## **Supporting Information**

## Multi-scale structure optimization of boron-doped hard carbon nanospheres boosting plateau capacity for high performance sodium ion battery

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Figure S1. SEM images of HCS-1200 and BHCS-1200 at different magnification rates.



Figure S2. SEM images of HCS-800 and BHCS-800 at different magnification rates.



Figure S3. SEM images of HCS-1600 and BHCS-1600 at different magnification rates.



**Figure S4.** TEM and HRTEM images of HCS-1200 and BHCS-1200 at different magnification rates.



Figure S5. Electron image of BHCS-1200.



Figure S6. XRD patterns of HCS-1200 and BHCS-1200.



Figure S7. XRD patterns of HCS-*x* and BHCS-*x*.



Figure S8. Deconvoluted XRD patterns of HCS-x and BHCS-x with  $d_{002}$  parameters.

**Table S1.** Structural parameters of microcrystals from XRD patterns for HCS-*x* and BHCS-*x*.

Samples	<i>d<sub>002</sub></i> (nm)	L <sub>a</sub> (nm)	<i>L<sub>c</sub></i> (nm)
HCS-800	0.393	2.766	1.419
BHCS-800	0.405	2.648	1.158
HCS-1000	0.388	3.329	1.305
BHCS-1000	0.386	3.171	1.258





**Figure S9.** Deconvoluted Raman spectras of HCS-*x* and BHCS-*x* with  $I_D / I_G$  parameters.



Figure S10. N<sub>2</sub> adsorption isotherms of HCS-800, HCS-1200 and HCS-1600.

Samples	BC <sub>3</sub> (%)	BC <sub>2</sub> O (%)	BCO <sub>2</sub> (%)	B <sub>4</sub> C (%)
BHCS-800	19.49	31.47	49.04	
BHCS-1200	44.13	28.77	27.10	
BHCS-1600	42.13	17.61	16.48	24.08

**Table S2.** Content of boron doping configurations from XPS spectrum for BHCS-800, BHCS-1200 and BHCS-1600.



**Figure S11.** Na<sup>+</sup> anodic performances of HCS-1200 using coin-type cells in 1 M NaPF<sub>6</sub> electrolyte with mass loading of 0.8-1.2 mg cm<sup>-2</sup>. (a) CV curves of HCS-1200 at the scan rate of 0.2 mV s<sup>-1</sup>. (b) Initial three discharge–charge curves of HCS-1200 at the current density of 0.03 A g<sup>-1</sup>.



Figure S12. Rate performances of HCS-x.



**Figure S13.** (a) CV curves of HCS-1200 at various scan rates. (b) *b*-value calculation according to the relationship between peak current and scan rate of HCS-1200.



**Figure S14.** Capacities calculated from the micropore filling (<0.03V) in the 2nd cycle of HCS-*x* and BHCS-*x*.

**Table S3.** HOMO, LUMO and band gap of carbon surface with different boron doping configurations.

	pristine carbon surface (eV)	BC <sub>3</sub> (eV)	BC <sub>2</sub> O (eV)	BCO <sub>2</sub> (eV)
НОМО	-5.095754	-5.252507	-5.326348	-5.142229
LUMO	-2.432218	-2.86461	-2.278184	-2.444216
Gap	2.663537	2.387897	3.048163	2.698013



Figure S15. Na<sup>+</sup> adsorption configurations on various carbon surfaces.



**Figure S16.** Galvanostatic intermittent titration technique (GITT) potential profiles of HCS-1200.



**Figure S17.** Initial three charge-discharge curves of NVP at the current density of 0.03 A  $g^{-1}$ 



**Figure S18.** Energy densities of HCS-1200//NVP and BHCS-1200//NVP full-cells at different rates.