

## Supporting Information

## Phenylenediamine-Formaldehyde Chemistry Derived N-Doped Hollow Carbon

## Spheres for High-Energy-Density Supercapacitors

Ming Xu<sup>a</sup>, Yuheng Liu<sup>a</sup>, Qiang Yu<sup>a</sup>, Shihao Feng<sup>a</sup>, Liang Zhou<sup>a,\*</sup> and Liqiang Mai<sup>a,\*</sup><sup>a</sup>State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China

\* Corresponding author.

E-mail address: liangzhou@whut.edu.cn

\* Corresponding author.

E-mail address: mlq518@whut.edu.cn

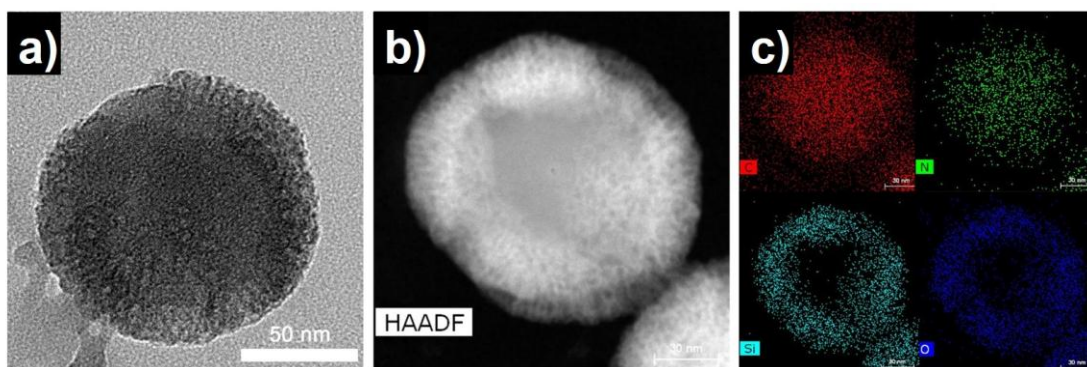


Fig. S1. TEM image (a), STEM-HAADF image (b), and the corresponding EDS elemental mappings of resin/SiO<sub>2</sub> (c).

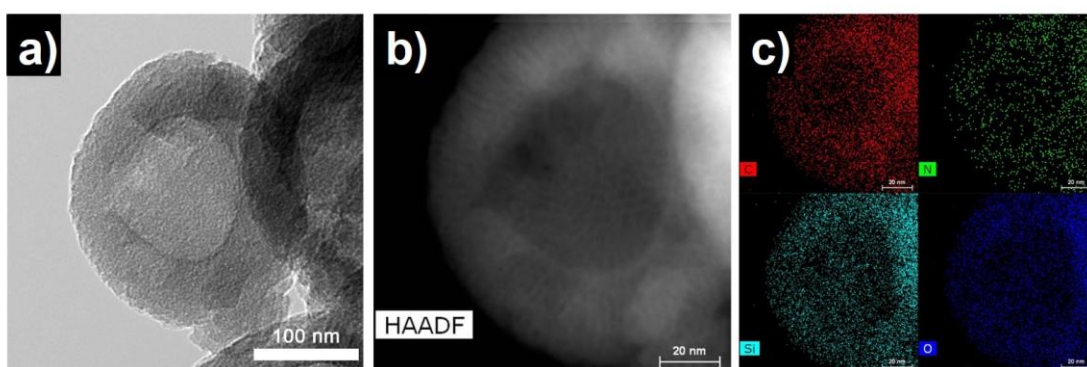


Fig. S2. TEM image (a), STEM-HAADF image (b), and the corresponding EDS elemental mappings of carbon/SiO<sub>2</sub> (c).

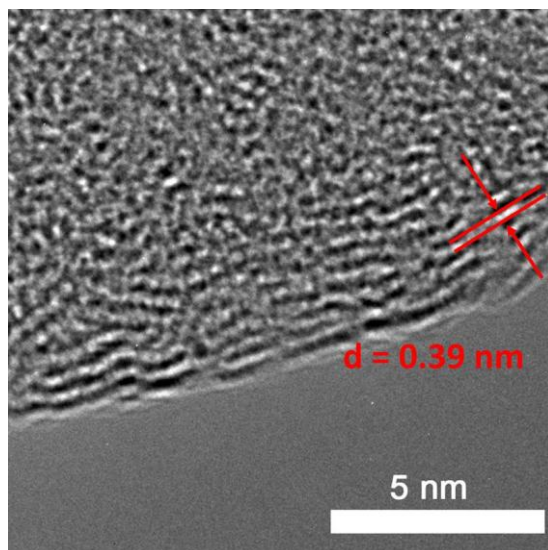


Fig. S3. HRTEM image of NHCSs.

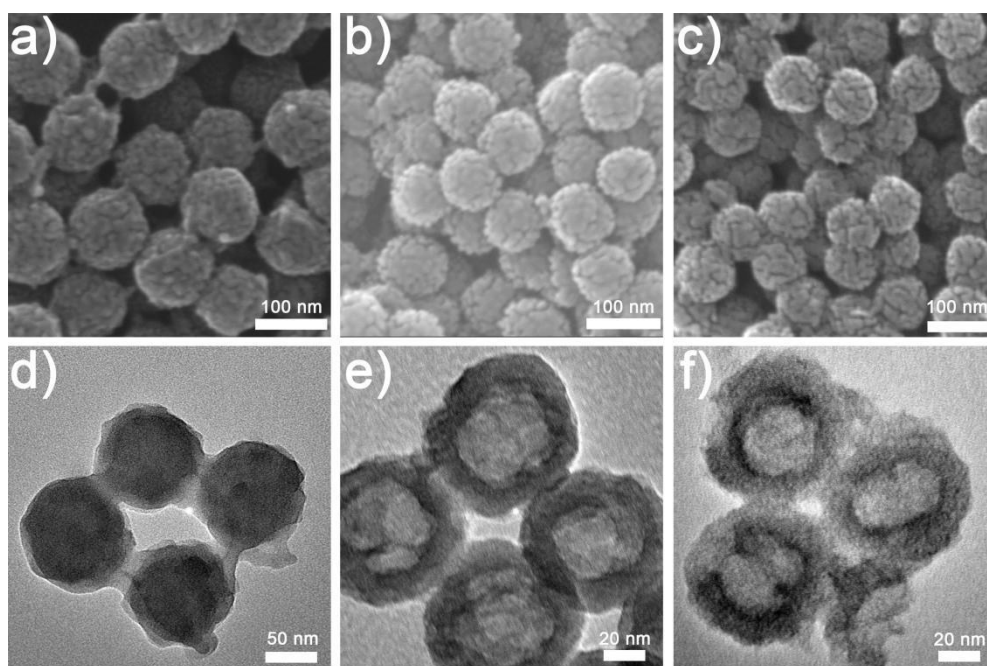


Fig. S4. SEM images of resin/SiO<sub>2</sub>-APF (a), carbon/SiO<sub>2</sub>-APF (b), and NHCSs-APF (c); TEM images of resin/SiO<sub>2</sub>-APF (d), carbon/SiO<sub>2</sub>-APF (e), and NHCSs-APF (f).

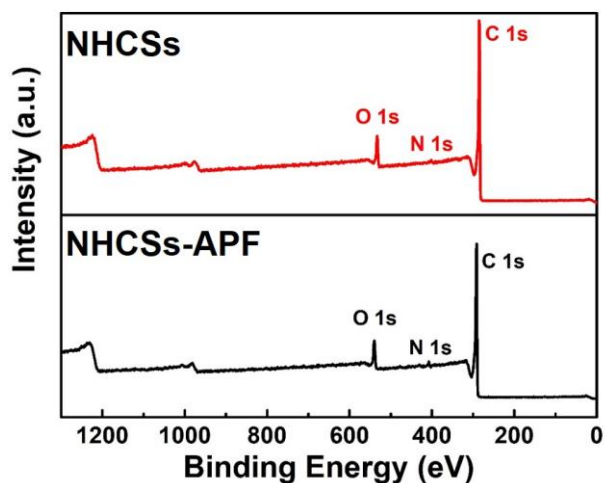


Fig. S5. XPS survey spectra of NHCSs and NHCSs-APF.

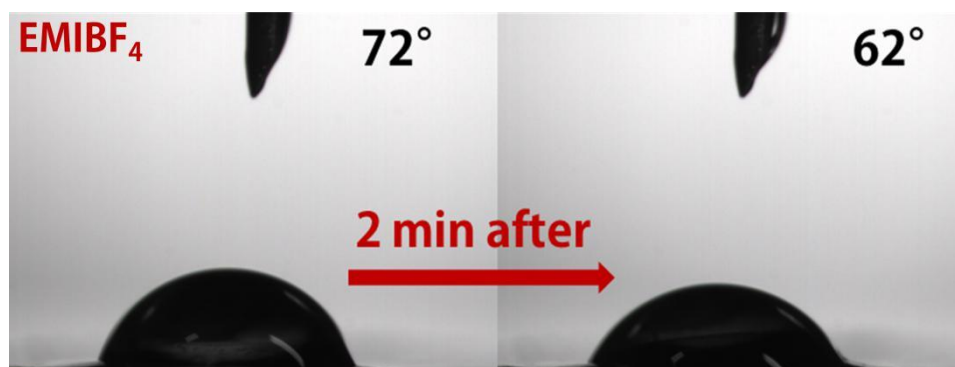


Fig. S6. Wetting angles of EMIBF<sub>4</sub> droplet on NHCSs based electrode film substrates.

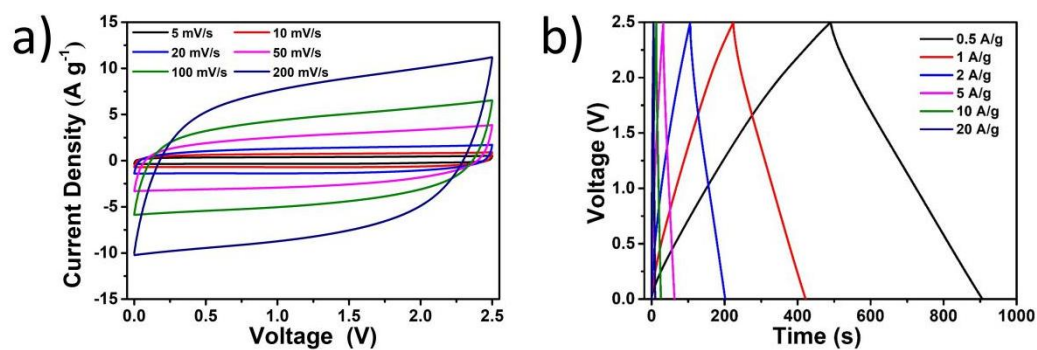


Fig. S7. CV curves of NHCSs-APF at different scan rates (a); GCD curves of NHCSs-APF at different current densities in TEABF<sub>4</sub>/AN (b).

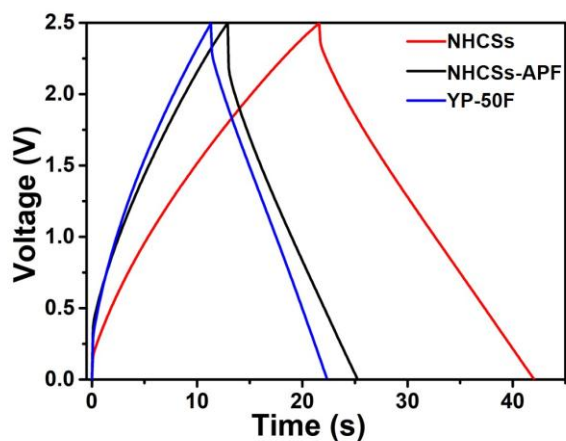


Fig. S8. GCD curves of NHCSs, NHCSs-APF and YP-50F at 10 A/g in TEABF<sub>4</sub>/AN.

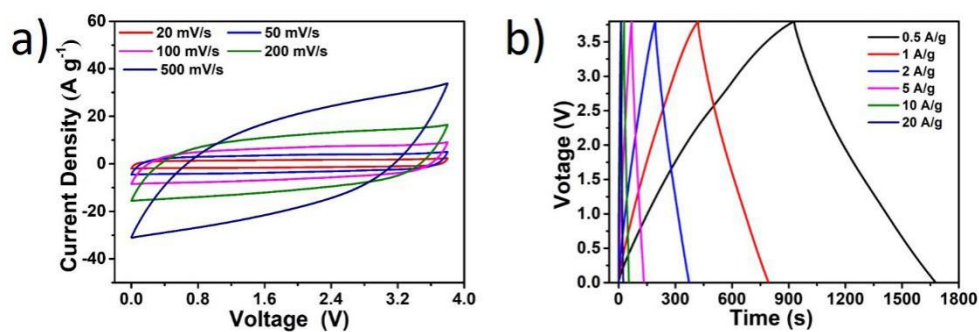


Fig. S9. CV curves of NHCSs-APF at different scan rates (a); GCD curves of NHCSs-APF at different current densities in EMIBF<sub>4</sub> (b).

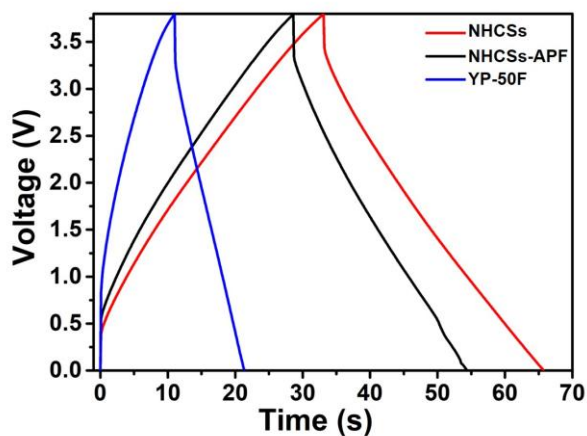


Fig. S10. GCD curves of NHCSs, NHCSs-APF and YP-50F at 20 A/g in EMIBF<sub>4</sub>.

Table S1. Synthesis conditions of resin/SiO<sub>2</sub> and resin/SiO<sub>2</sub>-APF.

Sample	mPD (g)	mAP (g)	Formaldehyde (mL)	TEOS (mL)	CTAB (g)	H <sub>2</sub> O (mL)	Ethanol (mL)	Ammonia (mL)	Temperature/ Time
resin/SiO <sub>2</sub>	0.2	-	0.28	0.46	0.26	20	4	0.15	25 °C /24 h
resin/SiO <sub>2</sub> - APF	-	0.2	0.28	0.46	0.26	20	4	0.15	25 °C /24 h

Table S2. Textural properties of NHCSs, NHCSs-APF, and YP-50F.

Sample	S <sub>BET</sub> (m <sup>2</sup> /g)	S <sub>t-Plot Micro</sub> (m <sup>2</sup> /g)	V <sub>P</sub> (cm <sup>3</sup> /g)	V <sub>t-Plot Micro</sub> (cm <sup>3</sup> /g)
NHCSs	2044	917	1.60	0.39
NHCSs-APF	1978	1208	1.85	0.50
YP-50F	1600	-	0.75	-

Table S3. Surface C, N, O atom contents measured from XPS results.

Sample	C (at%)	O (at%)	N (at%)
resin/SiO <sub>2</sub>	57.7	23.5	9.2
resin/SiO <sub>2</sub> -APF	63.6	21.5	7.8
carbon/SiO <sub>2</sub>	43.2	37.1	4.0
carbon/SiO <sub>2</sub> -APF	42.7	37.7	2.5
NHCSs	90.4	7.4	2.1
NHCSs-APF	90.4	8.0	1.6

Table S4. C, N, O atom contents measured from CHNS elemental analysis.

Sample	C (at%)	N (at%)
resin/SiO <sub>2</sub>	50.3	13.5
resin/SiO <sub>2</sub> -APF	50.9	7.2
carbon/SiO <sub>2</sub>	38.9	4.1
carbon/SiO <sub>2</sub> -APF	38.8	2.5
NHCSs	79.1	1.8
NHCSs-APF	80.5	1.5

Table S5. Comparison of this work and other works.

Capacitance (F/g)	Energy density (Wh/kg)	Electrolyte	Reference
160	50	EMI BF <sub>4</sub>	1
159	46.8	EMITFSI	2
173	81.4	EMI BF <sub>4</sub>	3
173	54.1	EMI BF <sub>4</sub>	4
113	38	EMI BF <sub>4</sub>	5
140	60.4	EMI BF <sub>4</sub>	6
176	75	EMI BF <sub>4</sub>	7
166	92	EMI BF <sub>4</sub>	8
<b>234</b>	<b>114.8</b>	<b>EMI BF<sub>4</sub></b>	<b>This work</b>
146	15	TEABF <sub>4</sub> /AN	9
102	30	TEABF <sub>4</sub> /AN	10
130	55	TEABF <sub>4</sub> /AN	11
181	45.3	TEABF <sub>4</sub> /AN	12
<b>221</b>	<b>47.7</b>	<b>TEABF<sub>4</sub>/AN</b>	<b>This work</b>

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