

## Supporting Information

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High-Performing All-Solid-State Sodium-Ion Batteries Enabled by the Presodiation of Hard Carbon

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## **Supporting Document**

## Achieving High-performing All-solid-state Sodium-ion Batteries by Presodiation of Hard Carbon

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**Figure S1**. High-resolution XPS C 1s spectra of a) HC and b) HCT during depth profiling. c) High-resolution XPS B 1s of HCP and NaBH<sub>4</sub>,



**Figure S2**. HR-TEM images with the area selected electron diffraction (inset) of a) HC, b) HCT, and c) HCP.



Figure S3 a) SEM image and b) Nyquist plot of NBH. c) Cyclic voltammogram of NBH+SS/NBH/Na<sub>9</sub>Sn<sub>4</sub>.



**Figure S4.** a) Potential profile and b) normalized capacity at different current density of HC composites with different weight ratios.



**Figure S5** a) First cycle dQ/dV of the respective electrode. Potential profile of b) desodiating HCP in first cycle, c) HCTT and d) HC+NaBH<sub>4</sub> without thermal treatment.



Figure S6 Potential profiles of a) HC, b) HCT, and c) HCP at different cycle.



**Figure S7** a) XRD profiles and b) initial potential profiles and c) reversible capacities of HCP-x and d) capacities observed via TGC and electrochemistry. e) EELS mapping of HCP-60.



**Figure S8** Potential profile of a) HC and b) HCT with CCCV. c) Total cell resistance evolution with cycle number.



**Figure S9** dQ/dV plots of a) HC, b) HCT, and c) HCP. Potential profiles of d) HC, e) HCT, and f) HCP differentiated according to the (de)sodiation mechanism.



Figure S10 a) Potential profile and b) capacity retention of Na<sub>9</sub>Sn<sub>4</sub>||NCO.



Figure S11 dQ/dV plots of  $AS^3iBs$  with a) Na<sub>9</sub>Sn<sub>4</sub>, b) HC, c) HCT, and b) HCP as the anode.



**Figure S12** Potential response of AS<sup>3</sup>iBs with a) HC, b) HCT, and c) HCP as anode at various current densities.