

Supporting Information

**N-doped carbon spheres with hierarchical micropore-nanosheet
networks for high performance supercapacitors**

Shoupei Wang, Jianan Zhang, Pei Shang, Yuanyuan Li, Zhimin Chen, Qun Xu**

College of Materials Science and Engineering, Zhengzhou University, Zhengzhou
450052, P. R. China

1. Experimental section

Synthesis of Nitrogen Containing Polymer spheres. Nitrogen containing polymer spheres were synthesized through a one-pot hydrothermal method. Namely, an aqueous solution was prepared by mixing 0.5 mL of ammonia aqueous solution, 40 mL of ethanol, and 100 mL of distilled water at 70 °C under vigorous agitation. Subsequently, 0.74 mL of formaldehyde (37 wt %) and 0.55 g resorcinol were added and stirred for 30 min until a complete dissolution occurred. Next, 0.55 mL of formaldehyde and 0.315 g melamine were added to the above mixture and stirred for 24 h continually. Finally, the reaction mixture was transferred to a Teflon container and placed in a sealed metal autoclave vessel, which was then placed in an oven at 120 °C for 24 h. The reddish brown powder was collected by centrifugation and washed with ethanol and water for several times, followed by a dry process at 80 °C for 24 h in air. The nitrogen containing polymer spheres were labeled as NPSs.

One-step carbonization and activation synthesis of HPSCSs. A mixture of 0.2 g of NPSs and 0.4 g of KOH was immersed in 10 mL of deionized water. After arefaction

at 110 °C for 24 h, the resulted powder was annealed at a rate of 5 °C/min to 800 °C, and kept for 2 h under N₂ flow. The as-prepared products were washed with deionized water until the pH of filtrate turned to neutral. The PCSs were prepared as the same way to HPSCSs except that the chemical reagent was changed to K₂CO₃. The CSs were obtaining by exposing NPSs to thermal treatment at 800°C at a heating rate of 5 °C/min under a N₂ atmosphere, dwelling for 2 h.

2. Characterizations.

The morphology of the samples was studied by a field-emission scanning electron microscope FE-SEM (JEORJSM-6700F) and a transmission electron microscope TEM (FEI Tecnai G2 20) with an accelerating voltage of 200 kV. The X-ray photoelectron spectroscopy (XPS) experiments were performed with an ESCA LAB 250 spectrometer using a focused monochromatic Al K α ($h\nu = 1486.6$ eV) X-ray beam with a diameter of 200 μm . X-ray diffraction (XRD) data were performed on a Y-2000 X-ray Diffractometer using copper K α radiation ($\lambda = 1.5406$ Å) at 40 kV, 40 mA. The Raman measurements were performed on a Renishaw spectrometer at 532 nm on a Reishaw Microscope System RM2000. The nitrogen sorption experiments were carried out at 77 K on a Micromeritics Tristar 2020 system with micropore analysis. The Brunauer-Emmett-Teller (BET) specific surface area was calculated using adsorption data at a relative pressure range of $P/P_0 = 0.05-0.25$. The pore volumes were estimated from the amounts adsorbed at a relative pressure (P/P_0) of 0.99. The micropore-size distribution was calculated with Horvath-Kawazoe (H-K) method.

3. Electrochemical testing

The electrochemical performances of the samples were characterized by cyclic voltammetry (CV), galvanostatic charge-discharge test (chronopotentionmetry, CP), cycling life measurement and electrochemical impedance spectroscopy (EIS). The cyclic voltammetry, galvanostatic charge-discharge test and electrochemical impedance spectroscopy were carried out on a CHI 660D electrochemical workstation (CHI Instruments Inc.). Cycling life measurement was performed using a Land battery electrochemical test CT 2001A (Jinnuo electronic Co., Ltd, Wuhan). The test electrodes were prepared by loading a slurry consisting of 80 wt % active materials, 10 wt % carbon black, and 10 wt % poly (tetrafluoroethylene) (used as a binder, PTFE 60 wt% dispersion in H₂O, Sigma-Aldrich) on a nickel foam (1 × 1 cm²) and dried at 80 °C for 24 h. As-made electrodes were pressed at a pressure of 10 MPa for 1 min. The electrochemical properties of samples were measured in a three-electrode cell in 6.0 M KOH aqueous solution with the smaller electrode as the test electrode, platinum foil as the counter electrode, Ag / AgCl electrode as the reference electrode. The CV curves were obtained at various scan rates with voltage ranging from -1 V to 0 V. The CP curves were obtained at various current densities with the same voltage range as CV. The electrochemical impedance spectroscopy (EIS) was measured in the frequency range of 10 mHz to 10 kHz at the open circuit voltage with an alternate current amplitude of 5 mV. All measurements were carried out at room temperature.

4. Figures

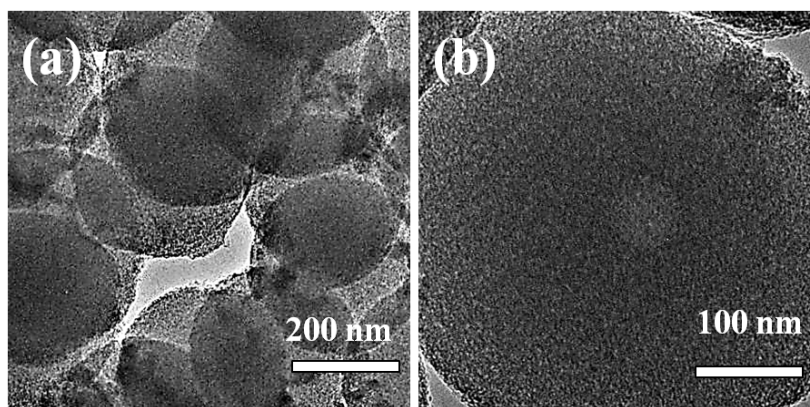


Fig. S1 TEM images of PCSs.

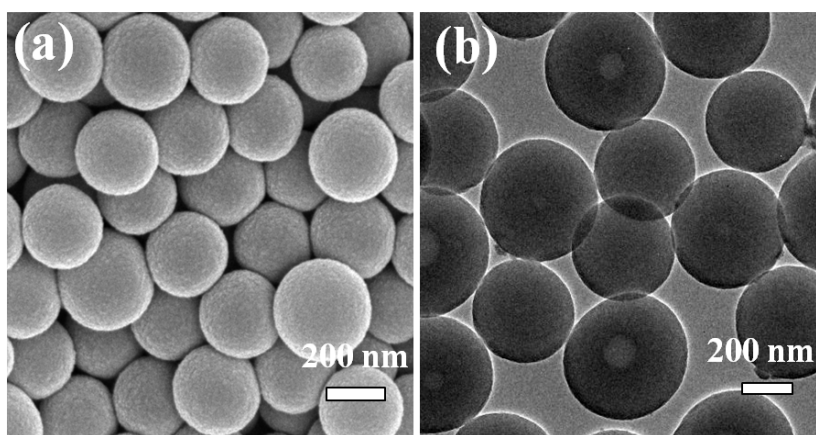


Fig. S2 TEM and SEM images of CSs.

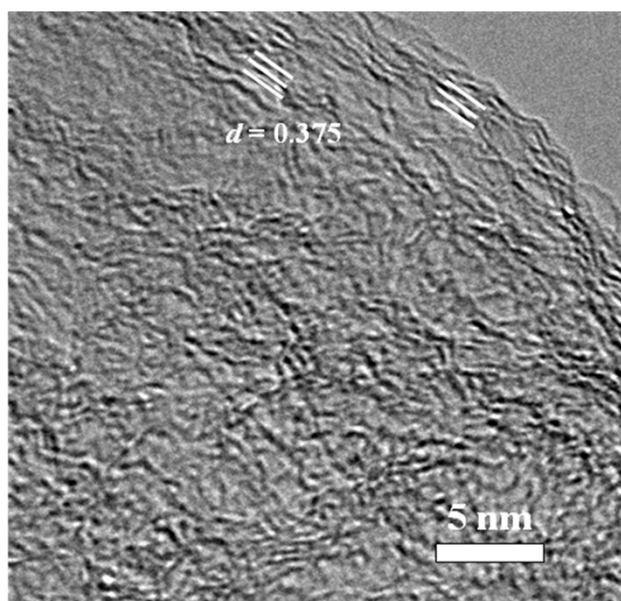


Fig. S3 HRTEM image of HPSCSs.

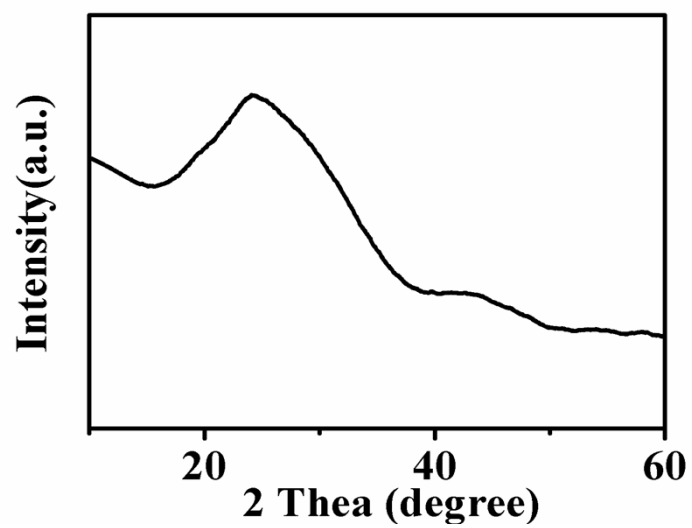


Fig. S4 XRD pattern of HPSCSs.

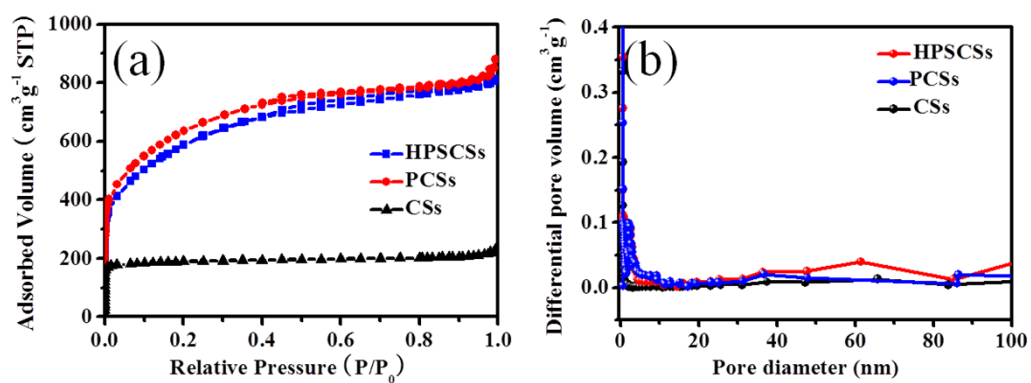


Fig. S5 (a) Sorption isotherms and (b) pore size distribution (estimated by the adsorption isotherm) of HPSCSs, PCSs and CSs.

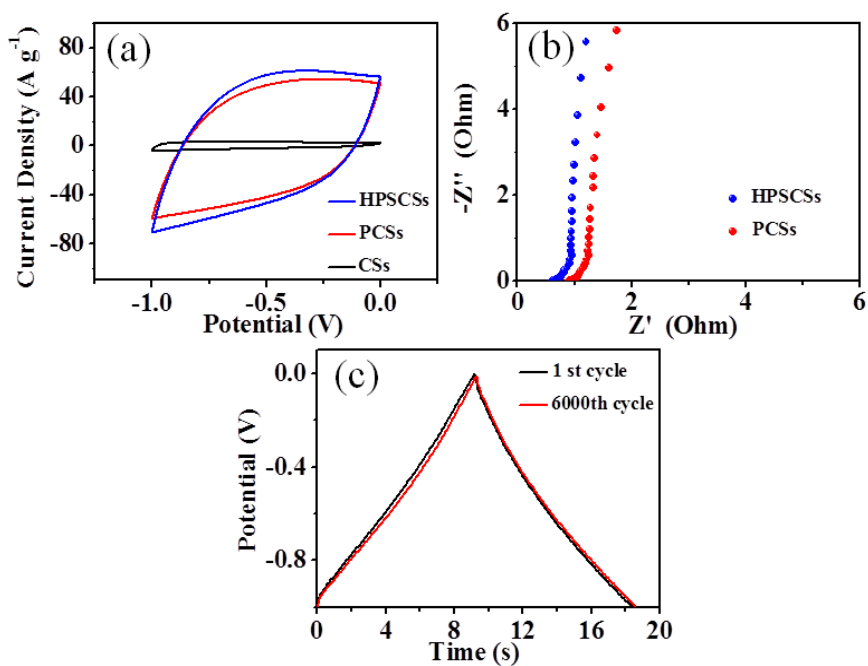


Fig. S6 (a) CVs of HPSCSs, PCSs, and CSs-based supercapacitors at a scan rate of 400 mV s^{-1} . (b) Electrochemical impedance spectra of HPSCSs and PCSs-based supercapacitors measured in the frequency range of 10 mHz to 10 kHz at the open circuit voltage with an alternate current amplitude of 5 mV . (c) Galvanostatic charge/discharge curves of HPSCSs-based supercapacitor before and after 6000 cycles measured at 10 A g^{-1} .

Table S1 Physicochemical properties of HPSCSs, PCSs and CSs.

Samples	BET surface area (m ² g ⁻¹)	t-method external surface area (m ² g ⁻¹)	t-Plot micropore volume (cm ³ g ⁻¹)	Average pore diameter (nm)	Horvath-Kawazoe pore diameter (nm)
HPSCSs	2117.0	1813.97	0.112	2.32	1.0567
PCSs	2279.0	1834.13	0.177	2.23	1.0442
CSs	580.4	81.62	0.230	2.10	0.6838

Table S2 Comparison of capacitance data reported for different carbon-based materials.

Samples	Electrolyte	Scan Rate	Specific capacitance (F g ⁻¹)	Capacitance Retention (cycles)	Ref.
Phenolic resin-derived carbon spheres	1 M H ₂ SO ₄	1 A g ⁻¹	242	~98% (8000)	1
Polypyrrole-derived carbon nanospheres	0.5 M H ₂ SO ₄	100 mV s ⁻¹	237.9	~98.7% (3000)	2
Carbon nanocages	1 M H ₂ SO ₄	10 mV s ⁻¹	251	~90% (10000)	3
Porous nanosheets from coconut shell	6 M KOH	1 A g ⁻¹	268	~99.5% (5000)	4
Carbon nanosheets from organic salt	Organic electrolyte	1 mV s ⁻¹	150	~94% (10000)	5
Carbon spheres/graphene nanosheets composite	6 M KOH	0.175 A g ⁻¹	198	~95% (1000)	6
This work	6 M KOH	1 mV s ⁻¹	407.9	~99.0% (6000)	

References

1. N. P. Wickramaratne, J. Xu, M. Wang, L. Zhu, L. Dai and M. Jaroniec, *Chem. Mater.*, 2014, **26**, 2820-2828.
2. F. Su, C. K. Poh, J. S. Chen, G. Xu, D. Wang, Q. Li, J. Lin and X. W. Lou, *Energy. Environ. Sci.*, 2011, **4**, 717-724.
3. K. Xie, X. Qin, X. Wang, Y. Wang, H. Tao, Q. Wu, L. Yang and Z. Hu, *Adv. Mater.*, 2012, **24**, 347-352.
4. L. Sun, C. Tian, M. Li, X. Meng, L. Wang, R. Wang, J. Yin and H. Fu, *J. Mater. Chem. A*, 2013, **1**, 6462-6470.
5. M. Sevilla and A. B. Fuertes, *ACS nano*, 2014, **8**, 5069-5078.
6. C. X. Guo and C. M. Li, *Energy. Environ. Sci.*, 2011, **4**, 4504-4507.