

## Electronic Supplementary Information

### **Rational Design of High Nitrogen-Doped and Core-Shell/Mesoporous Carbon Nanospheres with High Rate Capability and Cycling Longevity for Pseudocapacitive Sodium Storage**

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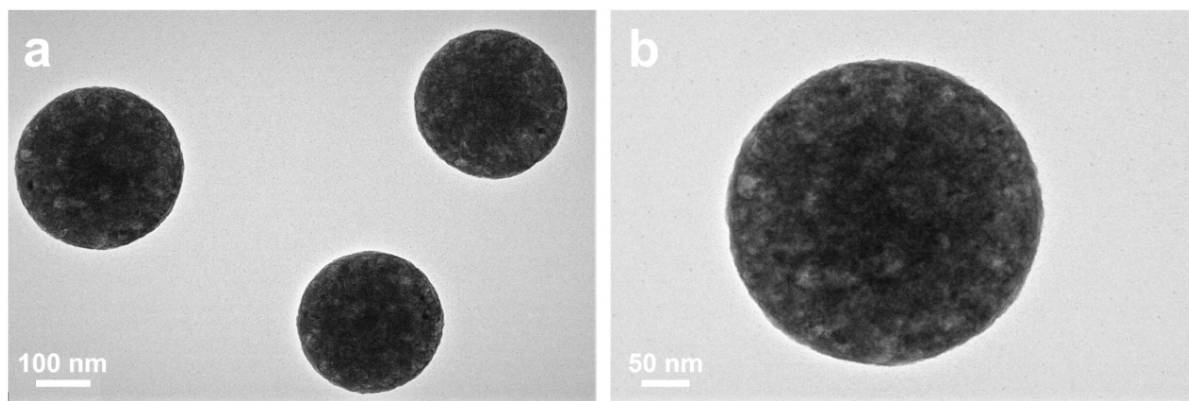
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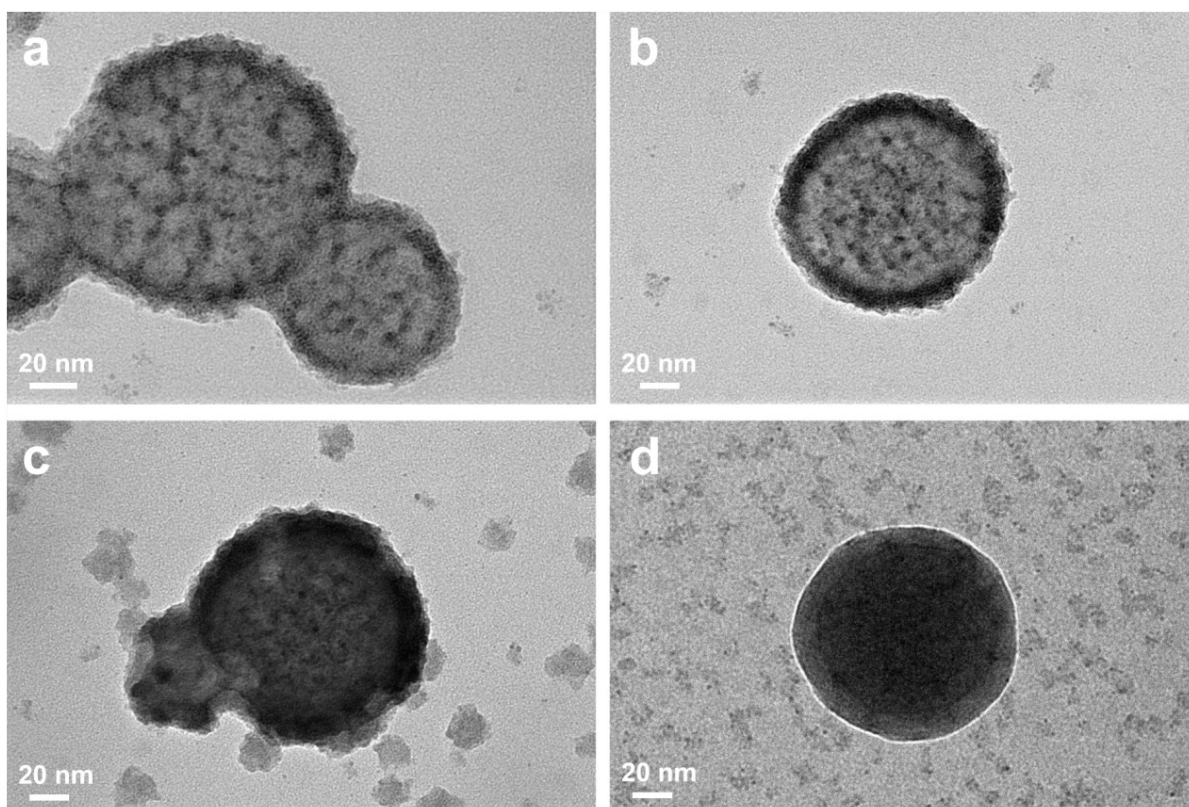
Fig. S1 – 17

Table S1 – 3

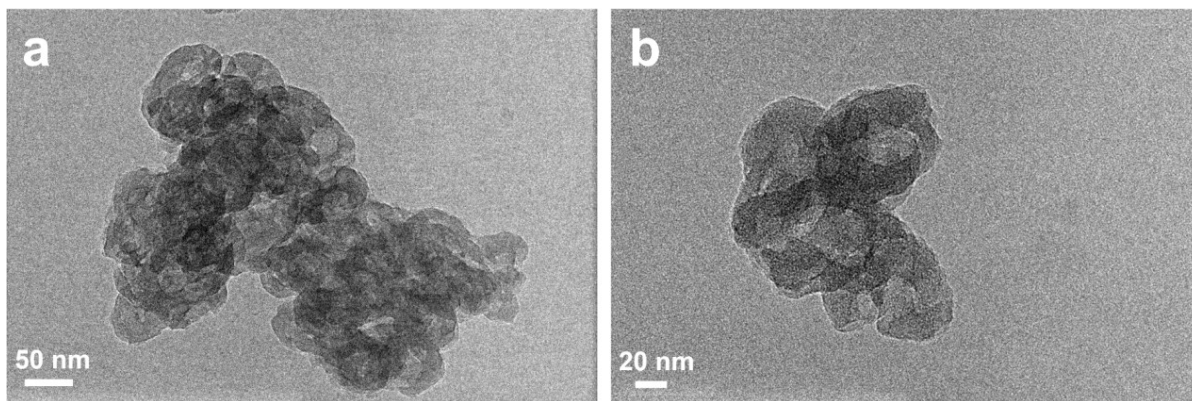
References S1-7



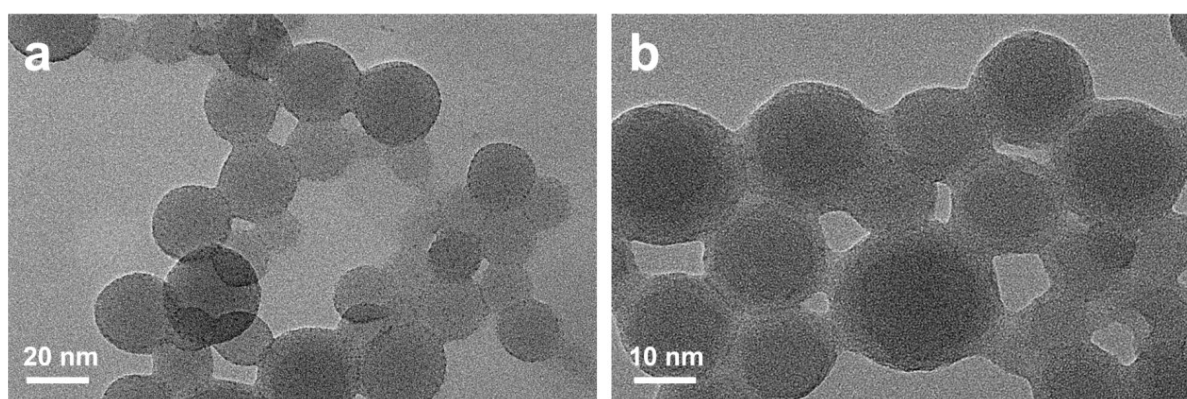
**Fig. S1** TEM images of spherical composite micelles at different magnifications.



**Fig. S2** TEM images of the composite micelles with PDA obtained by different reaction time periods: (a) 1 h, (b) 4 h, (c) 8 h, (d) 20 h.



**Fig. S3** TEM images of the control group synthesized in almost the same way as HN-CSMCNs without the addition of CATB.



**Fig. S4** TEM images of pure PS-*b*-PAA micelles.

**Table S1** BET surface areas, pore volumes and pore size distributions of HN-CSMCNs, HN-HCNs and N-CSMCNs.

| <b>Samples</b> | <b>Specific surface area (m<sup>2</sup> g<sup>-1</sup>)</b> | <b>Pore volume (cm<sup>3</sup> g<sup>-1</sup>)</b> | <b>Mesopore size (nm)</b> |
|----------------|---|--|---------------------------|
| HN-CSMCNs      | 449   | 0.60   | 14.8                      |
| HN-HCNs        | 310   | 0.34   | /                         |
| N-CSMCNs       | 415   | 0.53   | 15.6                      |

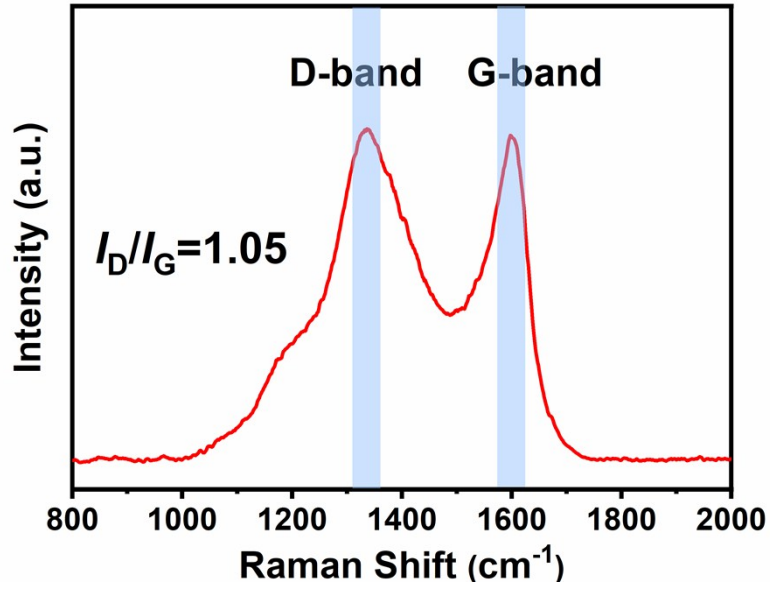


Fig. S5 Raman spectrum of HN-CSMCNs.

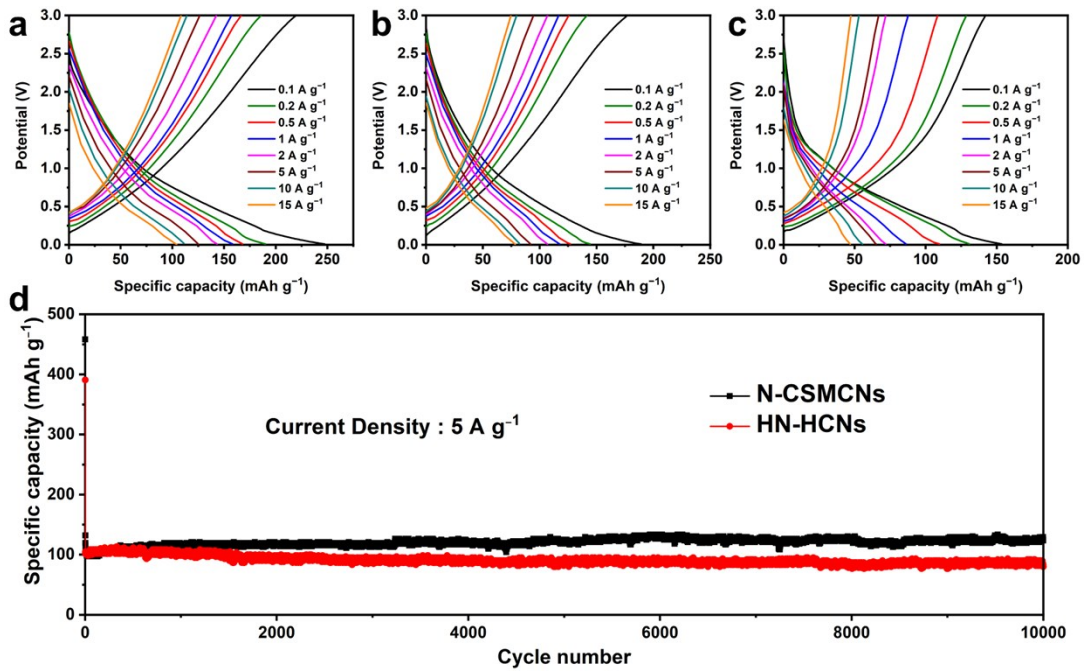
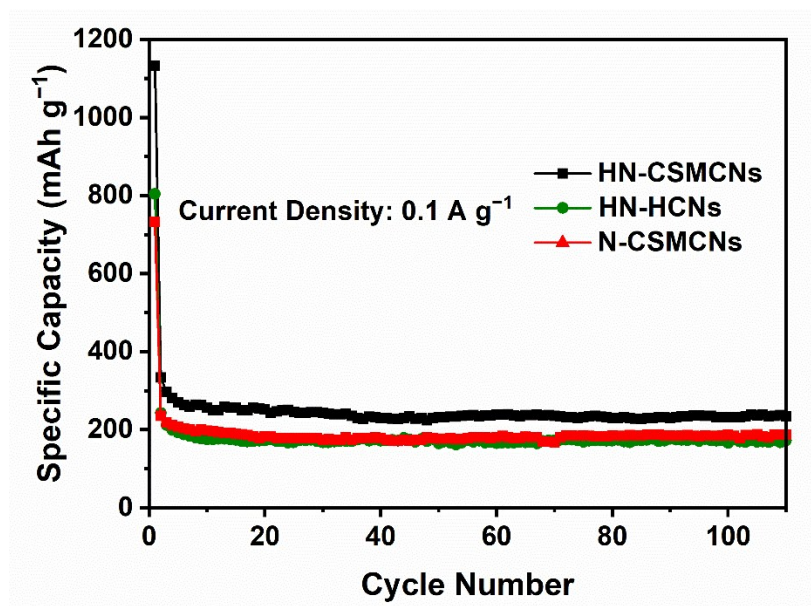


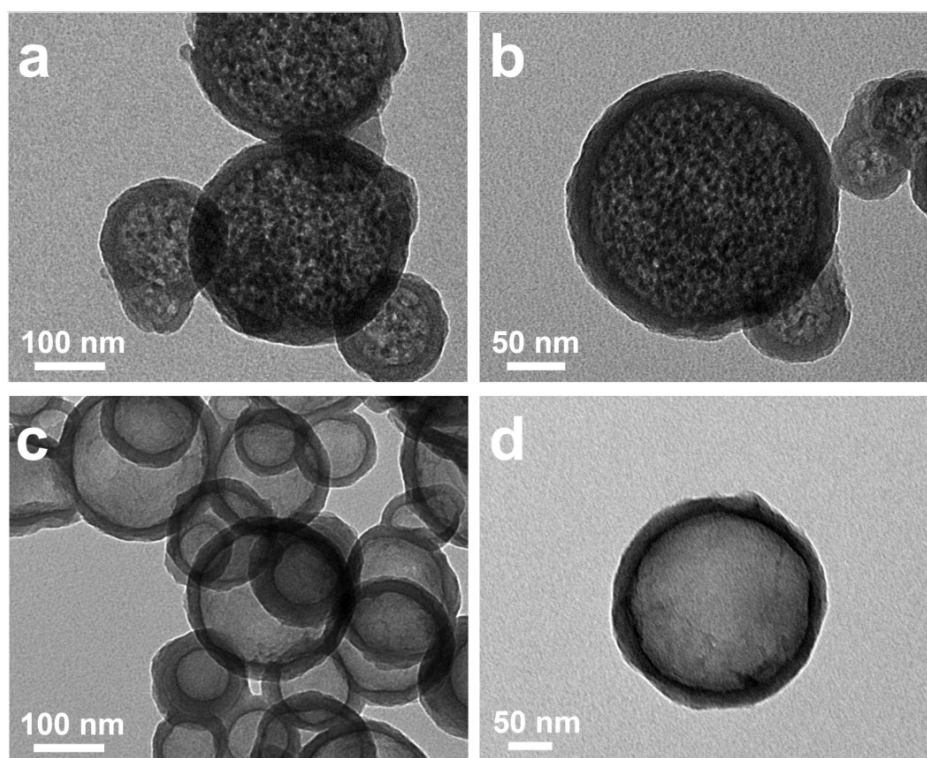
Fig. S6 (a-c) The galvanostatic discharge/charge curves of the HN-CSMCNs, HN-HCNs and N-CSMCNs, (d) the cycling performances of N-CSMCNs and HN-HCNs at 5 A g<sup>-1</sup>.

**Table S2** Comparison of detailed XPS results for HN-CSMCNs, HN-HCNs and N-CSMCNs.

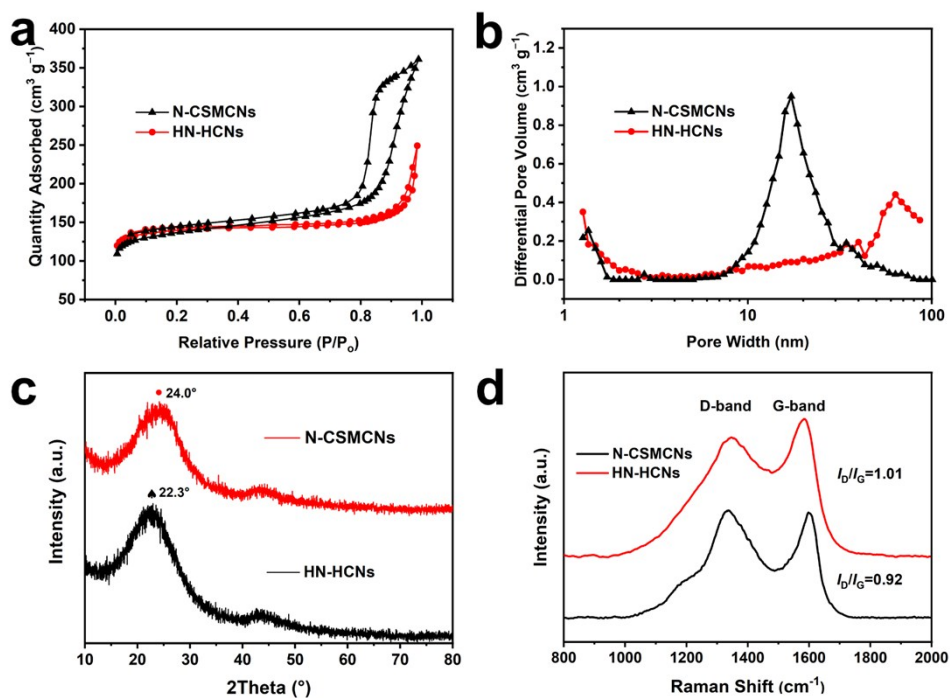
| Sample    | Carbon (wt%) | Nitrogen (wt%) | Oxygen (wt%) | Pyridinic N (%) | Pyrrolic N (%) | Graphitic N (%) | Oxidized N (%) |
|-----------|--------------|----------------|--------------|-----------------|----------------|-----------------|----------------|
| HN-CSMCNs | 85.45        | 10.07          | 4.48         | 32.80           | 25.48          | 32.80           | 8.92           |
| HN-HCNs   | 85.63        | 9.65           | 4.73         | 30.77           | 24.24          | 35.53           | 9.47           |
| N-CSMCNs  | 88.57        | 6.43           | 5.00         | 22.26           | 16.96          | 49.35           | 11.43          |



**Fig. S7** Cycling performances of HN-CSMCNs, HN-HCNs and N-CSMCNs at 0.1 A g<sup>-1</sup>.



**Fig. S8** TEM images of (a, b) N-CSMCNs and (c, d) HN-HCNs.



**Fig. S9** (a) Nitrogen adsorption/desorption isotherms, (b) BJH pore size distributions from absorption branches, (c) XRD patterns and (d) Raman spectra of N-CSMCNs and HN-HCNs.

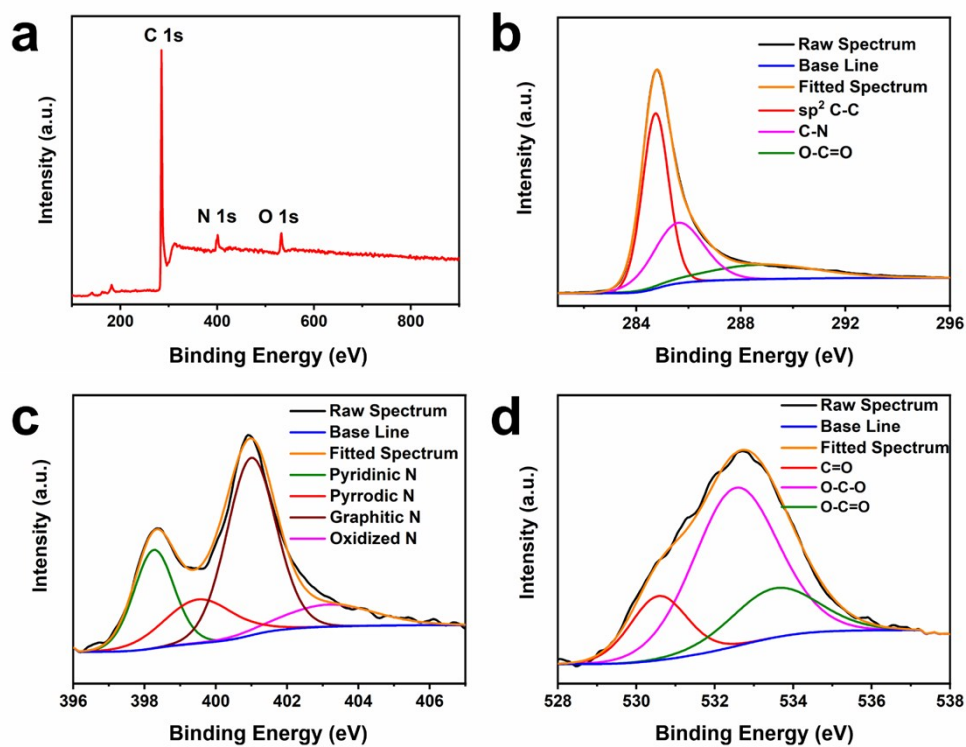


Fig S10. (a) XPS survey spectrum, (b) C 1s, (c) N 1s, and (d) C 1s spectra of N-CSMCNs.

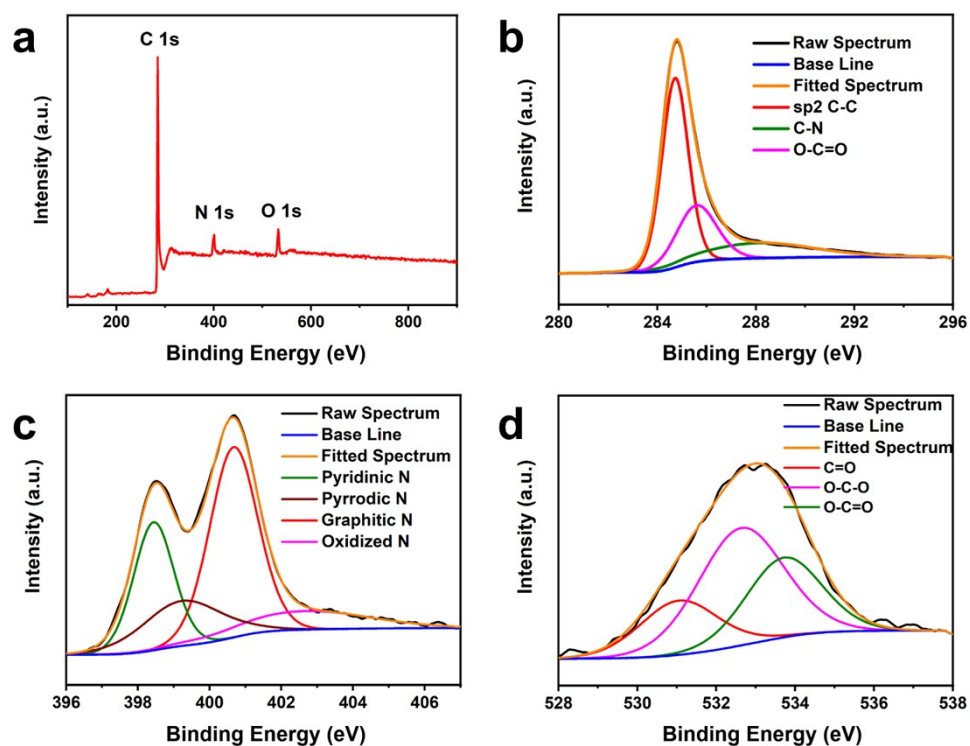
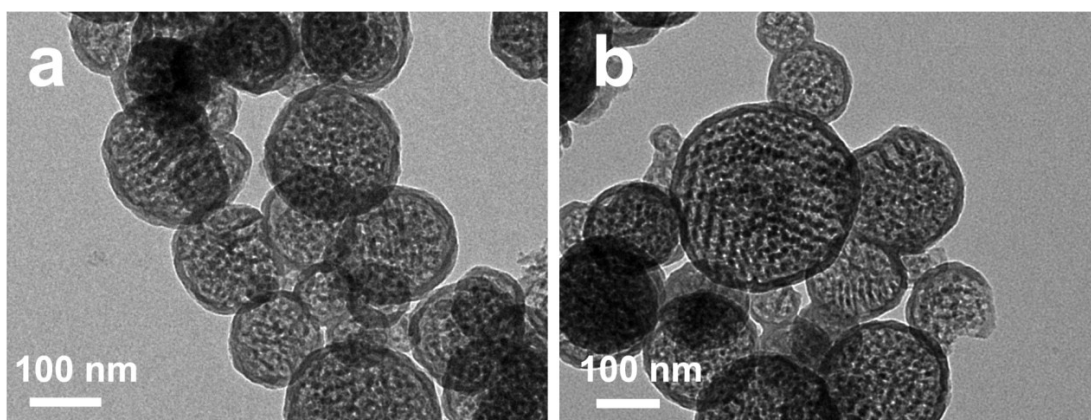
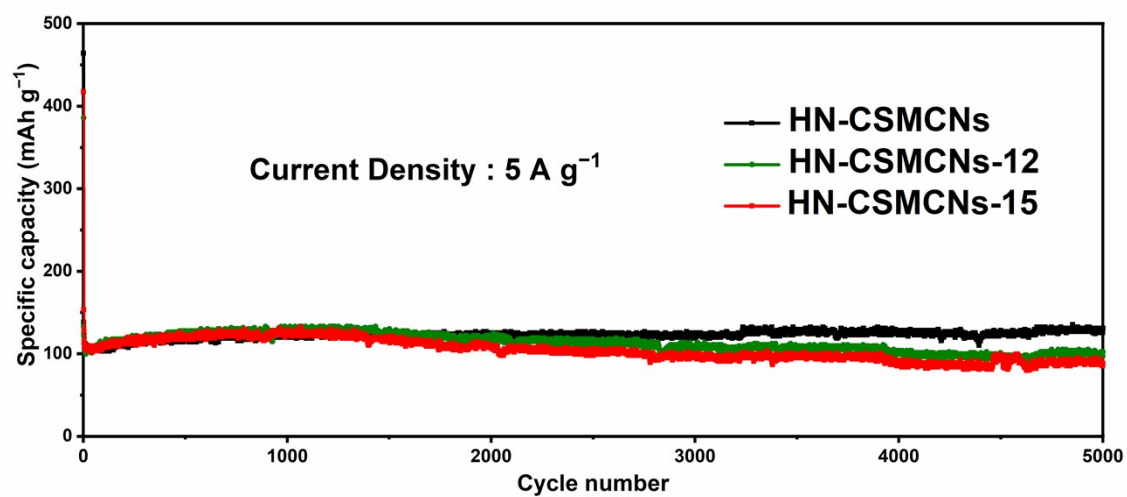


Fig. S11 (a) XPS survey spectrum, (b) C 1s, (c) N 1s, and (d) C 1s spectra of HN-HCNs.

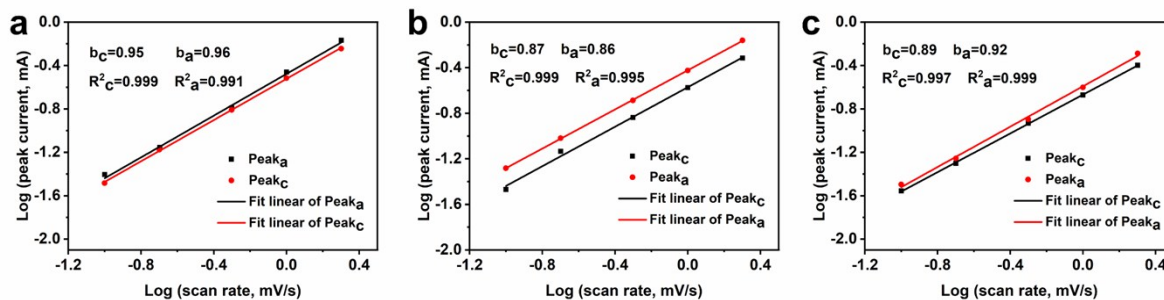


**Fig. S12** TEM images of (a) HN-CSMCNs-12 and (b) HN-CSMCNs-15.

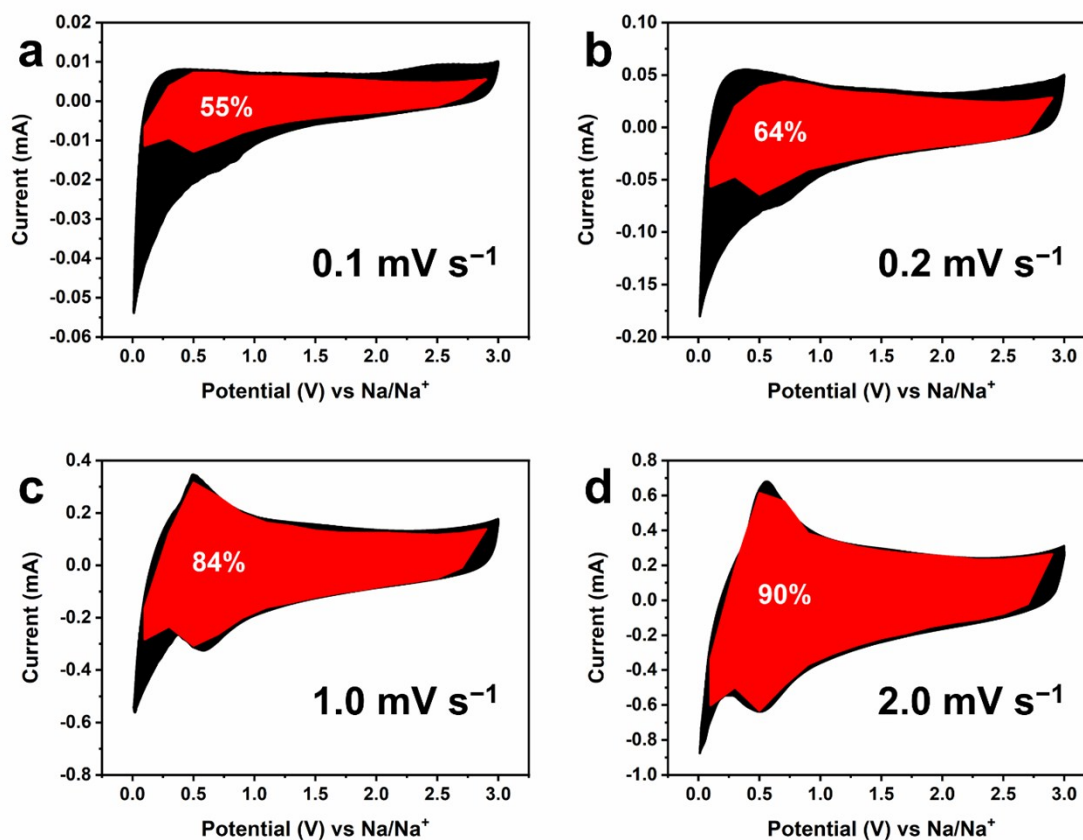


**Fig. S13** Cycling performances of HN-CSMCNs, HN-CSMCNs-12 and HN-CSMCNs-15 at 5 A g<sup>-1</sup>.

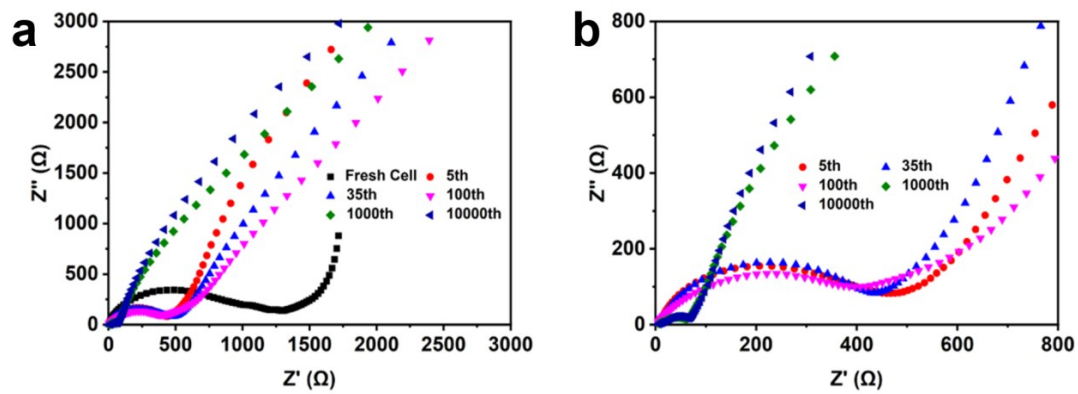




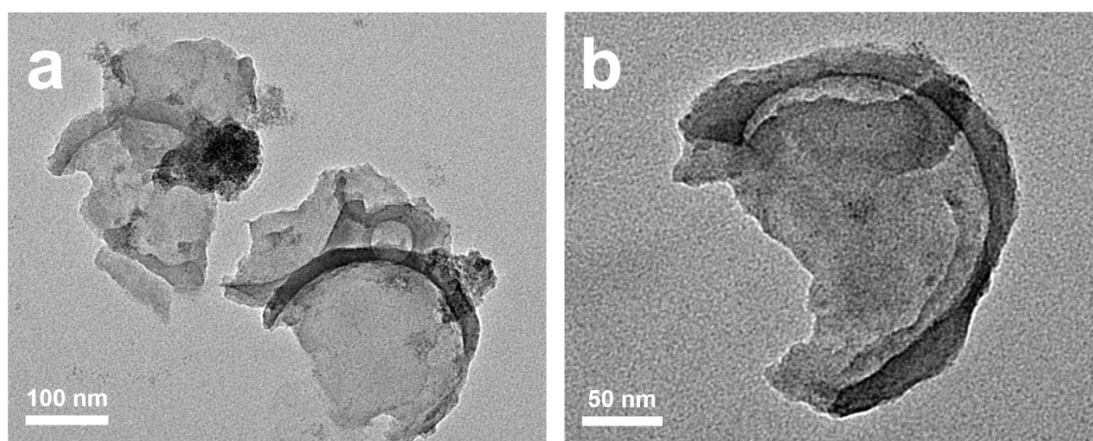
**Fig. S14** Log( $i$ ) vs. log( $v$ ) plots of the cathodic and anodic peaks for (a) HN-CSMCNs, (b) HN-HCNs and (c) N-CSMCNs.



**Fig. S15** Pseudocapacitive contributions (the red-filled area) of HN-CSMCNs at varied scan rates: (a)  $0.1 \text{ mV s}^{-1}$ , (b)  $0.2 \text{ mV s}^{-1}$ , (c)  $1.0 \text{ mV s}^{-1}$ , (d)  $2.0 \text{ mV s}^{-1}$ .



**Fig. S16** Nyquist plots of HN-CSMCNs before and after cycling for different cycles in different magnification.



**Fig. S17** TEM images of HN-HCNs after cycling for 10000 cycles at  $5 \text{ A g}^{-1}$ .

**Table S3** Comparison of the performances of various carbonaceous materials for SIBs anodes reported recently.

| Materials                            | Specific Capacity                                    | High-rate Capability                                | Cycling performance  | ICE   | Ref.      |
|--------------------------------------|--|---|--|-------|-----------|
| HN-CSMCNs                            | 251 mAh g <sup>-1</sup><br>at 0.1 A g <sup>-1</sup>  | 104 mAh g <sup>-1</sup><br>at 15 A g <sup>-1</sup>  | <ul style="list-style-type: none"> <li>■ 205 mAh/g after 1000 cycles at 0.5 A g<sup>-1</sup></li> <li>■ 163 mAh/g after 10000 cycles at 5 A g<sup>-1</sup></li> <li>■ 140 mAh/g after 20000 cycles at 10 A g<sup>-1</sup></li> </ul> | 27.3% | This work |
| Hierarchically Porous, Active Carbon | 248 mAh g <sup>-1</sup><br>at 0.1 A g <sup>-1</sup>  | 101 mAh g <sup>-1</sup><br>at 5 A g <sup>-1</sup>   | 169 mAh g <sup>-1</sup> after 270 cycles at 0.5 A g <sup>-1</sup>  | 18.5% | [S1]      |
| Nanocarbon Network                   | 280 mAh g <sup>-1</sup><br>at 0.1 A g <sup>-1</sup>  | 143 mAh g <sup>-1</sup><br>at 0.5 A g <sup>-1</sup> | 296 mAh g <sup>-1</sup> after 200 cycles at 0.05 A g <sup>-1</sup>   | 48.2% | [S2]      |
| N-doped Carbon Nanosheets            | 270 mAh g <sup>-1</sup><br>at 0.1 A g <sup>-1</sup>  | 139 mAh g <sup>-1</sup><br>at 5 A g <sup>-1</sup>   | 160 mAh g <sup>-1</sup> after 9500 cycles at 1A g <sup>-1</sup>  | 35.7% | [S3]      |
| N-doped Hard Carbon Nanoshells       | 247 mAh g <sup>-1</sup><br>at 0.1 A g <sup>-1</sup>  | 63 mAh g <sup>-1</sup><br>at 5 A g <sup>-1</sup>    | 174 mAh g <sup>-1</sup> after 200cycles at 0.1 A g <sup>-1</sup>   | 30.4% | [S4]      |
| N/S-doped Carbon Films               | 400 mAh g <sup>-1</sup><br>at 0.1 A g <sup>-1</sup>  | 92 mAh g <sup>-1</sup><br>at 2 A g <sup>-1</sup>    | 397 mAh g <sup>-1</sup> after 1000 cycles at 0.1 A g <sup>-1</sup>   | 63.5% | [S5]      |
| N-rich Hierarchically Porous Carbon  | 250mAh g <sup>-1</sup><br>at 0.1 A g <sup>-1</sup>   | 150 mAh g <sup>-1</sup><br>at 2 A g <sup>-1</sup>   | 101.4 mAh g <sup>-1</sup> after 10000 cycles at 5 A g <sup>-1</sup>  | 51.2% | [S6]      |
| 3D Amorphous Carbon                  | 240 mAh g <sup>-1</sup><br>at 0.15 A g <sup>-1</sup> | 81 mAh g <sup>-1</sup><br>at 4.8 A g <sup>-1</sup>  | 188 mAh g <sup>-1</sup> after 600 cycles at 0.3 A g <sup>-1</sup>  | 75%   | [S7]      |

## References

- [S1] X. Deng, W. Shi, Y. Zhong, W. Zhou, M. Liu, Z. Shao, *ACS Appl. Mater. Interfaces*, 2018, **10**, 21573–21581.
- [S2] H. Jia, N. Sun, M. Dirican, Y. Li, C. Chen, P. Zhu, C. Yan, J. Zang, J. Guo, J. Tao, *ACS Appl. Mater. Interfaces*, 2018, **10**, 44368–44375.
- [S3] J. Qin, H.M.K. Sari, C. He, X. Li, *J. Mater. Chem. A*, 2019, **7**, 3673–3681.
- [S4] S. Huang, Z. Li, B. Wang, J. Zhang, Z. Peng, R. Qi, J. Wang, Y. Zhao, *Adv. Funct. Mater.*, 2018, **28**, 1706294.
- [S5] J. Ruan, T. Yuan, Y. Pang, S. Luo, C. Peng, J. Yang, S. Zheng, *Carbon*, 2018, **126**, 9–16.
- [S6] X. Hu, X. Sun, S.J. Yoo, B. Evanko, F. Fan, S. Cai, C. Zheng, W. Hu, G.D. Stucky, *Nano Energy*, 2019, **56**, 828–839.
- [S7] P. Lu, Y. Sun, H. Xiang, X. Liang, Y. Yu, *Adv. Energy Mater.*, 2018, **8**, 1702434.