

# N/P co-doping regulates the local microcrystalline structure of hard carbon to facilitate sodium-ion storage

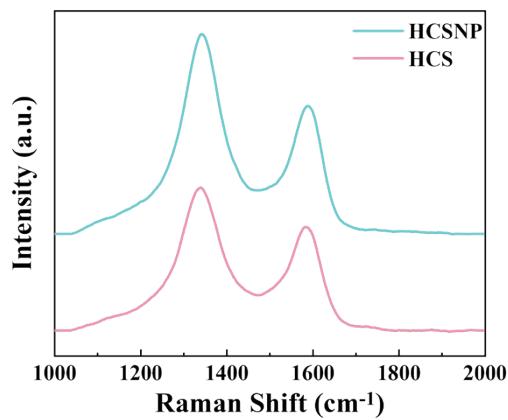
Yujie Guo <sup>a, 1</sup>, Ke Liu <sup>a, 1</sup>, Jie Xiao <sup>a</sup>, Xiaoyuan Zeng <sup>a, \*</sup>, Shun Ji <sup>a</sup>, Yanjia Zhang <sup>a</sup>,  
Peng Dong <sup>a, \*</sup>, Ziyi Zhu <sup>a, \*</sup>

<sup>a</sup> National and Local Joint Engineering Research Center for Lithium-ion Batteries and Materials Preparation Technology, Key Laboratory of Advanced Battery Materials of Yunnan Province, Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, China.

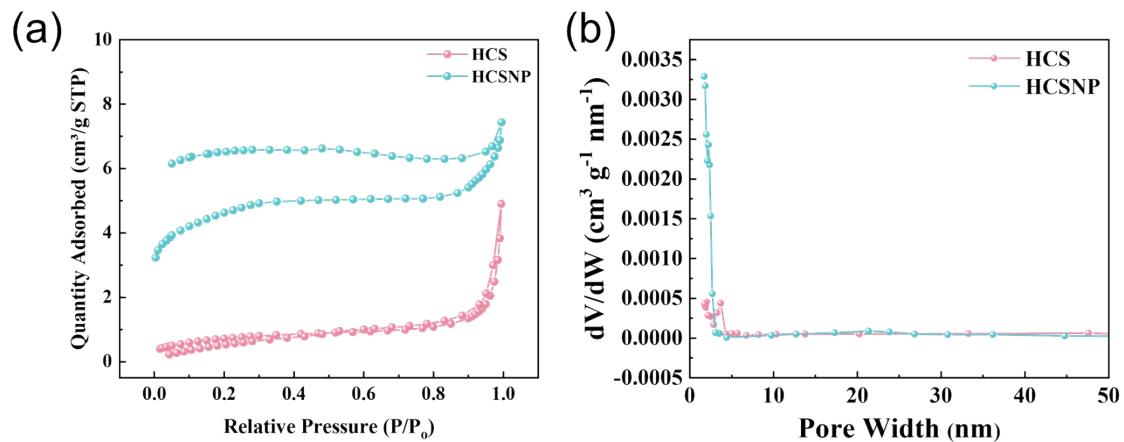
## Corresponding authors

\*E-mail: zengxiaoyuan@kust.edu.cn (X. Zheng); dongpeng2001@126.com (P. Dong); zyzhu23@kust.edu.cn (Z. Zhu).

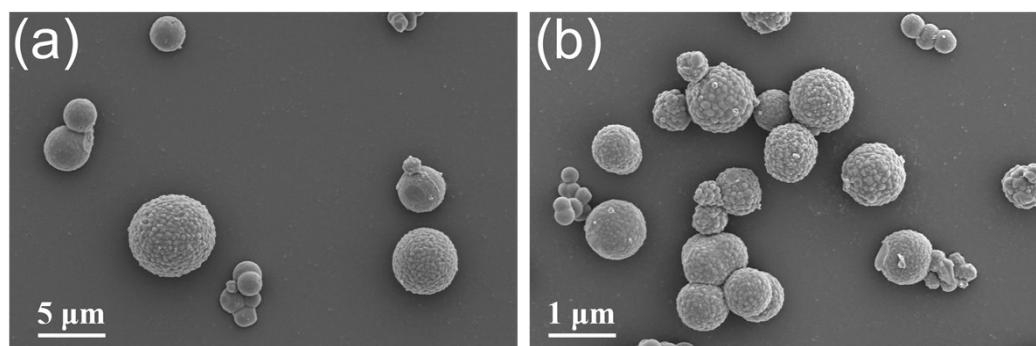
## 1 Figures



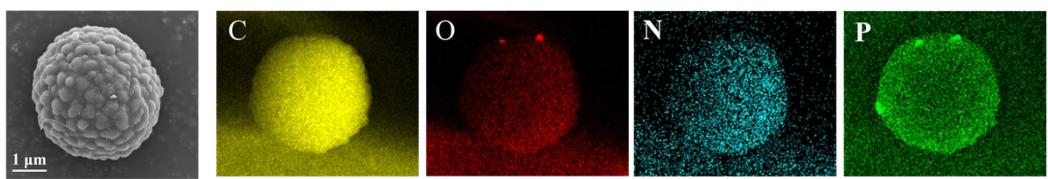
**Fig. S1.** Raman spectra of HCS and HCSNP.



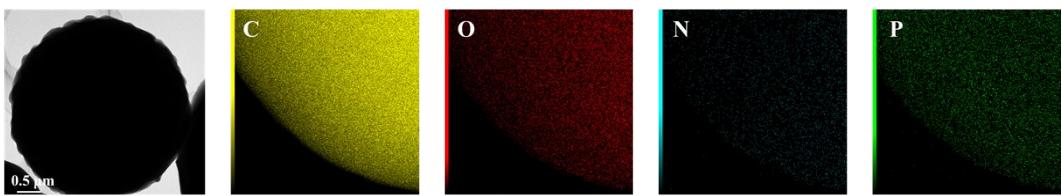
**Fig. S2.** (a) N<sub>2</sub> adsorption-desorption isotherms and (b) Pore width distributions of HCS and HCSNP.



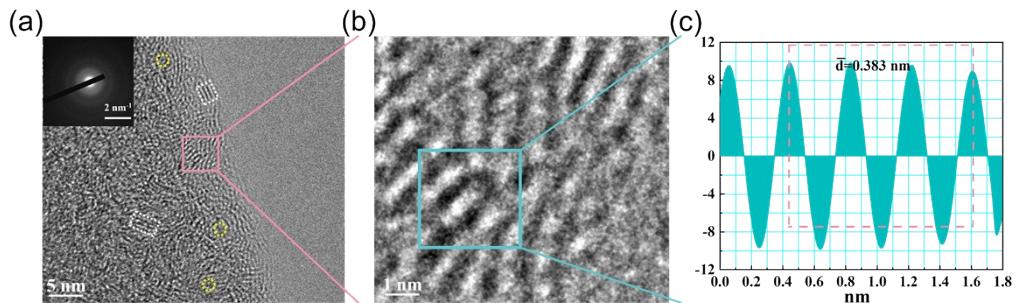
**Fig. S3.** SEM images of (a) HCS and (b) HCSNP.



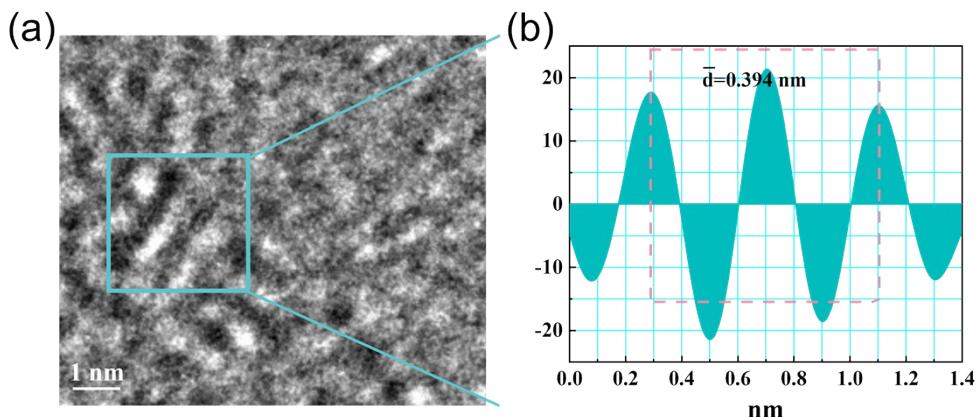
**Fig. S4.** SEM image and EDS energy spectrum of HCS.



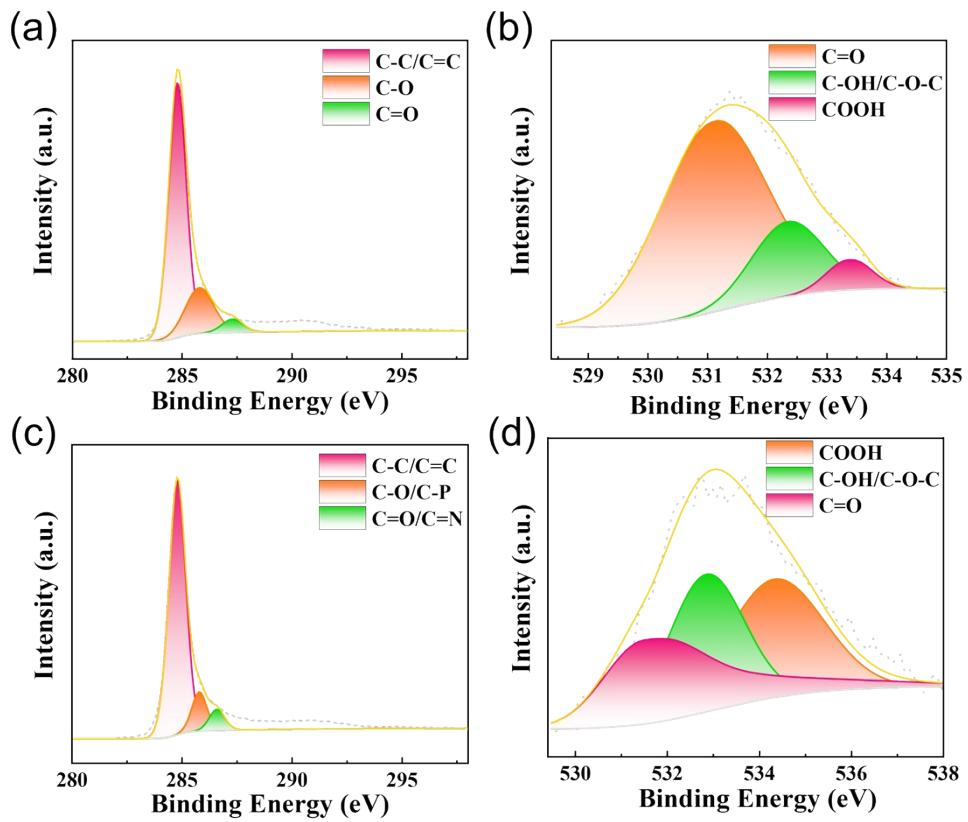
**Fig. S5.** TEM images of HCSNP and the corresponding Mapping elemental analysis.



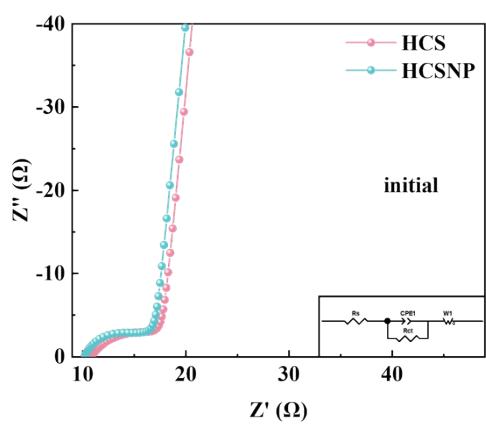
**Fig. S6.** (a, b) HRTEM images and the corresponding SAED images of HCS; (c) The lattice spacing after Fourier transformation.



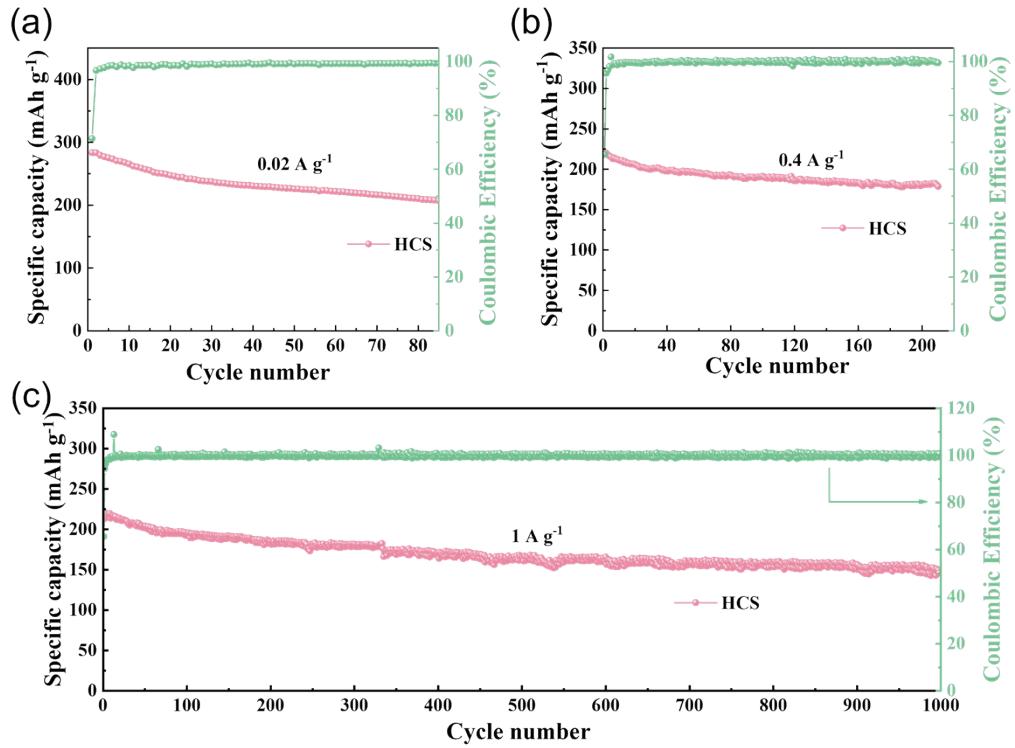
**Fig. S7.** (a) HRTEM images of HCSNP; (c) The lattice spacing after Fourier transformation.



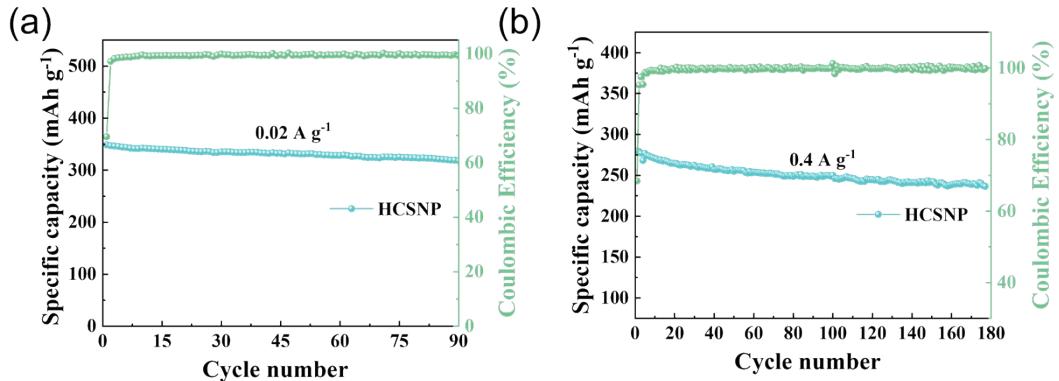
**Fig. S8.** High resolution energy spectra of C 1s and O 1s of (a, b) HCS and (c, d) HCSNP; (e, f) High resolution energy spectra of N 1s and P 2p of HCSNP.



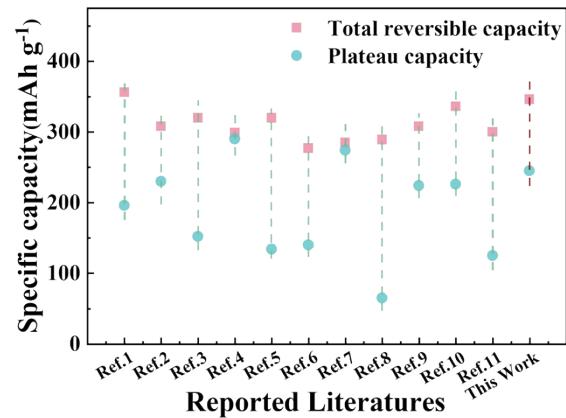
**Fig. S9.** EIS spectra and fitting circuits of HCS and HCSNP electrodes.



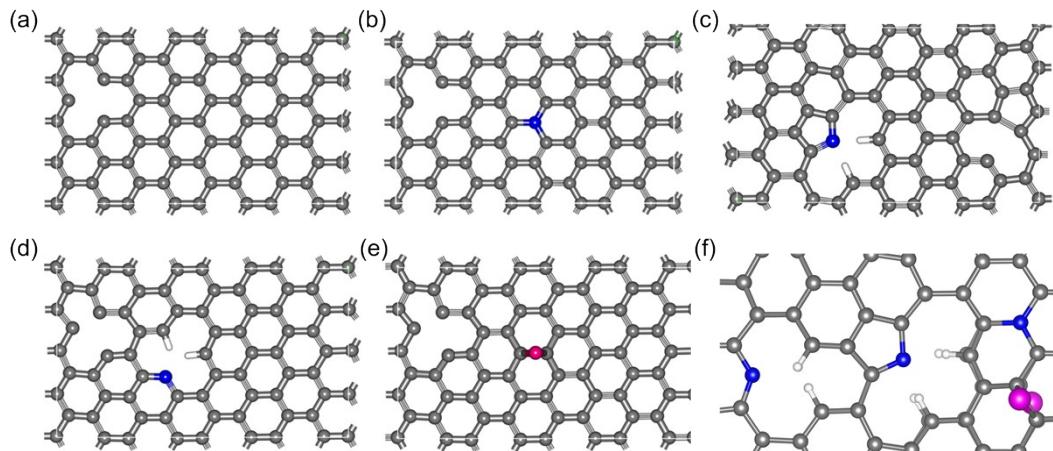
**Fig. S10.** Cycling performance of the HCS electrode: (a) at  $0.02 \text{ A g}^{-1}$ ; (b) at  $0.4 \text{ A g}^{-1}$ ; (c) at  $1 \text{ A g}^{-1}$ .



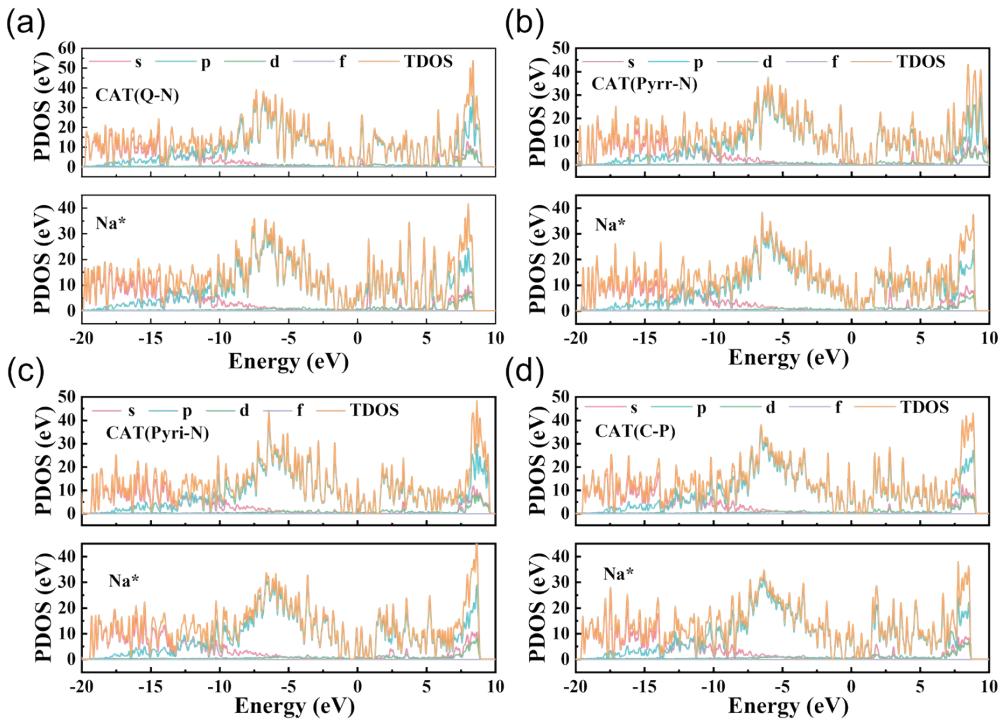
**Fig. S11.** Cycling performance of the HCSNP electrode: (a) at  $0.02 \text{ A g}^{-1}$ ; (b) at  $0.4 \text{ A g}^{-1}$ .



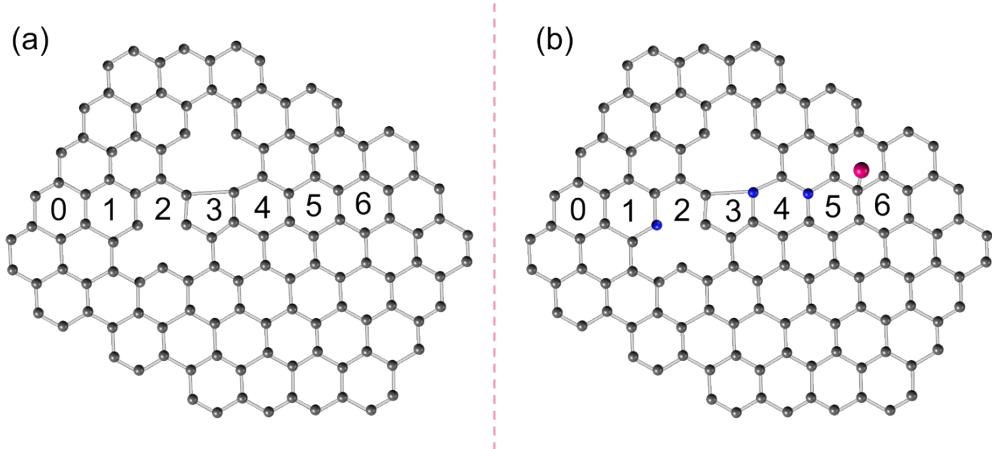
**Fig. S12.** Comparison diagram of the reversible specific capacity/plateau capacity of the HCSNP electrode with recently reported hard carbon anodes [1-11].



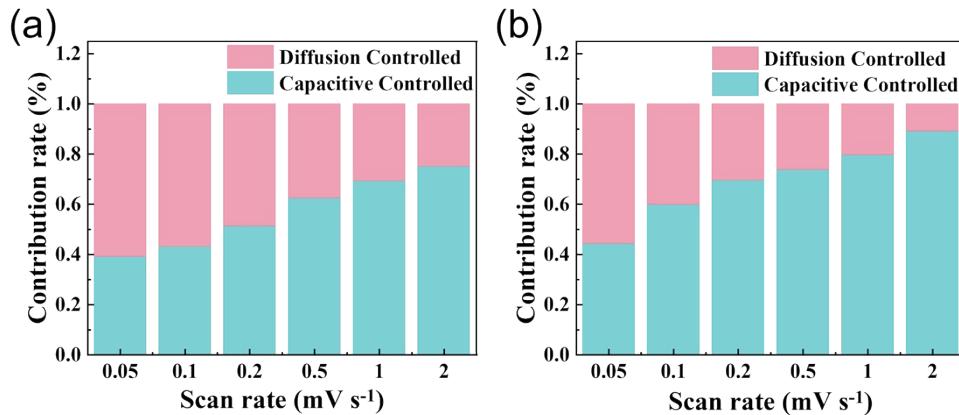
**Fig. S13.** Theoretical models: (a) PGs; (b) Q-NDGs; (c) Pyrr-NDGs; (d) Pyri-NDGs; (e) PDGs; (f) N/P-DGs.



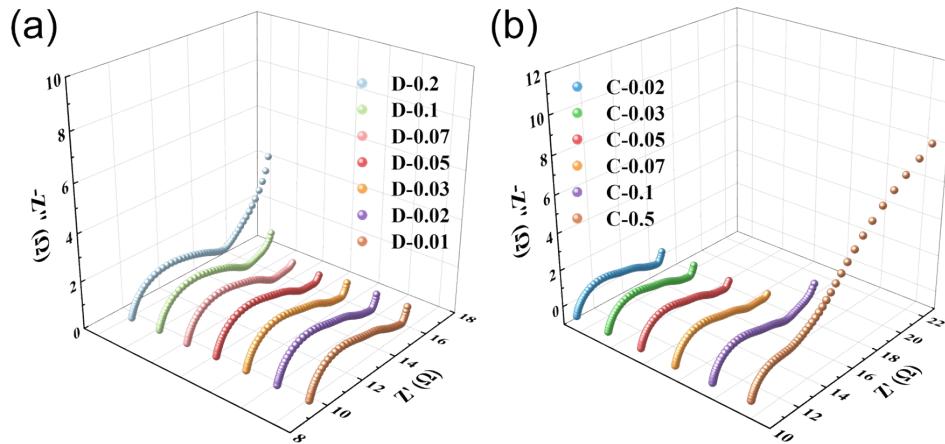
**Fig. S14.** The changes in the density of states of Na before and after adsorption in Q-NDGs, Pyrr-NDGs, Pyri-NDGs, and PDGs.



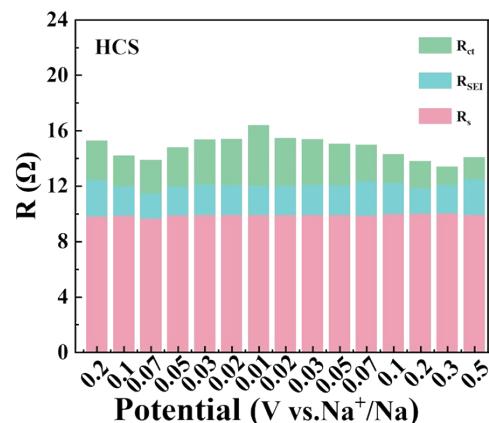
**Fig. S15.** Schematic diagrams of the diffusion position of Na in PGs and N/P-DGs.



**Fig. S16.** The proportion of diffusion-controlled behavior and capacitive controlled behavior at different scan rates: (a) HCS electrode and (b) HCSNP electrode.



**Fig. S17.** In-situ EIS spectra of the HCS electrode: (a) the discharging process and (b) the charging process.



**Fig. S18.** Fitted impedance values of the HCS electrode.



**Fig. S19.** Color changes of the reference samples reacting with a 1% phenolphthalein ethanol solution: The samples from left to right are the original HCSNP electrode, the fully discharged HCSNP electrode, and metallic sodium.

## 2 Tables

**Table 1** Fitting of  $R_s$ ,  $R_{SEI}$ ,  $R_{ct}$  and  $W$  based on the equivalent circuit.

**Table 1 (a)** Fitting information of the initial HCS and HCSNP electrodes.

Initial	HCS	HCSNP
$R_s (\Omega)$	10.79	10.05
$R_{ct} (\Omega)$	4.458	3.484
$W (\Omega)$	10.11	7.29

**Table 1 (b)** Fitting information of the HCS and HCSNP electrodes after one cycle.

After the 1 <sup>st</sup> cycle	HCS	HCSNP
$R_s (\Omega)$	8.207	9.147
$R_{SEI} (\Omega)$	5.455	14.887
$R_{ct} (\Omega)$	6.186	87.121
$W (\Omega)$	911.7	763.7

**Table 1 (c)** Fitting information of the HCS and HCSNP electrodes after ten cycles.

After the 10 <sup>th</sup> cycle	HCS	HCSNP
$R_s (\Omega)$	8.205	9.1243
$R_{SEI} (\Omega)$	4.13	11.12
$R_{ct} (\Omega)$	5.809	15.27
$W (\Omega)$	926.2	897.3

## References

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