume retention, while delivering specific strengths as high as  $0.13 \text{ GPa g}^{-1} \text{ cm}^3$ —placing it among

the strongest known pyrolytic carbon foams derived from polymeric templates. These results enable the translation of nanoscale strength benefits to macroscopic geometries and hold promise for structural components in the automotive, aerospace, and packaging sectors, where weight reduction and simultaneous strength enhancement are critical.

Chapter 3 builds on this foundation by optimizing the framework to address the density–retention trade-off, which often limits the mass scalability of carbon architectures. Using polybenzoxazine coatings paired with engineered polystyrene-DVB templates, this chapter introduces a thermal compatibility criterion that ensures structural inheritance. The optimized system achieves volume retention exceeding 90% and enables tunable final densities spanning  $\sim 0.1$  to  $0.7 \text{ g cm}^{-3}$ , marking an unprecedented level of control in the lightweight materials regime. Benchmarking these materials against a broad literature dataset reveals that they occupy a previously inaccessible region of the density–retention landscape, demonstrating that the strategy is not only generalizable but also highly effective for designing materials with application-specific density constraints, including thermal insulation, filtration, and wearable protective systems.

In Chapter 4, the strategy is extended to 3D-printed lattices, shifting the focus to the trade-off between strength and toughness—a particularly challenging set of mutually exclusive materials properties to co-optimize among pyrolytic carbon architectures. Here, partial carbonization is utilized as a new approach to create hybrid materials comprising both carbonized and polymeric domains. These lattices, pyrolyzed at intermediate temperatures (e.g.,  $700^\circ\text{C}$ ), achieve specific strengths of  $\sim 115 \text{ MPa g}^{-1} \text{ cm}^3$ , moduli of up to  $531 \text{ MPa g}^{-1} \text{ cm}^3$ , and peak toughness values of  $\sim 32 \text{ J g}^{-1}$ , all while retaining  $\sim 80\%$  of their original dimensions. The resulting architectures occupy the upper-right quadrant of the toughness–shrinkage map, outperforming many nanostructured carbon systems that require high-resolution lithography or sacrificial templating. By leveraging architectural hierarchy and hybrid microstructure, this approach delivers mechanical synergies that are not accessible through



conventional pyrolysis routes, laying the foundation for impact-absorbing, damage-tolerant carbon materials at usable, real-world scales.

This work introduces a novel template-coating pair framework for designing and fabricating macroscopic porous carbon materials with remarkable mechanical properties, thereby overcoming the limitations imposed by thermally unstable precursors and nanoscopic systems that rely on shrinkage to exploit size effects. The template-coating platform decouples the structural blueprint—the template—from the primary carbon source—the coating—which significantly expands the design space, affording independent control over macroscale geometry, microscale pore distribution, bulk density and mechanical behavior. As such, the template-coating pair design strategy affords access to a new paradigm of hierarchically porous carbon architectures that can challenge longstanding trade-offs in materials science, such as those between density and strength and design complexity and fabrication scalability. Drawing inspiration from natural materials such as bone, wood, and nacre, which exhibit exceptional combinations of properties that are otherwise mutually exclusive, this research presents a new route towards harnessing size-based mechanical enhancement effects that are emergent at the nanoscale, using pyrolytic carbon systems at the macroscale.

## **5.2 Outlook and Future Directions**

The versatility and tunability of the template-coating framework position it as a promising platform technology with potential applications that extend beyond the mechanical domains explored in this thesis. Moving forward, two key directions illustrate the broader impact and adaptability of this approach: (1) the development of metal–carbon interpenetrating phase composites for structural applications, and (2) the use of hierarchically porous carbons in electrochemical systems for ion capture and energy storage.

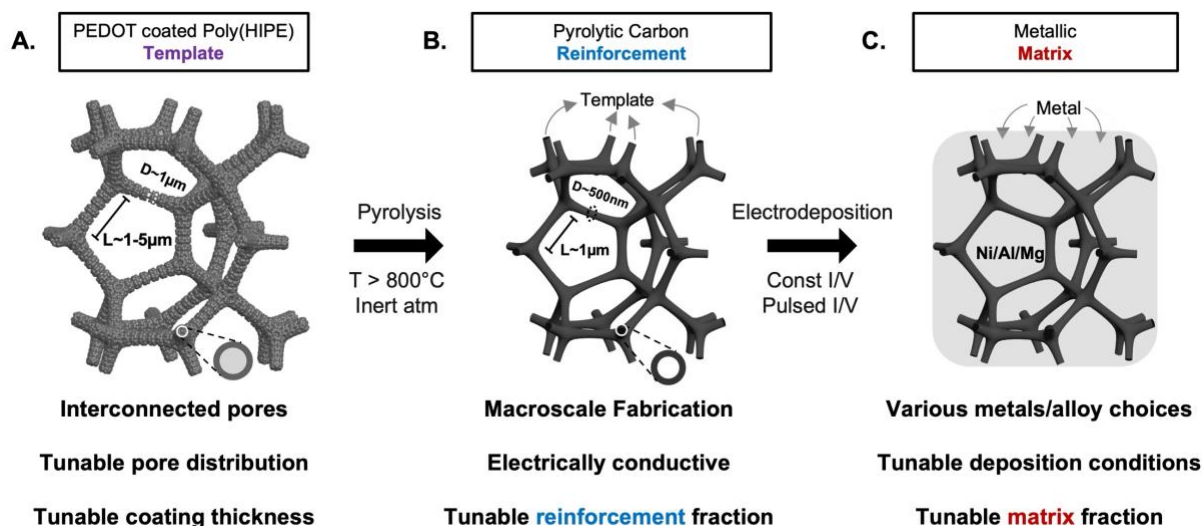
### **5.2.1 Interpenetrating Phase Composites: Integrating Strength and Toughness**

Building on the principles explored in Chapter 4, where partial carbonization was used to balance strength and toughness, a natural extension of this work lies in the development of interpenetrating phase composites (IPCs)<sup>[1]</sup>. These composites integrate a ductile or tough matrix phase composed of metal<sup>[2]</sup> or ceramic<sup>[3–5]</sup>, with a stiff carbon framework to produce materials that can simultaneously resist deformation and absorb energy<sup>[6]</sup>, two properties that are frequently mutually exclusive<sup>[7–9]</sup>.

At the nanoscale, interpenetrating phase composites such as nickel–pyrolytic carbon architectures have demonstrated exceptional mechanical properties by harnessing extreme material size effects<sup>[10]</sup>. These composites combine the strength of pyrolytic carbon, amplified by its nanoscale architecture, with the ductility of electrodeposited nickel. The result is a co-continuous structure that exhibits both high compressive strength and excellent strain energy absorption. By combining multiple size-dependent properties, these nanoscale IPCs access unique regimes of mechanical performance that were previously unreachable by conventional foams or lattices, offering multifunctional capabilities that extend beyond structural applications. At larger length scales, macroscopic IPCs—such as magnesium/nickel–titanium composites created by melt infiltration—have also demonstrated enhanced strength, damage tolerance, and energy dissipation<sup>[11,12]</sup>. However, these approaches often

rely on high-temperature processing and do not retain the mechanical enhancement conferred by size effects emergent at the nanoscale.

Inspired by these systems, our work explores a macroscale, low-temperature route to IPC fabrication by electrodepositing metals into hierarchically porous carbon scaffolds derived from PEDOT-coated poly(HIPE) templates (Fig. 1A). These pyrolyzed foams are dimensionally stable, electrically conductive, and exhibit tunable pore architecture across multiple length scales (Fig. 1B). Their hierarchical porosity makes them ideal scaffolds for metal backfilling, while their conductivity allows them to function as working electrodes in an electrochemical deposition process (Fig. 1C).

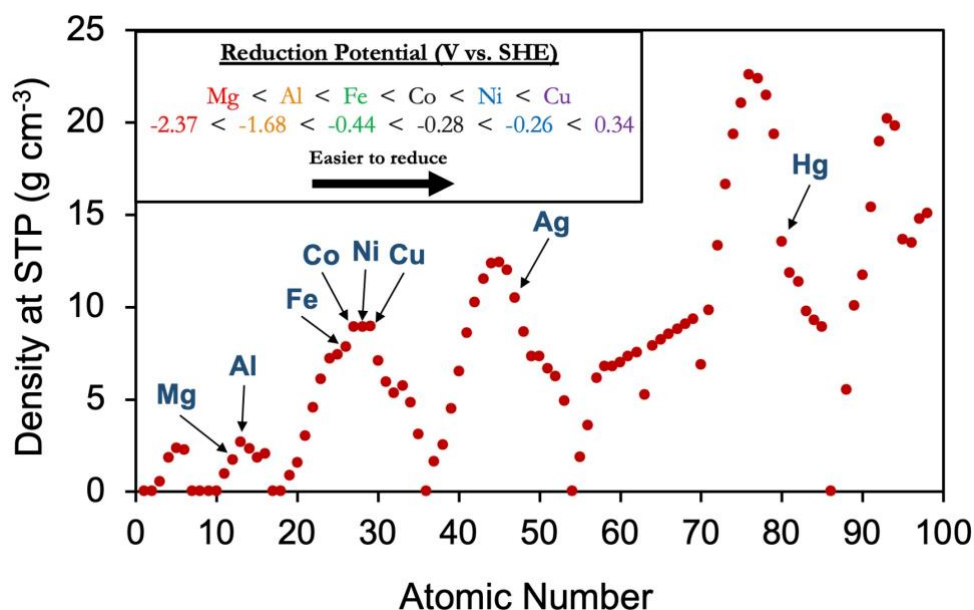


**Figure 1.** Schematic overview of the macroscale fabrication strategy for metal–carbon interpenetrating phase composites. **A)** A poly(HIPE) template is conformally coated with a carbonizable polymer (e.g., PEDOT), forming a thermally mismatched template-coating pair. **B)** Upon pyrolysis, the coating carbonizes before template decomposition, yielding a hierarchically porous, dimensionally stable pyrolytic carbon scaffold. **C)** The resulting conductive carbon architecture is backfilled with a metal phase (e.g., Ni) via electrodeposition, forming a co-continuous composite with tunable reinforcement and matrix fractions.

A unique feature of this approach is the ability to tune the volume fractions of the two constituent phases independently. The reinforcement fraction—i.e., the carbon content—can be varied by adjusting the initial coating thickness applied to the polymer template, which dictates the amount of carbon retained after pyrolysis. The matrix fraction, corresponding to the volume of

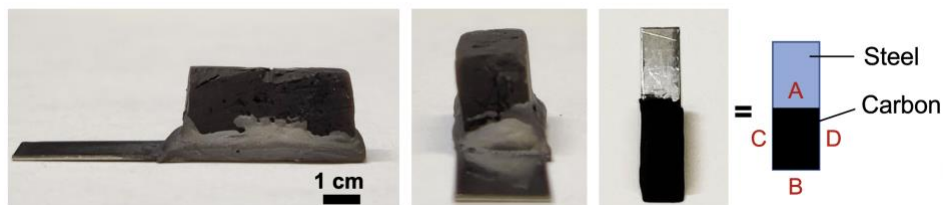
infiltrated metal, is controlled through the electrodeposition parameters: electrolyte concentration, deposition time, and current mode (e.g., constant current vs. pulsed current), each of which influences the extent and uniformity of infiltration.

In selecting the matrix metal, factors such as density, melting point, and reduction potential must be considered. Lighter metals such as magnesium<sup>[13]</sup> and aluminum<sup>[14]</sup> offer superior strength-to-weight potential but are challenging to deposit electrochemically<sup>[15]</sup> due to their low reduction potentials (Fig. 2). In contrast, nickel is denser but more easily deposited, making it an ideal proof-of-concept system for validating the infiltration process. Ultimately, this strategy can be extended to lower-density metals to produce interpenetrating composites with optimized strength-to-toughness-to-weight ratios.



**Figure 2.** Elemental density versus atomic number, highlighting key candidate metals for matrix infiltration into porous carbon scaffolds. Elements of interest—Mg, Al, Fe, Co, Ni, and Cu—are labeled, spanning a range of densities from 1.74 g cm<sup>-3</sup> to 8.96 g cm<sup>-3</sup>, in that order. Inset (top left) shows standard reduction potentials (vs. SHE), which indicate relative ease of electrodeposition. Magnesium offers the lowest density but has the most negative reduction potential, making it the most challenging to deposit electrochemically. Nickel, although denser, is far easier to reduce and serves as a practical proof of concept for infiltration. This trade-off informs the selection of matrix metals for optimizing strength-to-weight and toughness-to-weight ratios in IPC design.

To realize this, we developed an experimental setup involving constant-current electrodeposition. The pyrolytic carbon foam was adhered to a stainless-steel plate using a graphene-based conductive paste, forming the working electrode (Fig. 3). A nickel wire served as the counter electrode, and a platinum wire immersed in silver nitrate solution was used as a reference. The organic electrolyte consisted of a 4:1 mixture of dimethylformamide (DMF) and acetonitrile (ACN), with nickel chloride hexahydrate ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ) as the metal source.

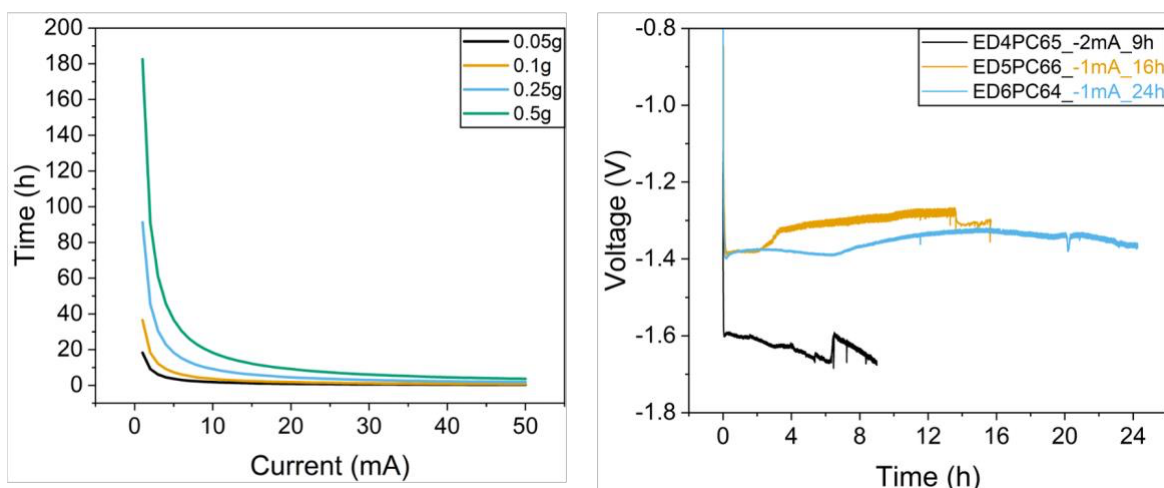


**Figure 3.** Working electrode made by pasting the porous carbon reinforcement on a steel plate.

The Faraday equation was then used to estimate the deposition time required to achieve complete infiltration based on the mass of the working electrode. The primary equation governing Faraday's electrodeposition is:

$$m = \frac{Q \cdot E}{F} = \frac{I \cdot t \cdot M}{z \cdot F}$$

where  $m$  is the mass of the substance deposited,  $Q$  is the total electric charge passed,  $E$  is the equivalent weight of the metal, and  $F$  is the Faraday constant ( $\sim 96,485 \text{ C mol}^{-1}$ ). This equation highlights the direct proportionality between the mass of material deposited and the total charge delivered. As shown in Figure 4A, these calculations revealed that deposition time is highly sensitive to both the applied current and the electrode mass. For example, a 0.05 g carbon scaffold deposited at 1 mA required approximately 20 hours for complete infiltration, whereas a 0.5 g scaffold required nearly 180 hours under the same conditions. These results were experimentally validated and demonstrated an exponential decrease in the necessary deposition time with increasing current. However, higher current densities were observed to induce non-uniform metal deposition due to rapid ion depletion near the

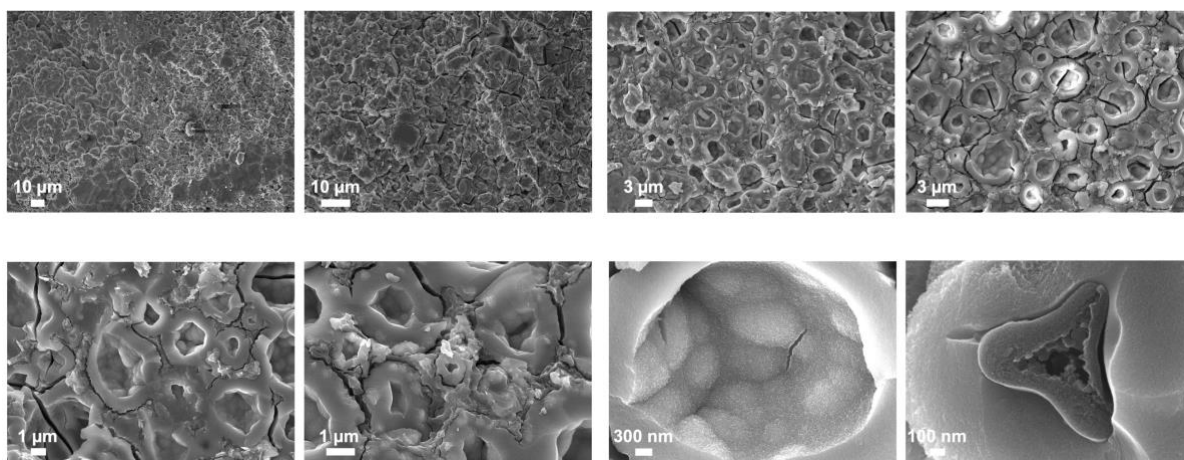


**Figure 4.** Electrodeposition time as a function of applied current for nickel infiltration into a pyrolytic carbon scaffold, estimated using the Faraday equation. As expected, deposition time decreases nonlinearly with increasing current. The sharp decay illustrates the sensitivity of deposition time to current, particularly in the low-current regime. While higher currents reduce process duration, they can lead to non-uniform deposition due to rapid ion depletion near the electrode surface, highlighting the importance of balancing deposition rate with infiltration quality.

electrode surface. This trade-off underscores the importance of optimizing deposition conditions: low currents improve deposition uniformity but increase processing time, while higher currents accelerate deposition but risk inhomogeneous filling. These findings highlight the importance of striking a balance between electrode mass and current to achieve practical deposition durations.

To further evaluate the deposition process, we recorded voltage–time profiles under constant-current conditions for three trials:  $-2$  mA for 9 h,  $-1$  mA for 16 h, and  $-1$  mA for 24 h (Fig. 4B). In all cases, the voltage initially decreased and then plateaued as the deposition progressed. For the  $-1$  mA conditions, the voltage stabilized at approximately  $-1.35$  V. In contrast, the  $-2$  mA trial reached a more negative plateau of approximately  $-1.6$  V, consistent with faster nickel ion consumption at higher current densities. The relatively steady but noisy profiles likely result from electrolyte stirring, which was used to minimize mass transport limitations and ensure uniform metal ion availability near the electrode surface. These results confirmed that deposition conditions could be tuned to promote sustained infiltration without hitting diffusion-limited regimes or incurring unstable overpotentials.

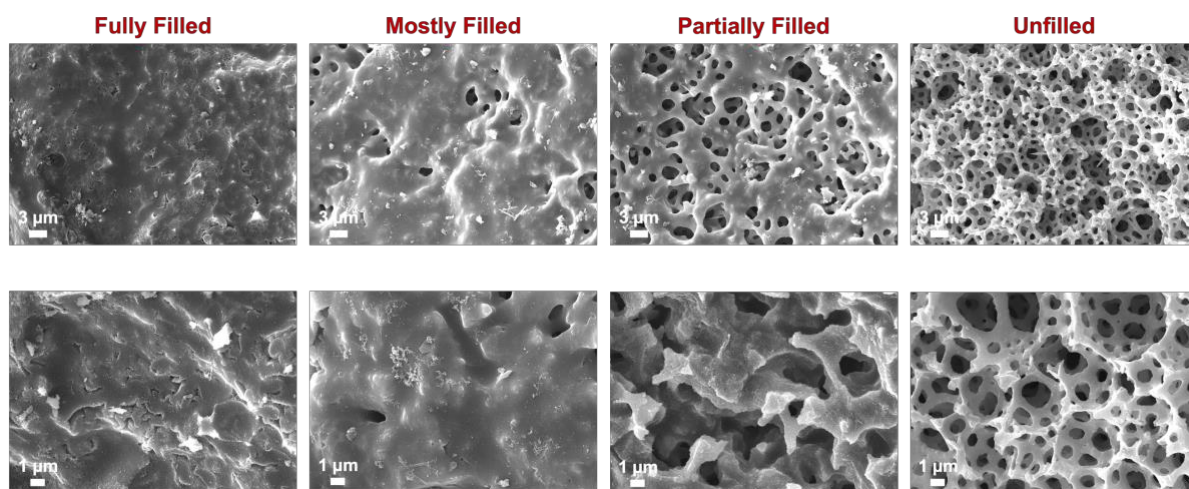
With these considerations in mind, we selected a 0.25 g pyrolytic carbon foam as the working electrode and subjected it to constant-current electrodeposition at  $-1$  mA for three days. This approach enabled the gradual and uniform infiltration of nickel into the carbon architecture. Post-deposition, the sample exhibited a significant increase in mass consistent with nickel uptake, confirming that metal deposition had occurred. Scanning electron microscopy (SEM) further validated the result, revealing distinct and co-continuous phases of nickel and carbon throughout the architecture, clear evidence of interpenetrating phase formation (Fig. 5).



**Figure 5.** Preliminary evidence of interpenetrating phase composite (IPC) formation following electrodeposition of nickel into a pyrolytic carbon scaffold. Scanning electron microscopy (SEM) images at increasing magnifications (from left to right) reveal distinct and co-continuous nickel and carbon domains. These observations confirm successful metal infiltration across multiple length scales and support the formation of a hierarchical nickel–carbon IPC.

SEM analysis also revealed multiple regimes of pore filling within the same structure. In the fully filled regime, the characteristic hierarchical porosity was almost entirely obscured by the metal, indicating complete infiltration. The mostly filled regime showed substantial metal deposition, but some of the underlying pore structure remained visible. In the partially filled regime, the carbon architecture remained primarily evident, with complete metal deposition occurring only in certain regions. Finally, the unfilled regime showed the original porous structure with minimal metal infiltration (Fig. 6).





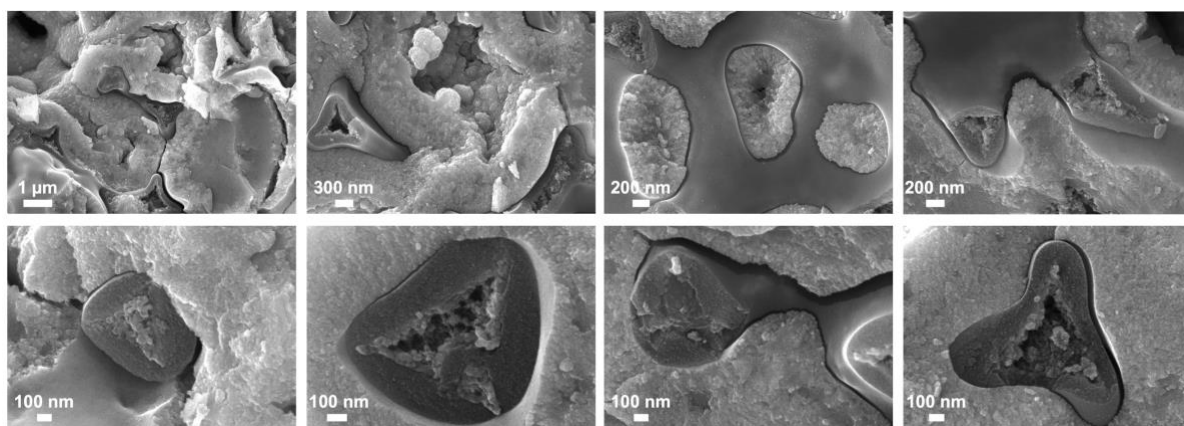
**Figure 6.** Representative SEM images illustrating the distinct regimes of nickel infiltration observed within the pyrolytic carbon scaffold following electrodeposition. Fully filled regions show complete occlusion of the original pore structure by deposited nickel. Mostly filled regions retain visible carbon features interspersed with dense metal deposits. Partially filled regions exhibit limited metal growth along select surfaces, whereas unfilled regions retain the original porous carbon morphology with minimal or no nickel infiltration. These regimes highlight the spatial variability in infiltration and inform future strategies for achieving uniform composite formation.

A closer examination revealed a critical limitation: in several regions, the reinforcement and matrix phases were not in direct physical contact, resulting in voids or poorly bonded interfaces between the carbon ligaments and the deposited metal (Fig. 7). This is nontrivial seeing as, in composite materials, an intact interphase is essential for efficient load transfer and synergistic performance<sup>[16]</sup>. This transitional region—neither purely matrix nor reinforcement—mediates stress redistribution and suppresses interfacial failure modes such as debonding or crack propagation. In well-engineered metal–carbon interpenetrating composites, the interphase enables metal ligaments to bridge carbon fractures, thereby enhancing both strength and toughness simultaneously. Absent or weak interfaces undermine these benefits by allowing slippage or debonding under load, while overly strong, brittle interfaces may suppress energy dissipation mechanisms such as crack deflection or fiber pullout. Engineering the interphase—whether through nanoscale topological roughness, chemical functionalization of the carbon scaffold, or surface activation—ensures compatibility between dissimilar materials, mitigates thermal mismatch stresses, and unlocks multifunctionality, including self-healing, conductivity, and damage sensing. These findings emphasize that future efforts must



focus not only on infiltration completeness but also on interfacial quality, which will ultimately determine whether these composites can realize their full mechanical potential.

To that end, future efforts will focus on engineering a robust interphase between the pyrolytic carbon framework and the infiltrated metal matrix. Several pathways are being explored to improve



**Figure 7.** SEM images reveal an interfacial gap between the pyrolytic carbon scaffold and the deposited nickel, indicating incomplete contact between the reinforcement and matrix phases. Such separation compromises load transfer across the interface, highlighting the need for future interphase engineering to ensure mechanical integration. Improving contact quality will be critical for unlocking the full strength and toughness potential of these macroscopic metal–carbon IPCs.

contact and compatibility between phases. These include surface activation of the carbon scaffold before deposition (e.g., via oxygen plasma or acid functionalization) and use of pulsed-current deposition protocols to promote more conformal growth within high-aspect-ratio pores. In parallel, composite characterization using cross-sectional SEM, EDS mapping, and mechanical testing under load will help quantify the effects of interfacial quality on overall performance. The goal is to create a fully co-continuous metal–carbon architecture in which mechanical load is efficiently transferred between phases, enabling new combinations of stiffness, strength, toughness, and damage tolerance in macroscopic, lightweight materials. By integrating interphase design into the template-coating strategy, this future work has the potential to transform the framework from a structural concept into a fully functional composite platform.

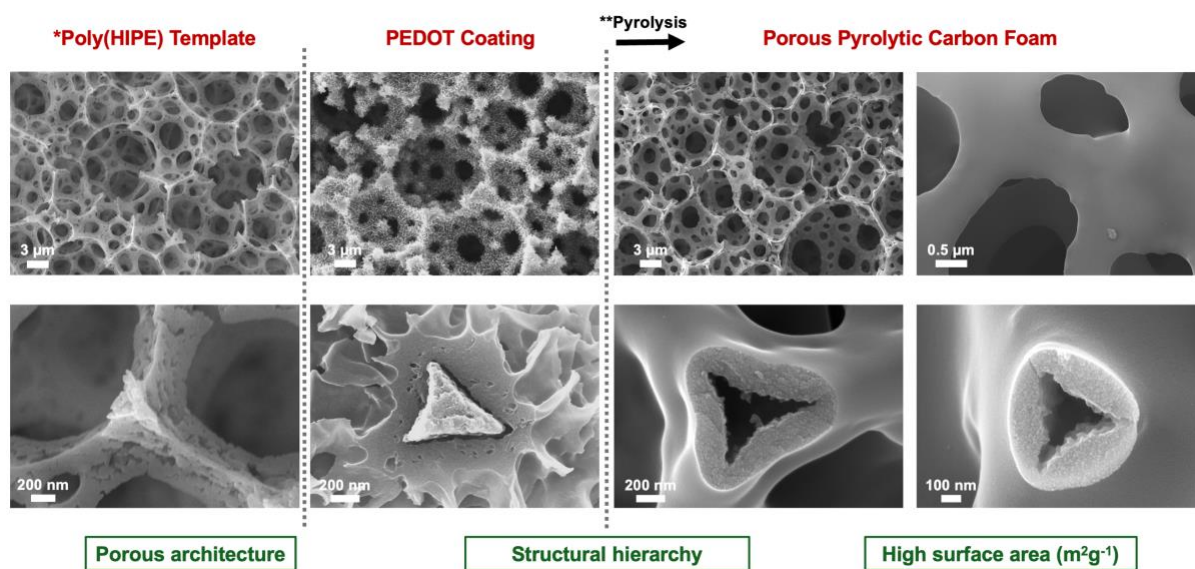
### 5.2.2 Hierarchically Porous Carbons for Ion Capture and Energy Storage

In parallel with structural applications, hierarchically porous carbons derived from the template-coating strategy show significant promise for capacitive electrochemical systems, particularly in capacitive deionization (CDI) and supercapacitive energy storage. Both technologies rely on a common mechanism: the reversible, non-faradaic adsorption of ions onto an electrically conductive surface. Because this process is surface-driven and diffusion-limited, the performance of such systems is tightly coupled to the architecture and electronic properties of the electrode material.

The ideal material for capacitive ion storage must satisfy three demanding criteria. First, it must possess a high surface area to enable substantial ion adsorption. Second, it must feature hierarchical porosity to support fast ion transport across length scales—from electrolyte flow through macropores, to ion diffusion through mesopores, to surface access at the nanoscale. Third, it must be electrically conductive to enable efficient charge redistribution and minimal resistive losses during rapid cycling. Many materials used in this space—such as activated carbons, carbon aerogels, and polymer-derived carbons—meet one or two of these requirements, but rarely all three in tandem. Emulsion-templated polymers, such as poly(HIPEs), offer an unmatched structural hierarchy but are electrically insulating. Conductive additives, filler incorporation, or surface functionalization strategies can add conductivity, but often at the expense of pore accessibility or structural fidelity.

This thesis proposes an alternative and fundamentally different approach: instead of trying to make poly(HIPEs) conductive, we transform them into carbon. Through the template-coating strategy developed in earlier chapters, a poly(HIPE) serves as a sacrificial structural template, while a conformal, high-char-yield coating (e.g., PEDOT or polybenzoxazine) supplies the carbon mass. Upon pyrolysis, this pairing yields an electrically conductive, hierarchically porous carbon foam that inherits the architecture of the original poly(HIPE) but gains the functional advantages of a pyrolytic carbon network.

This inversion of conventional thinking—carbonizing for conductivity rather than modifying to accommodate it—preserves the hierarchical porosity that makes poly(HIPEs) attractive while endowing the structure with electronic functionality (Figure 8). It eliminates the need for blending or post-processing additives and decouples carbon supply from geometric design. The resulting carbon scaffold is not only conductive but also tunable in mass and density, depending on coating thickness and pyrolysis temperature. Because both architecture and conductivity are built into the system from the start, these carbons are poised to serve as highly effective electrodes for ion storage and separation technologies.



**Figure 8.** SEM images of template-coating pair-derived hierarchically porous carbons, ideally suited for applications in ion adsorption (separation and energy storage).

This approach has the potential to address a central bottleneck in CDI and supercapacitor design: the trade-off between ion accessibility and electrode conductivity. Instead of navigating this trade-off through additive blending or architectural compromise, the template–coating strategy may provide a route to producing monolithic structures in which pore hierarchy, surface area, and conductivity are built in from the outset. While still in the early stages of investigation, this framework

presents a promising path toward scalable, structurally robust, and electrochemically functional carbon electrodes that go beyond the capabilities of conventional powders or composite slurries.

Early characterization of these template-derived carbon architectures reveals several attributes that make them well-suited for electrochemical applications. Using nitrogen adsorption measurements, we observe BET surface areas as high as  $650 \text{ m}^2 \text{ g}^{-1}$  for non-activated samples—values that already rival commercial activated carbons. These surface areas can be further enhanced to over  $1000 \text{ m}^2 \text{ g}^{-1}$  through post-pyrolysis surface activation, as detailed in Chapter 2. Importantly, this surface area is not confined to micropores alone; evidence from SEM and pore volume analysis confirms a hierarchical pore structure, with interconnected macro- and mesopores that facilitate rapid ion transport and electrolyte access throughout the architecture.

In addition to pore hierarchy, SEM also reveals hollow struts within the carbon network—a structural feature that, while still under investigation, could significantly increase the electrochemically accessible surface area by providing internal voids accessible to electrolyte ions. Electrical conductivity measurements show values ranging from  $100\text{--}200 \text{ S m}^{-1}$ , depending on coating thickness, confirming that the pyrolytic carbon network is not only architected for ion transport but also intrinsically conductive. This combination of porosity and conductivity eliminates the need for conductive additives or composite slurries, enabling monolithic carbon electrodes with built-in electronic functionality.

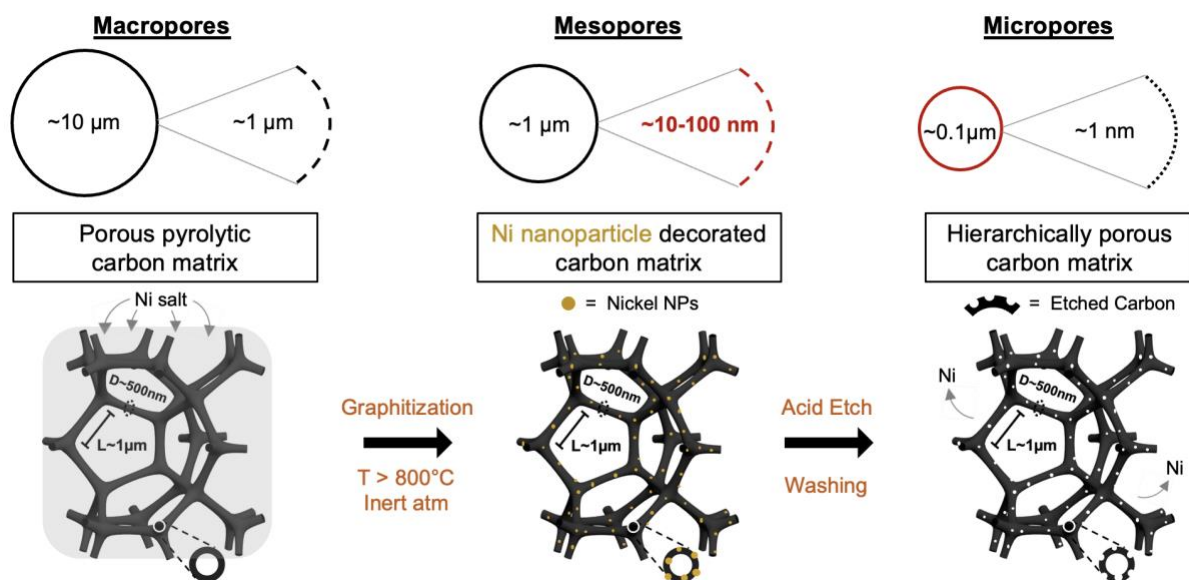
Because electrode thickness plays a critical role in determining both specific capacitance and ion transport kinetics, this ability to control form factor without compromising architecture is particularly valuable. Many conventional carbon-based electrodes must trade off thickness and performance: Thicker electrodes store more charge but suffer from transport limitations, while thinner electrodes lose capacity due to low mass loading. The hierarchical, tunable nature of these carbon

foams may provide a way to escape this trade-off, maintaining fast kinetics even in thicker monoliths or enabling conformal integration in microscale architectures.

While macroscale form factor plays a key role in dictating electrode performance—especially in terms of device integration, resistance, and mass transport—ion accessibility is equally governed by microstructural details. Specifically, if the carbon struts or cell walls become too thick, the interior surfaces, including the inner volume of hollow struts, may become electrochemically inaccessible. This impairs both gravimetric and volumetric performance by creating regions that are physically present but functionally inactive.

To address microstructural inaccessibility, we propose a post-pyrolysis etching and graphitization scheme based on nickel nanoparticle-mediated catalytic graphitization (Figure 9). In this approach, the pyrolyzed carbon scaffold is saturated with a nickel nitrate  $[\text{Ni}(\text{NO}_3)_2]$  solution, which diffuses throughout the hierarchical pore network. Upon heating to 800 °C under an inert atmosphere, the salt decomposes and reduces to form dispersed nickel nanoparticles within the matrix. These particles then catalyze a solid-state dissolution–precipitation reaction between disordered carbon and the metal catalyst. In this mechanism, amorphous carbon dissolves into the metal nanoparticle, reorganizes at elevated temperature, and is then re-precipitated as more ordered graphitic carbon, often leaving behind voids in the process.

In effect, the nickel particles behave like nanoscale tunnel borers, selectively etching and reorganizing the thick, disordered carbon walls from within. This process not only opens otherwise inaccessible interior regions but also enhances the crystallinity of the remaining carbon, potentially improving both electrochemical accessibility and electronic conductivity. Importantly, it introduces porosity in a structure-directed manner—guided by the local nickel distribution—without global collapse of the foam. This catalytic graphitization strategy offers a promising route to maximize active surface area and internal connectivity in carbon scaffolds that would otherwise be limited.



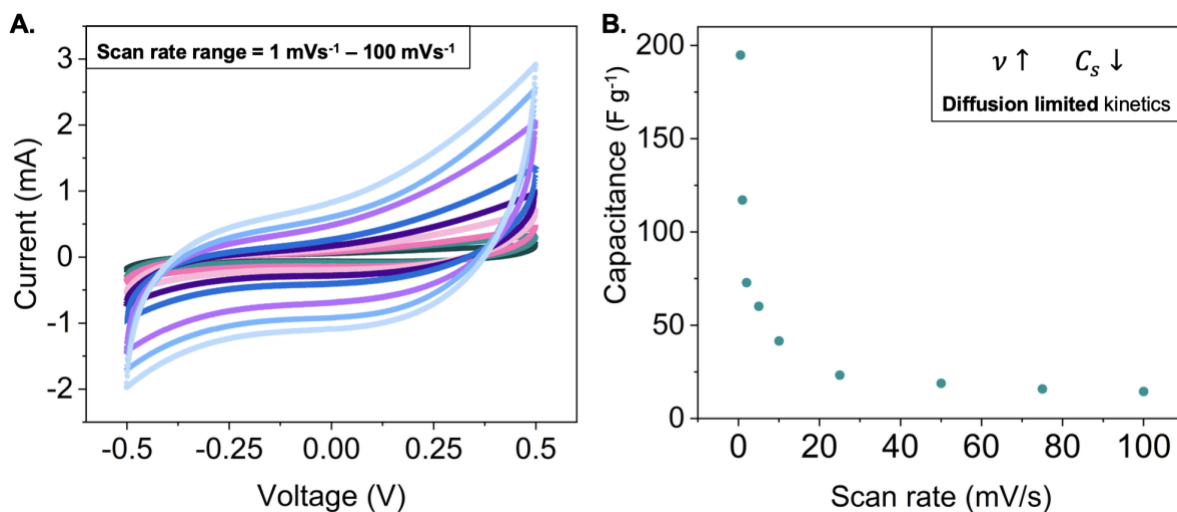
**Figure 9.** Schematic of catalytic graphitization via nickel nanoparticles.  $\text{Ni}(\text{NO}_3)_2$  is infused into the porous carbon scaffold and thermally reduced at 800 °C to form Ni nanoparticles. These catalyze a solid-state dissolution–precipitation reaction with disordered carbon, selectively etching thick struts and enhancing graphitic order. The process could increase internal surface area accessibility and conductivity by opening previously obscured regions.

Initial electrochemical testing of the holey carbon scaffolds produced via nickel nanoparticle etching revealed modest performance in their current form. Cyclic voltammetry (CV) conducted at scan rates ranging from 1 to 20  $\text{mV s}^{-1}$  showed specific capacitance values between 20 and 100  $\text{F g}^{-1}$ , respectively. While these values confirm capacitive behavior, they remain significantly lower than the theoretical potential implied by the materials' high surface area and hierarchical porosity. This suggests that a large fraction of the internal surface may be electrochemically inaccessible, or that sluggish ion transport and internal resistance are limiting performance.

These findings point to a critical limitation—form factor. Although the carbon foams are architecturally porous and exhibit intrinsic electrical conductivity in the range of 100–200  $\text{S m}^{-1}$ , their monolithic geometry in the initial studies was relatively thick, limiting ion transport and internal accessibility. This suggests that structural improvements alone are insufficient unless paired with geometry optimization at the device level. To address this, we shifted our focus to fabricating ultrathin,

hierarchically porous carbon electrodes using doctor-blade-cast poly(HIPE) templates. These thin films preserve the multiscale architecture of the original foams but drastically reduce diffusion distances, offering a direct route to improved electrochemical performance without compromising structural integrity.

To evaluate this strategy, we prepared a thin, monolithic carbon film and tested it in a three-electrode configuration (Figure 10). The working electrode consisted of a thin carbon layer, the counter electrode was a carbon foam, and the reference electrode was a Pt wire in 100 mM TBAPF<sub>6</sub> and 10 mM AgNO<sub>3</sub>. The electrolyte—a mixed 1 M LiClO<sub>4</sub> aqueous/organic (20 vol% acetonitrile) system—was selected to provide both ionic strength and adequate wetting of the hierarchical structure.



**Figure 10.** Electrochemical performance of a thin-film porous carbon electrode. **(A)** Cyclic voltammograms at increasing scan rates. **(B)** Specific capacitance as a function of scan rate, showing rapid decay with increasing rate.

CV curves revealed capacitive behavior with pronounced rate dependence. At low scan rates (1 mV s<sup>-1</sup>), the specific capacitance reached approximately 200 F g<sup>-1</sup>, indicating excellent ion accessibility and effective utilization of the internal surface area. However, as the scan rate increased, the capacitance exponentially decayed, falling to ~40 F g<sup>-1</sup> at 10 mV s<sup>-1</sup> and plateauing near 10 F g<sup>-1</sup> at

100 mV s<sup>-1</sup>. This trend suggests that while the thin-film architecture improves performance over thicker monoliths, rate-dependent transport limitations persist, likely due to remaining microstructural barriers or tortuosity within the pore network. Nonetheless, the enhancement in gravimetric capacitance relative to prior thick electrodes validates the approach of form factor optimization and highlights the potential for further improvement through microstructural refinement and electrolyte engineering.

Taken together, these preliminary studies demonstrate that template–coating-derived carbon foams possess the essential features of an effective electrochemical platform: high surface area, hierarchical porosity, intrinsic conductivity, and tunable geometry. While initial capacitance values remain modest under high-rate conditions, the observed improvements in thin-film architectures suggest that further optimization of form factor and microstructure can unlock significantly enhanced performance. Future directions will focus on tailoring strut connectivity, reducing tortuosity, and incorporating selective ion sorption functionality—advancing these materials toward real-world applications in energy storage and ionic separations.



### 5.3 References

- [1] D. R. Clarke, *J. Am. Ceram. Soc.* **1992**, *75*, 739.
- [2] R. Schaller, *J. Alloys Compd.* **2003**, *355*, 131.
- [3] N. Kota, M. S. Charan, T. Laha, S. Roy, *Ceram. Int.* **2022**, *48*, 1451.
- [4] J. Binner, H. Chang, R. Higginson, *J. Eur. Ceram. Soc.* **2009**, *29*, 837.
- [5] Z. Wang, K. M. Schmalbach, R. L. Penn, D. Poerschke, A. Antoniou, N. A. Mara, A. Stein, *ACS Appl. Mater. Interfaces* **2021**, *13*, 32126.
- [6] L. D. Wegner, L. J. Gibson, *Int. J. Mech. Sci.* **2001**, *43*, 1771.
- [7] R. O. Ritchie, *Nat. Mater.* **2011**, *10*, 817.
- [8] F. Bouville, E. Maire, S. Meille, B. Van De Moortèle, A. J. Stevenson, S. Deville, *Nat. Mater.* **2014**, *13*, 508.
- [9] N. Song, Y. Zhang, Z. Gao, X. Li, *Nano Lett.* **2018**, *18*, 5812.
- [10] J. Bauer, M. Sala-Casanovas, M. Amiri, L. Valdevit, *Sci. Adv.* **2022**, *8*, eabo3080.
- [11] M. Zhang, N. Zhao, Q. Yu, Z. Liu, R. Qu, J. Zhang, S. Li, D. Ren, F. Berto, Z. Zhang, R. O. Ritchie, *Nat. Commun.* **2022**, *13*, 3247.
- [12] M. Zhang, Q. Yu, Z. Liu, J. Zhang, G. Tan, D. Jiao, W. Zhu, S. Li, Z. Zhang, R. Yang, R. O. Ritchie, *Sci. Adv.* **2020**, *6*, eaba5581.
- [13] T. M. Pollock, *Science* **2010**, *328*, 986.
- [14] E. Guinea, A. Salicio-Paz, A. Iriarte, H. Grande, E. Medina, E. García-Lecina, *ChemistryOpen* **2019**, *8*, 1094.
- [15] Z. Song, Z. Zhang, A. Du, S. Dong, G. Li, G. Cui, *Adv. Mater.* **2021**, *33*, 2100224.
- [16] Y. Chen, X. Liu, T. Zhang, H. Xie, N. Zhao, C. Shi, C. He, J. Li, E. Liu, *Comput. Mater. Sci.* **2019**, *169*, 109131.