Supplementary information

A Selective Etching Approach to Pore Structure Control of Polymeric Precursor: Creating Hierarchical Porous N, P Co-doped Carbon Nanospheres For Semi-Solid-State Supercapacitor

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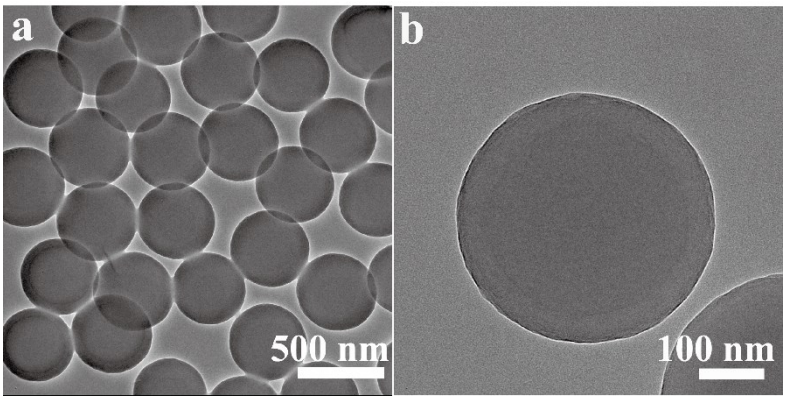

Fig. S1. TEM images of IDPs.

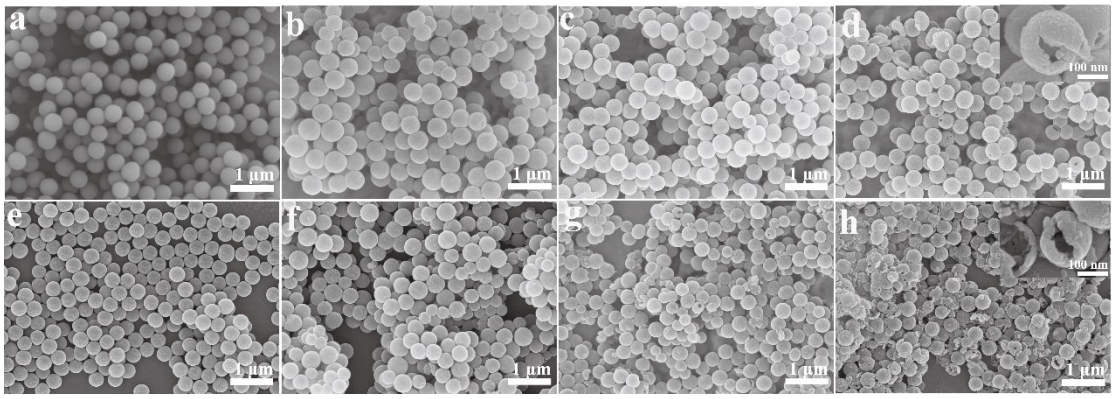

Fig. S2. SEM images of (a) IDPs, (b) PIDP1, (c) PIDP2, (d) PIDP3, (e) CNP, (f) PCNP1, (g) PCNP2, (h) PCNP3; the insets are the corresponding magnified SEM images.

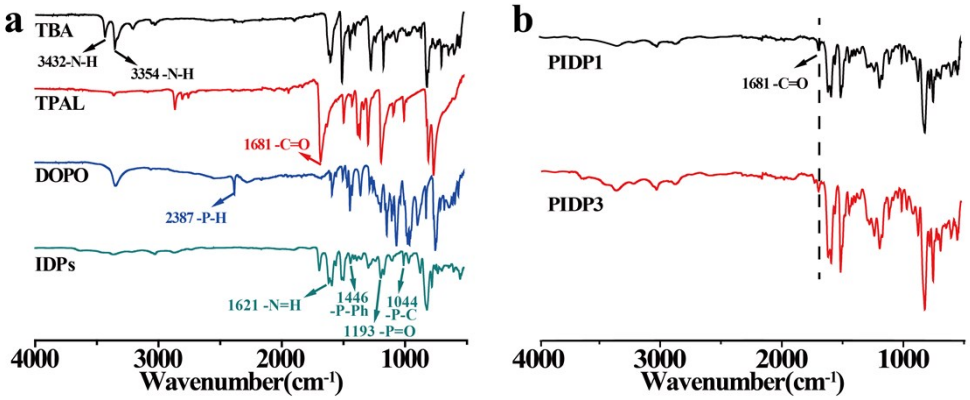

Fig. S3. FT-IR spectra of starting materials and IDPs (a); FT-IR spectra of PIDP1 and PIDP3 (b).

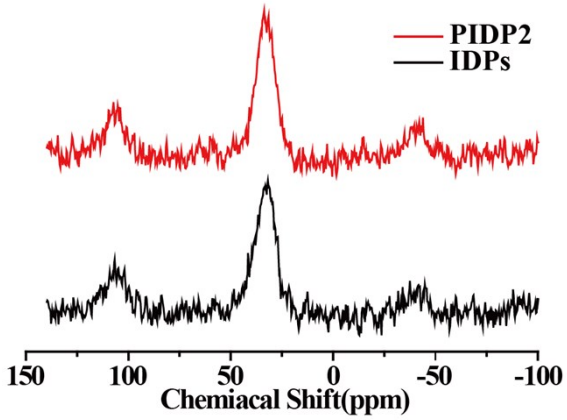

Fig. S4. Solid-state ^{31}P NMR spectra of IDPs and PIDP2.

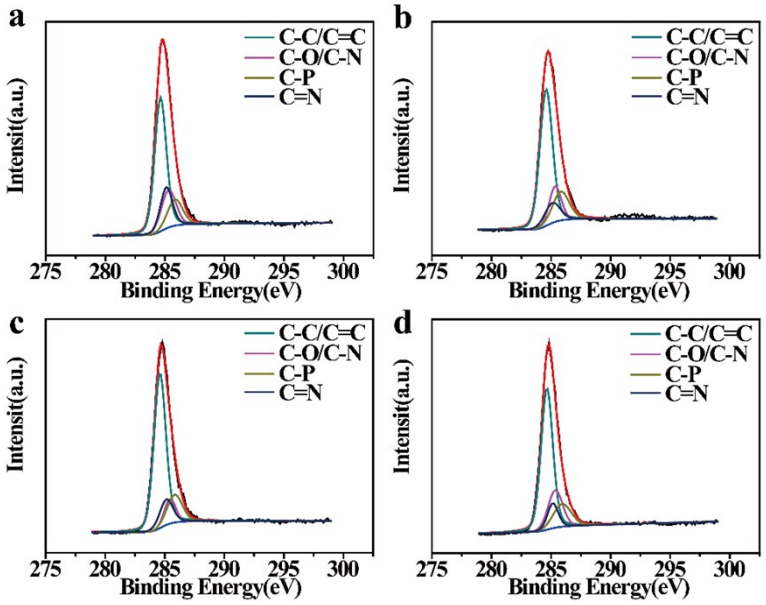

Fig. S5. High-resolution XPS spectra of C 1s for (a) IDPs, (b) PIDP1, (c) PIDP2 and (d) PIDP3.

All samples have similar C 1s spectra. Curve-fitting of these spectra indicates the presence of C-C and C=C bonding (284.8 eV), C-O and C-N bonding (285.4 eV), C-P bonding (285.7 eV) and C=N bonding (285.1 eV).[1-3]

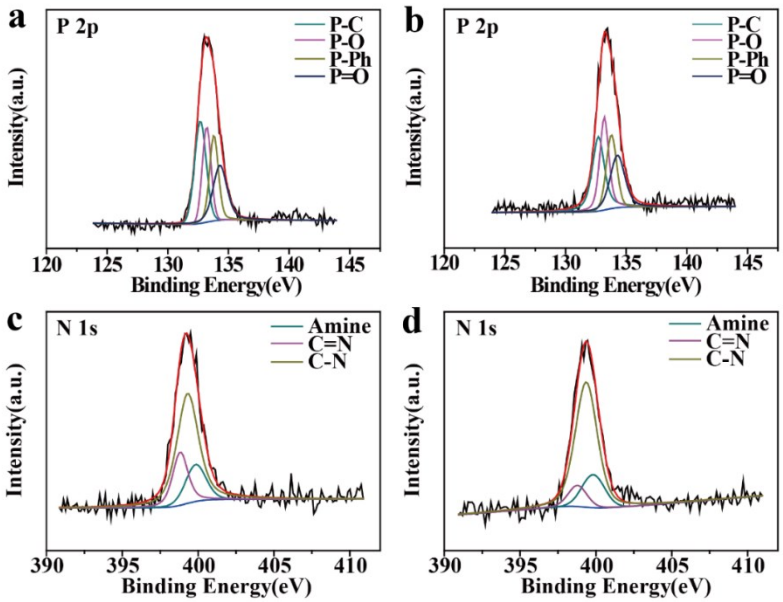

Fig. S6. High-resolution XPS spectra of P 2p for (a) PIDP1, (b) PIDP3 and N 1s for (c) PIDP1 and (d) PIDP3.

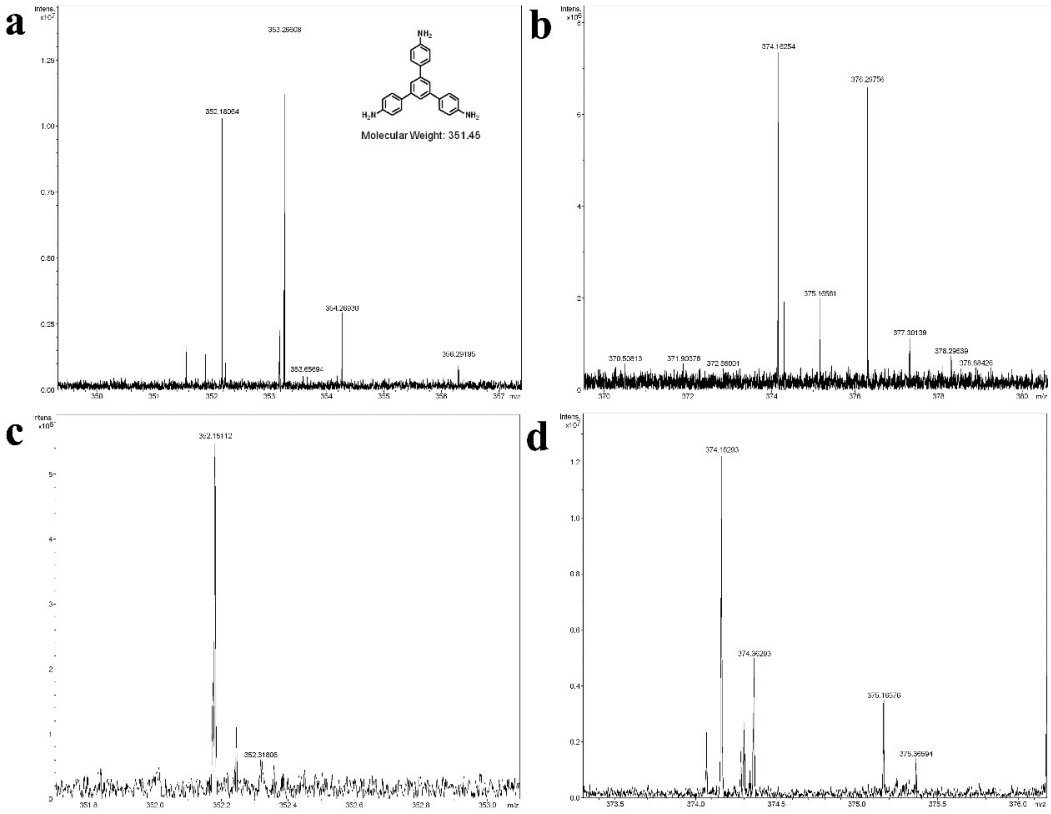

Fig. S7. The mass spectra of (a, b) TBA and (c, d) the supernatant after the reaction between aniline and IDPs.

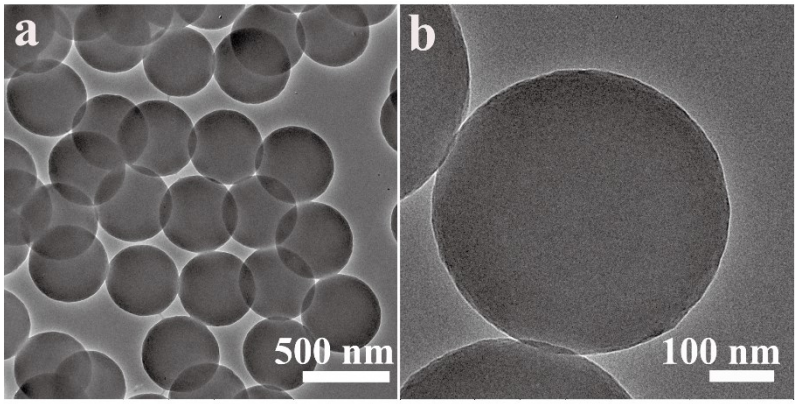

Fig. S8. TEM images of IDPs after treating with aniline (0.02 mol/L).

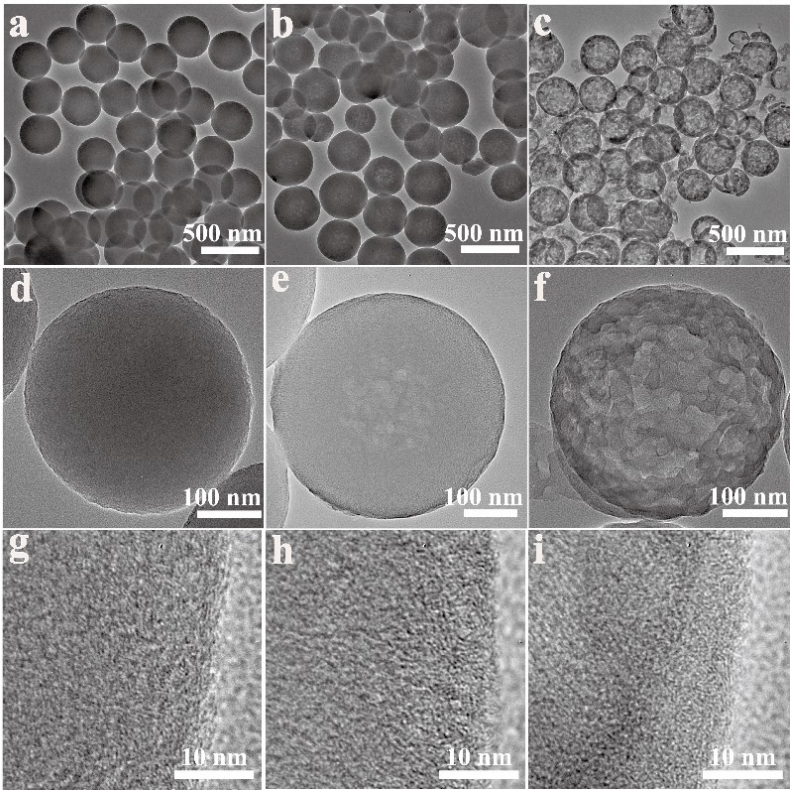

Fig. S9. TEM images of (a) CNP, (b) PCNP1, (c) PCNP3; (d-f) are the corresponding magnified TEM images of (a-c); (g-i) are the corresponding high resolution TEM images.

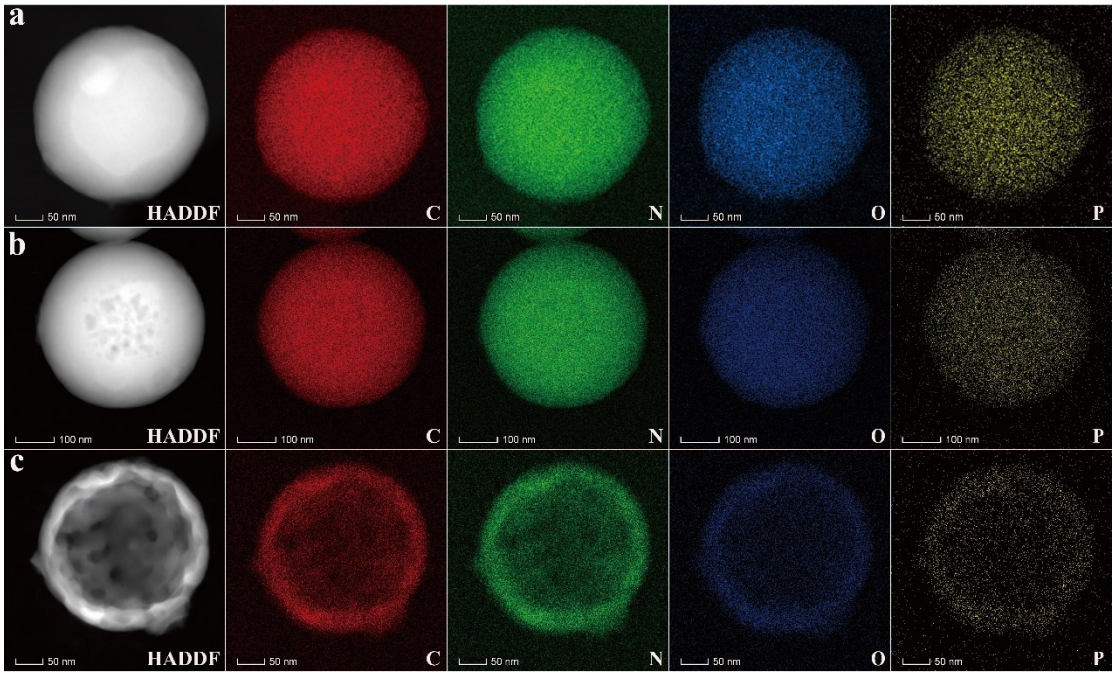

Fig. S10. HAADF-STEM image and EDX element mapping of (a) CNP, (b) PCNP1, (c) PCNP3.

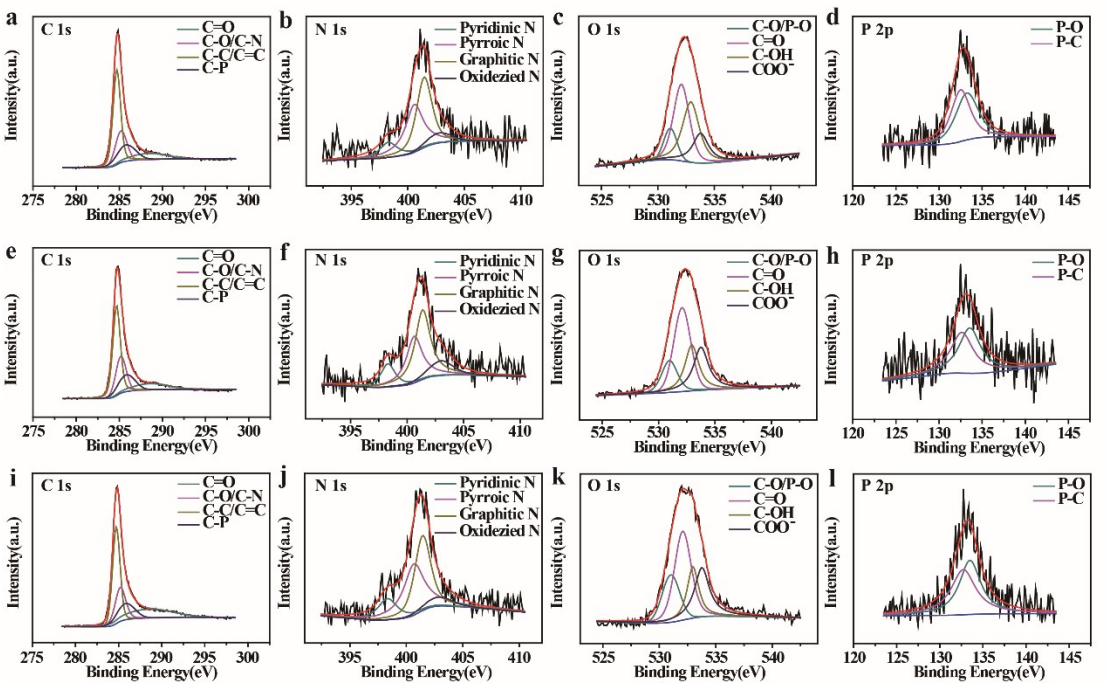

Fig. S11. High-resolution XPS spectra of PCNPs. (a) C 1s, (b) N 1s, (c) O 1s and (d) P 2p for CNP; (e) C 1s, (f) N 1s, (g) O 1s and (h) P 2p for PCNP1; (i) C 1s, (j) N 1s, (k) O 1s and (l) P 2p for PCNP3.

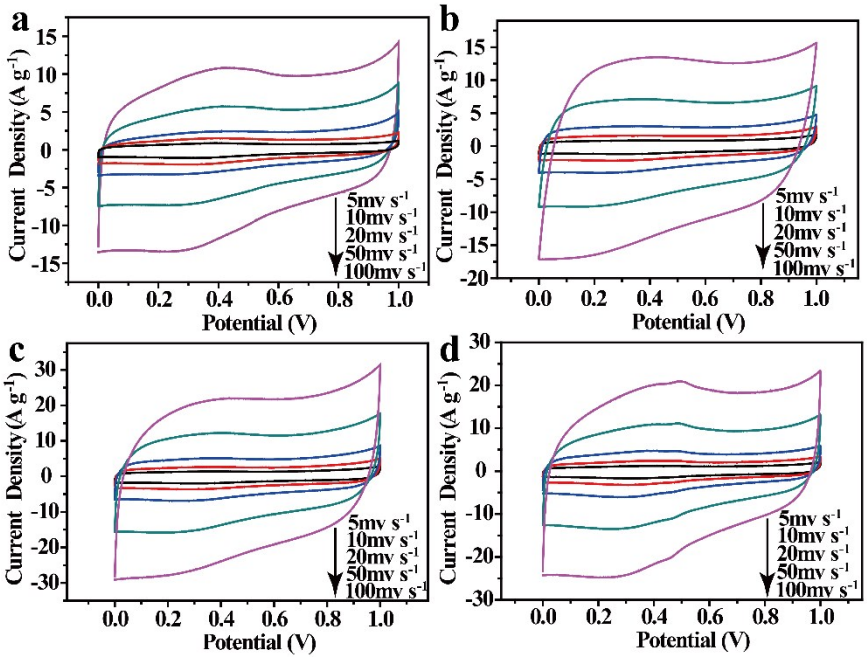

Fig. S12. CV curves of (a) CNP, (b) PCNP1 (c) PCNP2, and (d) PCNP3 at scan rate ranging from 5 to 100 mV s^{-1}.

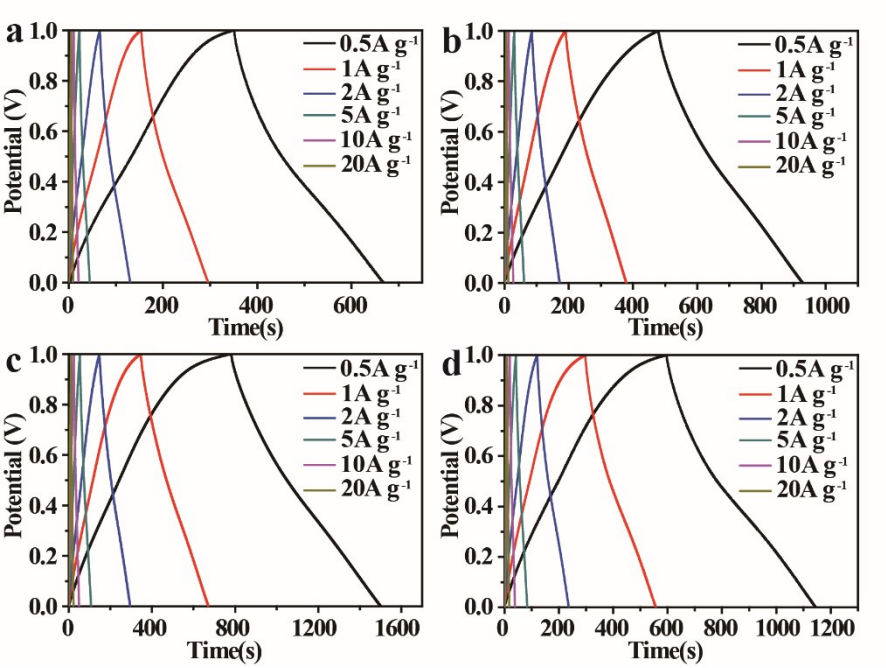

Fig. S13. GCD profiles of (a) CNP, (b) PCNP1, (c) PCNP2 and (d) PCNP3 at current density ranging from 0.5 to 20 A g^{-1}.

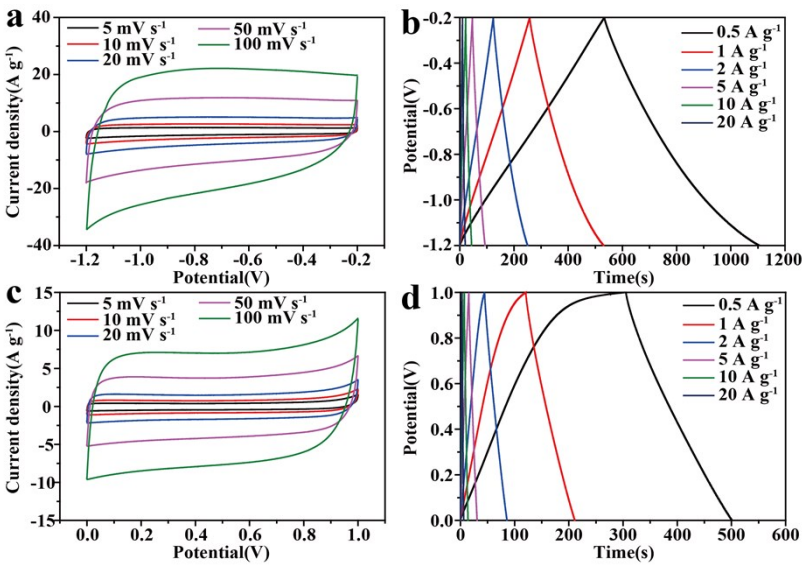

Fig. S14. CV curves (a) and GCD curves (b) of PCNP2 measured in 6M KOH aqueous solution; CV curves (c) and GCD curves (d) of PCNP2 measured in 1M Na_2SO_4 aqueous solution.

The CV curves of PCNP2 in both 6M KOH and 1M Na_2SO_4 aqueous solutions exhibit a quasi-rectangular shape. The results of GCD curves show that PCNP2 delivers specific capacitances of 284.5 and 98.0 F g^{-1} in 6M KOH and 1M Na_2SO_4 aqueous solutions, respectively, at a current density of 0.5 A g^{-1}.

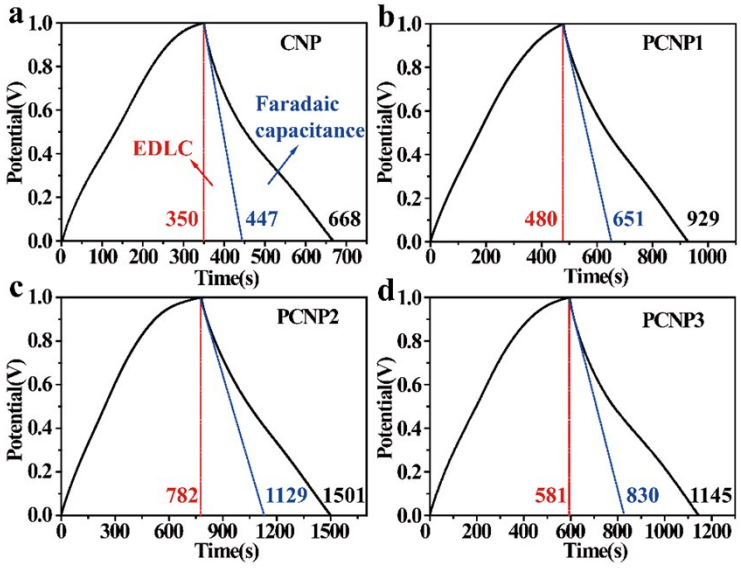

Fig. S15. GCD curves of CNP (a), PCNP1 (b), PCNP2(c) and PCNP3 (d) at 0.5 A g^{-1} in 1 M H_2SO_4 with the estimated EDLC and faradaic capacitance contributions obtained from the discharge portions of differing slopes.

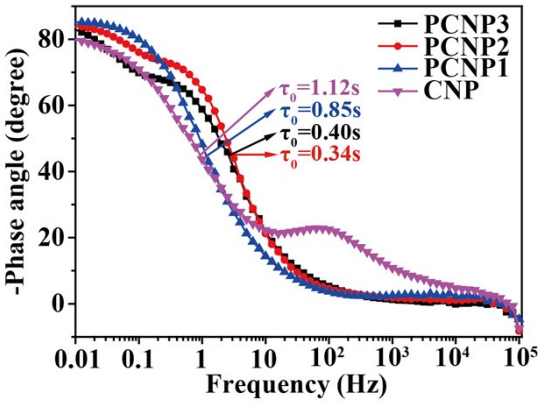

Fig. S16. Bode plots of CNP, PCNP1, PCNP2 and PCNP3. The time constants of CNP, PCNP1, PCNP2 and PCNP3 are 1.12, 0.85, 0.34 and 0.40 s, respectively.

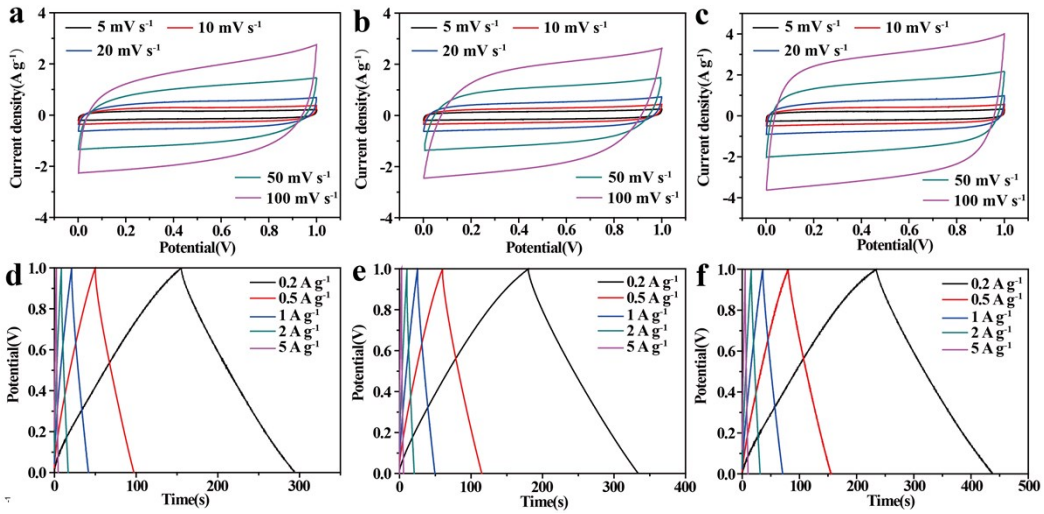

Fig. S17. CV curves of symmetric supercapacitors based on (a) CNP, (b) PCNP1 and (c) PCNP3 with various scan rates at a potential range of 0-1 V; GCD curves of (d) CNP, (e) PCNP1 and (f) PCNP3 based symmetric supercapacitors at various current densities.

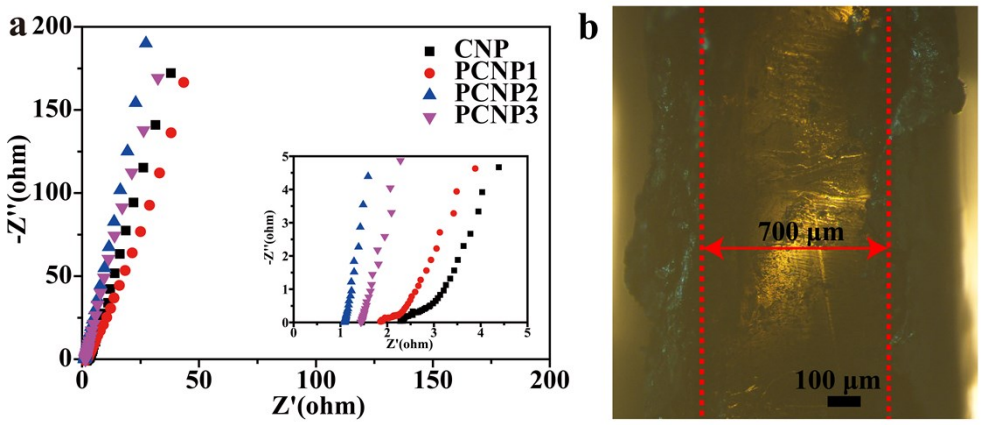

Figure S18. Over view of Nyquist plots of the symmetric supercapacitor devices based on CNP, PCNP1, PCNP2 and PCNP3 and the inset is the magnified version of Nyquist plots (a); optical microscope picture of a symmetric supercapacitor based on PCNP2 (b).

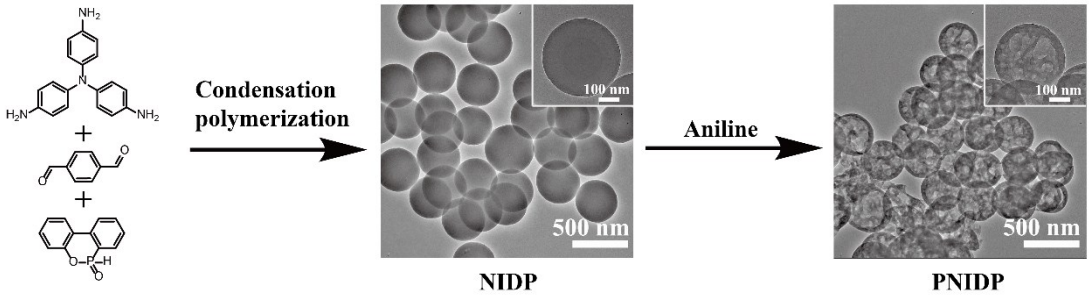

Fig. S19. Synthetic process of porous polymer nanosphere PNIDP.

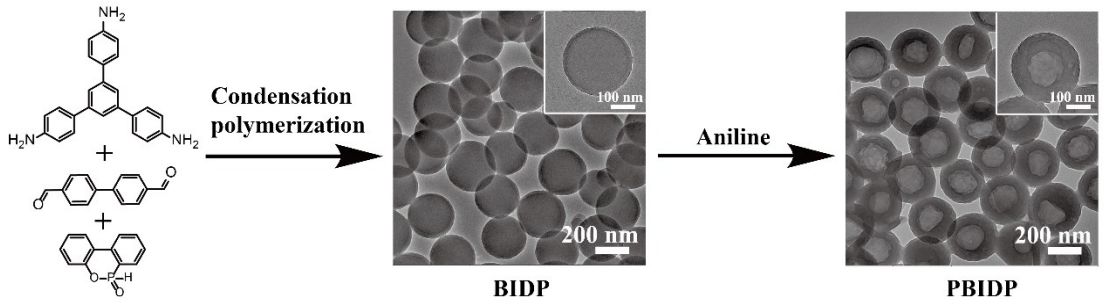

Fig. S20. Synthetic process of porous polymer nanosphere PBIDP.

Synthetic procedure of PNIDP and PBIDP

Materials. Tris(4-aminophenyl)amine (TAA) was obtained from the J&K Chemical. 4, 4'-biphenyldicarboxaldehyde (BPAL) was purchased from the Aladdin company. All chemicals were used as received without further purification.

Preparation of PNIDP. Typically, 30 mg (0.10 mmol) TAA and 67 mg DOPO (0.31 mmol) were dissolved in a mixture solution containing 15 mL ethanol and 15 mL dichloromethane, 21 mg (0.15 mmol) TPAL was dissolved in 30 mL ethanol. The TPAL solution was added dropwise into the solution of TAA and DOPO under vigorous stirring. After overnight reaction at room temperature, red product of solid polymer nanosphere (denoted as NIDP) was collected by centrifugation, followed by washing with ethanol for 3 times. Then, NIDP was dispersed in 12.5 mL ethanol with 1.6 mol/L aniline by sonication to form a dispersion. After 24 h reaction, red product was collected by centrifugation, followed by washing with ethanol for 3 times and drying in vacuum at 60 ^{o}C. The resultant product was denoted as PNIDP.

Preparation of PBIDP. In brief, 30 mg (0.08 mmol) TBA and 56 mg DOPO (0.26 mmol) were dissolved in a mixture solution containing 15 mL ethanol and 15 mL dichloromethane, 27 mg (0.13 mmol) BPAL was dissolved in 30 mL ethanol. The BPAL solution was added dropwise into the solution of TBA and DOPO under vigorous stirring. After overnight reaction at room temperature, tan product of solid polymer nanosphere (denoted as BIDP) was collected by centrifugation, followed by washing with ethanol for 3 times. Then, BIDP was dispersed in 12.5 mL ethanol with 0.8 mol/L

aniline by sonication to form a dispersion. After 24 h reaction, tan product was collected by centrifugation, followed by washing with ethanol for 3 times and drying in vacuum at 60 ^{o}C. The resultant product was denoted as PBIDP.

Table S1 Surface elemental composition (atomic %) of the prepared polymer precursors.

Samples	Elemental Composition[a]				C=N	NH_2+C-N
	C%	N%	O%	P%		
IDPs	82.66	4.34	10.63	2.38	22.47	77.53
PIDP1	84.14	4.74	8.86	2.26	20.77	79.23
PIDP2	82.56	4.12	11.47	1.84	14.99	85.01
PIDP3	84.58	3.46	10.69	1.28	9.84	90.16
PIDP0.02	83.16	4.47	10.14	2.24	/	/

[a] Atomic percent of elements obtained from XPS analysis.

Table S2 Performance of the some reported heteroatom doped carbon materials for supercapacitors.

Materials	Electrode System	Electrolyte	Current Density (A g^{-1})	Capacitance (F g^{-1})	Ref.
PCNP2	Three	1M H_2SO_4	0.5	359.5	This work
YCS-C	Three	6M KOH	0.2	330	4
PNPC	Three	6M KOH	1	318	5
N, S co-doping PCNs	Three	6M KOH	0.5	298	6
N,P,S-HCS-800	Three	6M KOH	0.5	274	7
MCC-6H	Three	6 M KOH	0.2	301	8
TNNs-500	Three	1M H_2SO_4	0.2	299	9
PS_{230}-*b*-PAA_{156}	Three	1M H_2SO_4	0.2	252	10
N-OMC	Three	1M H_2SO_4	0.1	216	11
CS3-6A	Three	1M H_2SO_4	1	388	12

Reference

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