Supporting Information

Materials: Triblock copolymer poly(styrene-*b*-2-vinyl pyridine-*b*-ethylene oxide) $PS_{(20,000)}$-*b*-$P2VP_{(15,000)}$-*b*-$PEO_{(27,000)}$ was purchased from Polymer Source. Methanol, tetrahydrofuran (THF), 35% hydrochloric acid, phenol, formaldehyde, aniline were obtained from Nacalai Tesque. Ammonium persulfate $((NH_4)_2S_2O_8)$ was purchased from Alfa Aesar. All chemicals were used directly without further purification.

Synthesis of HCNs: The phenolic resol solution was prepared first. A low-molecular-weight (M_w=500-5000) phenolic resol was generated by a typical process. 0.61 g of phenol was melted at 40 °C, and then 0.13 g of 20% NaOH was added slowly over 10 min under stirring. 1.03 g of formaldehyde was added into above solution and reacted at 70 °C for 1 h. After cooling to room temperature, 0.6 M HCl was used to adjust solution to pH 7.0. Water was removed from the solution under vacuum at 45 °C, yielding a gel. A 20 wt% phenolic resol solution was prepared by diluting the gel in methanol prior to use.

In a typical synthesis of HCNs, 5 mg of triblock copolymer PS-*b*-P2VP-*b*-PEO was completely dissolved in 1 mL of THF. Then 20 uL of 35% HCl solution and 100 uL of H_2O were added under mixing. Next, the solution was diluted again with 1.5 mL methanol. The solution was mixed with 29.4 mg of phenolic resol resin and the micellization was stimulated with 150 uL of 35% HCl solution. The solution was stirred for 2 hours then transferred into a 25 uL autoclave and continuously heated at 130 °C for 10 hours. The products were collected by centrifugation and washed by ethanol for several times. A brown dried powder was calcined at different temperatures (800 °C, 900 °C, and 1000 °C) in N_2 atmosphere for 4 h. The final black products were obtained and kept for further characterization.

For synthesis of small-sized HCNs, 83.3 mg of triblock copolymer PS-*b*-P2VP-*b*-PEO was dissolved in 16.66 mL THF. Then, 333 uL of 35% HCl was added to stimulate micellization. This mixed solution was transferred into a dialysis membrane tube (Mw cut-off: 14,000 Da) and dialyzed in methanol for 6 cycles to completely remove THF. Then, the polymeric micelle solution with a dense PS core was obtained. 5 mg of triblock copolymer PS-*b*-P2VP-*b*-PEO in 1.5 mL methanol was used to synthesize small-sized HCNs. The following process is the same as the above-mentioned method.

Characterization: Field emission scanning electron microscope (SEM, HITACHI SU-8000) was used to observe morphology of HCNs with the accelerating voltage of 5 kV. Transmission electron microscope (TEM, JEOL JEM-2100F) was operated to investigate the interior structure at 200 kV. The hydrodynamic diameter (D_h) of polymeric micelles were measured with an Otsuka ELSA particle analyzer. Wide angle X-ray diffraction (XRD: RIGAKU) was performed at a scanning rate of $1° \cdot min^{-1}$ with a Cu Kα radiation (40 kV, 30 mA). Small angle X-ray scattering (Rigaku NANO-Viewer) was used to evaluate the diameter of hollow center with a Cu Kα radiation (40 kV, 30 mA) and the camera length is 700 mm. Nitrogen adsorption-desorption isotherms were obtained by using a Belsorp 28 apparatus (Bel Japan, Inc.) to investigate the surface area of

the HCNs by the Brunauer-Emmett-Teller (BET) method. Raman spectra were collected on a Horiba-Jovin Yvon T64000 instrument with a λ=514.5 nm excitation laser.

Electrochemical measurements: A three-electrode cell consists of a reference electrode (Ag/AgCl electrode), a counter electrode (Pt wire) and a working electrode (the graphite substrate of 1 cm^2). 0.8 mg of HCNs materials was mixed with 0.2 mg of poly(vinylidine difluoride) and dissolved in 0.1 mL of N-methylpyrrolidinone solvent. A homogeneous slurry was prepared by ultrasonication and coated on a graphite substrate. Each electrode keeps the same loading weight. For comparison, HCNs-8, HCNs-9, and HCNs-10 were synthesized under 800 °C, 900 °C, and 1000 °C, respectively. Supercapacitor test was carried out using a CHI 842B electrochemical analyzer (CHI Instrument, USA) in 1.0 M H_2SO_4 to investigate cyclic voltammetry (CV) and galvanostatic charge-discharge measurements. The same potential window of 0.0 to 0.8 V was selected and the current density varied from 1 to 10 A g^{-1}. The specific capacitance was calculated from CVs using the equation:

$$C = \frac{1}{ms(Vf - Vi)} \int_{Vi}^{Vf} I(V)dV$$

where, I is the current (A), s is the sweep rate (V s^{-1}), V is the potential window (V) and m is the mass (g). According to galvanostatic charge-discharge curves, the specific capacitance was attained from the formula:

$$C = \frac{I \times \Delta t}{\Delta V \times m}$$

where, I is the applied current (A), Δt is the discharge time (s), ΔV is the voltage change during the discharge (V) and m is the mass (g).
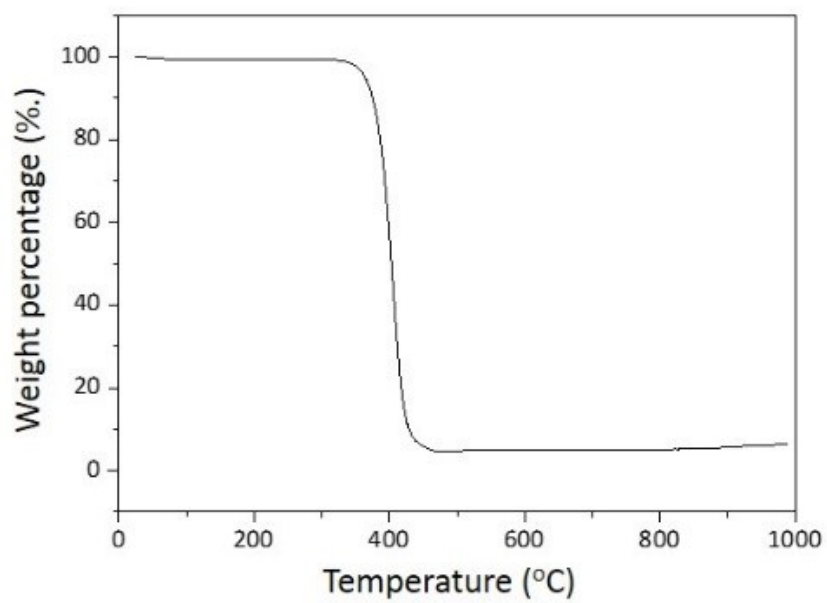
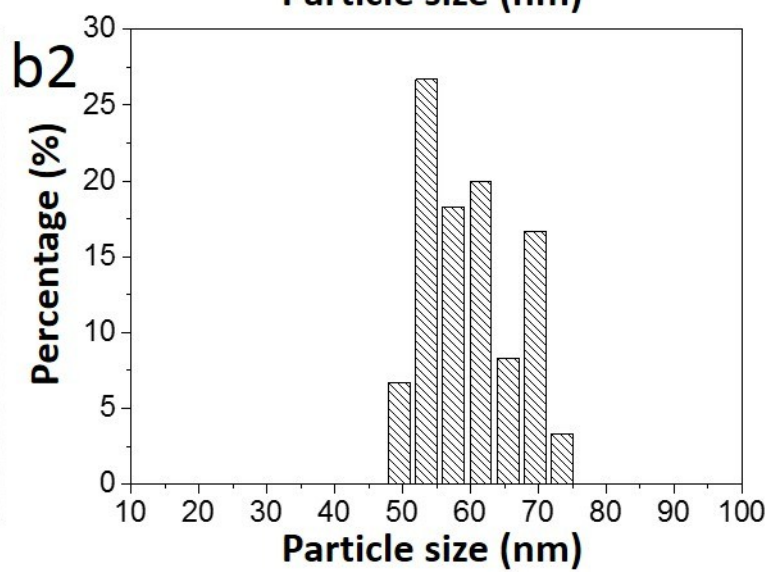**Figure S1** TGA of triblock copolymer PS-*b*-P2VP-*b*-PEO under the protection of N_2 gas.
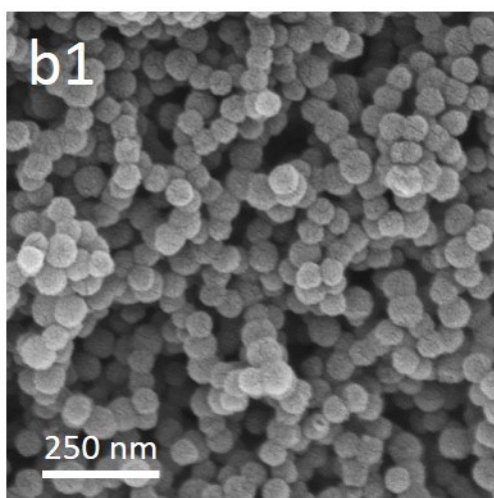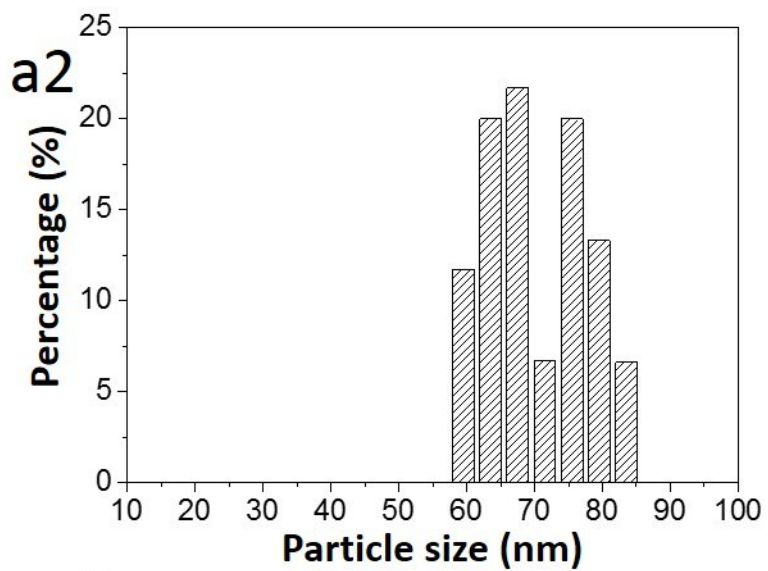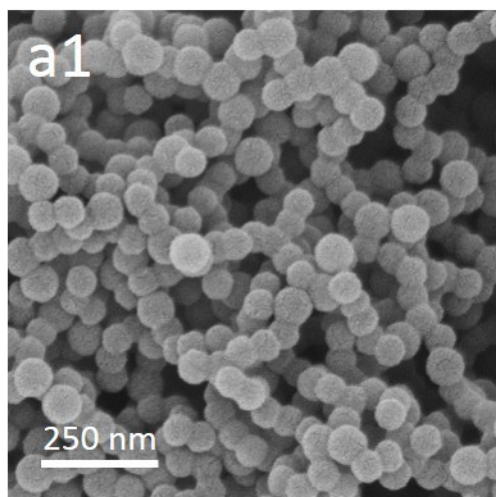
Figure S2 SEM images and particle size distributions of the samples before (a1 and a2) and after (b1 and b2) annealing at 800 °C for 4 h.

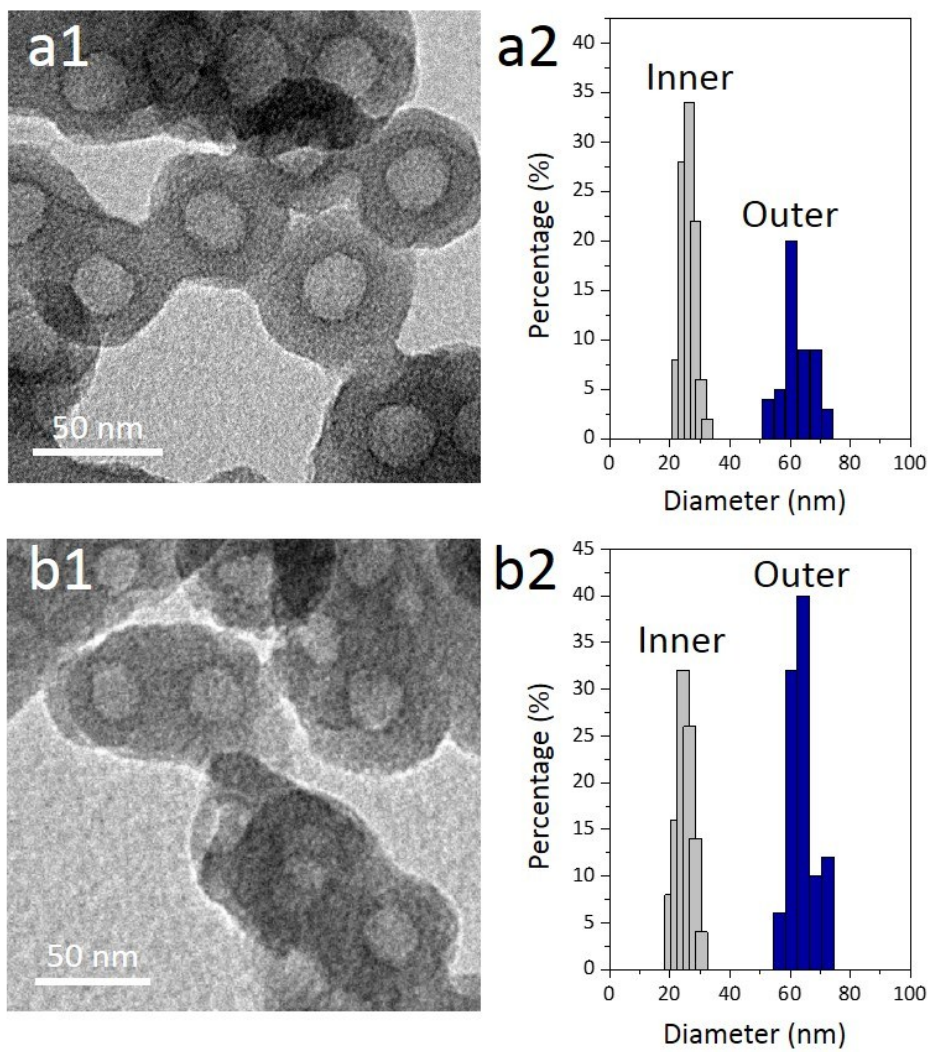**Figure S3** (a1 and b1) TEM images and (a2 and b2) inner and outer diameter distributions of HCN-900 and HCN-1000.
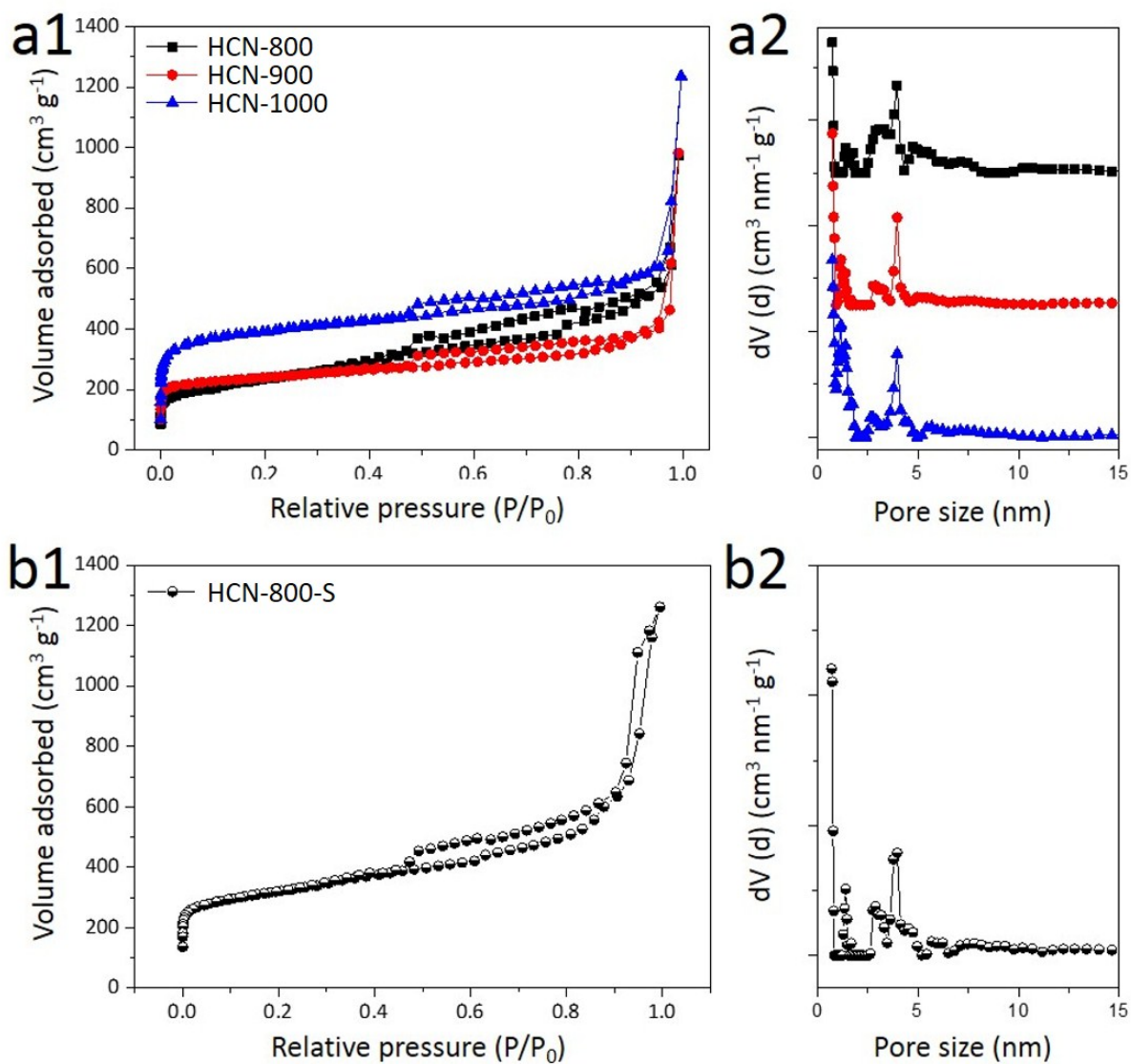
Figure S4 N_2 adsorption-desorption isotherms and pore size distribution of (a) HCN-800, HCN-900, and HCN-1000, and (b) HCN-800-S.
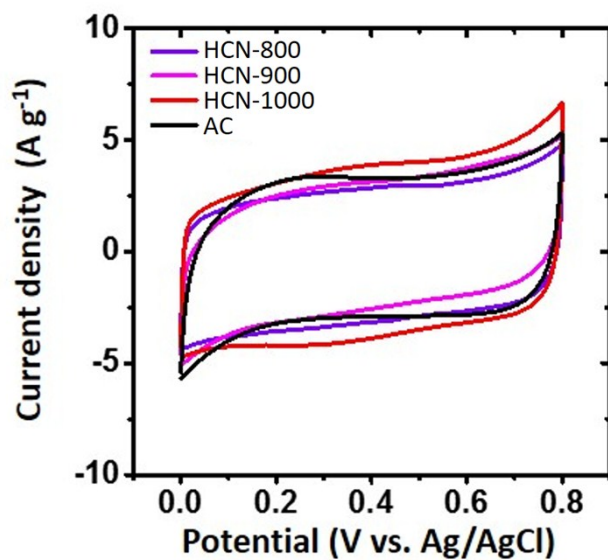
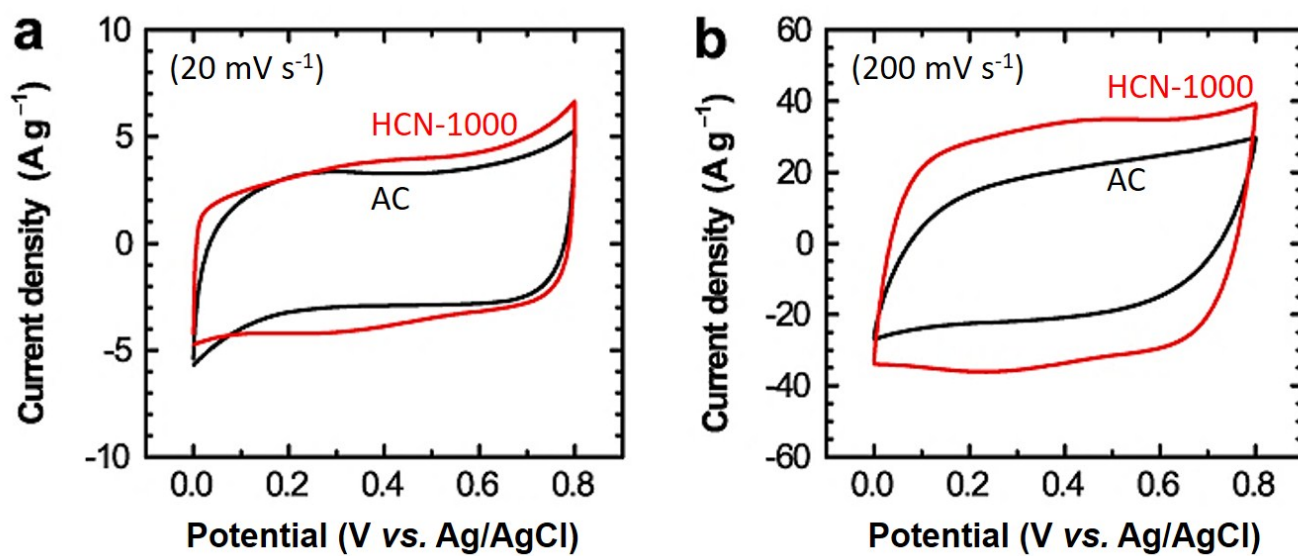**Figure S5** Comparison of CV curves for HCN-800, HCN-900, HCN-1000 and AC recorded at 5 mV s^{-1}.

Figure S6 CV curves of HCN-1000 (red) and AC (black) recorded at (a) 20 mV s^{-1} and (b) 200 mV s^{-1}, respectively.

Table S1. The summary of inner diameters, outer diameters, and templates of the HCNs from literatures.

Templates	Inner diameter (nm)	Outer diameter (nm)	Ref.
PS-*b*-PVP-*b*-PEO	19, 26	43, 63	This work
Triton X-100	26	69	1
PMMA-EA-AA	290	450	2
SnO$_2$ hollow spheres	150-350	300-500	3
Emulsion droplets	100-550	180-800	4
SiO$_2$ templates	7, 40, μm sized	12, 70, μm sized	5
SiO$_2$ templates	350	400	6
SiO$_2$ templates	200	180	7
PS templates	300	220	8
PS templates	100	80	9
MF templates	200	300	10
Co templates	33-49	33-49	11
Fe templates	20-50	40-70	12*

*This approach provides a wide range of particle size distribution (40-70 nm), and only the smallest particle size is indeed smaller than the average diameter of our HCN.

Supplementary References in Table S1

1   F. Xu, Z. Tang, S. Huang, L. Chen, Y. Liang, W. Mai, H. Zhong, R. Fu and D. Wu, *Nat. Comm.*, 2015, 6, 7221.

2   Z. Wang, S. Zhang, L. Zhang, R. Lin, X. Wu, H. Fang, Y. Ren, *J. Power Sources*, 2014, 248, 337.

3   C. Zhang, H. B. Wu, C. Yuan, Z. Guo, X. W. Lou, *Angew. Chem. Int. Ed.*, 2013, 51, 9592.

4   Z.-A. Qiao, B. Guo, A. J. Binder, J. Chen, G. M. Veith and S. Dai, *Nano Lett.*, 2013, 13, 207.

5   F. Böttger-Hiller, P. Kempe, G. Cox. A. Panchenko, N. Janssen, A. Petzold, T. Thurn-Albrecht, L. Borchardt, M. Rose, S. Kaskel, C. Georgi, H. Lang and S. Spange, *Angew. Chem. Int. Ed.*, 2013, 52, 6088.

6   J. Tang, J. Liu, R. R. Salunkhe, T. Wang and Y. Yamauchi, *Chem. Commun.*, 2016, 52, 505.

7   G. He, S. Evers, X. Liang, M. Cuisinier, A. Garsuch, L. F. Nazar, *ACS Nano*, 2013, 7, 10920.

8   A. H. Lu, T. Sun, W. C. Li, Q. Sun, F. Han, D. H. Liu and Y. Guo, *Angew. Chem. Int. Ed.*, 2011, 50, 11765.

9   R. J. White, K. Tauer, M. Antonietti and M.-M. Titirici, *J. Am. Chem. Soc.*, 2010, 132, 17360.

10   Y. Wang, H. Zou, S. Zeng, Y. Pan, R. Wang, X. Wang, Q. Sun, Z. Zhang and S. Qiu, *Chem. Commun.*, 2015, 51, 12423.

11   C. J. Hofer, R. N. Grass, M. Zeltner, C. A. Mora, F. Krumeich and W. J. Stark, *Angew. Chem. Int. Ed.*, 2016, 55, 8761.

12   C. Zhang, G. Bhargava, M. D. Elwell, S. Parasher, B. Zhou, D. Yates, I. Knoke, I. Neitzel and Y. Gogotsi, *J. Mater. Sci.*, 2014, 49, 1947.

Table S2. The summary of surface area and total pore volume of HCN-1000, HCN-900, HCN-800 and HCN-800-S.

Sample	V_{pore} (cm^3 g^{-1})	V_{micro} (cm^3 g^{-1})	V_{micro}/V_{pore} (%)	S_{BET} (m^2 g^{-1})
HCN-1000	1.911	0.400	20.9	1475.5
HCN-900	1.519	0.238	15.7	906.3
HCN-800	1.505	0.104	6.9	835.2
HCN-800-S	1.953	0.233	11.9	1163.5
AC	1.951	0.947	48.5	3104.4

Table S3. Comparison of specific capacitance value with various literatures for hollow carbon nanomaterials.

Electrode	Electrolyte	Specific capacitance (F g^{-1})	Scan rate (mV s^{-1})	Specific current (A g^{-1})	Voltage window (V)	S_{BET} (m^2 g^{-1})	Diameter (nm)	Ref.
Hollow Carbon Spheres								
HCMSs	H$_2$SO$_4$ (2 M)	251	50	-	0.0-0.8	1704	360	1
HCN	KOH (6 M)	269	-	0.5	(-1.0)-0.0	658	100	2
HCSF	KOH (1 M)	227	2	-	(-1.0)-0.0	1286	micrometers	3
Nitrogen-doped Hollow Carbon Spheres								
PNHCS	KOH (6 M)	213	-	0.5	(-1.0)-0.0	213	600	4
NPC	KOH (5 M)	230	-	0.5	(-1.0)-0.0	525	130	5
N-/O- HCSs	KOH (6 M)	210	-	0.5	(-0.8)-0.2	355	900	6
N-HMSCCs	KOH (6 M)	206	-	1	(-1.0)-0.0	718	200	7
GNHCSs	KOH (6 M)	122	-	0.5	(-1.0)-0.0	124	720	8

HCMSs: Mesoporous Shell Carbon Nanospheres; HCN: Hollow Carbon Spheres; HCSF: Hollow Carbon Spheres with Foam-like Shells; PNHCS: Porous N-doped Hollow Carbon Spheres; NPC: N-rich Porous Carbon; N-/O-HCSs: N-/O-doped Hollow Carbon Spheres; N-HMSCCs: N-doped Hollow Mesoporous Spherical Carbon Capsules; GNHCSs: GO Decorated N-doped Hollow Carbon Spheres.

Supplementary References in Table S3

1. B. You, J. Yang, Y. Sun and Q. Su, *Chem. Commun.*, 2011, 47, 12364.

2. Y. Han, X. Dong, C. Zhang and S. Liu, *J. Power Sources*, 2012, 211, 92.

3. X. Fang, J. Zang, X. Wang, M.-S. Zheng and N. Zheng, *J. Mater. Chem. A*, 2014, 2, 6191.

4. J. Han, G. Xu, B. Ding, J. Pan, H. Dou and D. R. MacFarlane, *J. Mater. Chem. A*, 2014, 2, 5352.

5. X. Liu, L. Zhou, Y. Zhao, L. Bian, X. Feng and Q. Pu, *ACS Appl. Mater. Interfaces*, 2013, 5, 10280.

6. C. Yuan, X. Liu, M. Jia, Z. Luo and J. Yao, *J. Mater. Chem. A*, 2015, 3, 3409.

7. A. Chen, K. Xia, L. Zhang, Y. Yu, Y. Li, H. Sun, Y. Wang, Y. Li and S. Li, *Langmuir*, 2016, 32, 8934.

8. L. Liu, S.-D. Xu, Q. Yu, F.-Y. Wang, H.-L. Zhu, R.-L. Zhang and X. Liu, *Chem. Commun.*, 2016, 52, 11693.