Supporting Information

Dual Tuning of 1 D heteroatoms doped porous carbon nanoarchitectures for supercapacitors: the role of balanced P/N doping and core@shell nano-networks

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1. **Experimental section**

1.1 **Synthesis of PN-CNTs**

Single-wall CNTs were first pre-treated in a HNO_3/H_2SO_4 (v/v=1:3) mixed solution and refluxing at 70 °C for 2 h. The obtained solid was filtered using filter polytetrafluoroethylene menbrane, and washed with deionized water until the pH of the filtrate reached 7 followed by drying in vacuum at 60 °C for 4 h. For the preparation of resorcinol-melamine-formaldehyde coated CNTs (CNT@RMF), 0.37 mL of formaldehyde (37 wt %) and 0.275 g of resorcinol were added a mixture containing 30 mg CNTs, 50 mL of water, 20 mL of ethanol and 0.25 mL of ammonia at 70 °C under stirring. After 30 min, 0.63 g melamine and 1.105 mL of formaldehyde were added to the above mixture and continued stirring for another 24 h, followed by hydrothermal treatment at 120 °C for 24 h. The obtained CNT@RMF were collected by centrifugation, washed with ethanol and water for several times, and dired at 60 °C.

For the preparation of PN-CNTs, the above prepared CNT@RMF precursors (100 mg) and triphenylphosphine (TPP) were immersed in 10 mL of deionized water. The mixture was stirred for 2 h, and further sonicated for 2 h. Then, the solvent was slowly evaporated at 80 °C for 24 h. The resulted powder was annealed at a rate of 5 °C/min to 800 °C under an N2 gas flow. Afterwards, the sample was allowed to cool naturally to room temperature. The mass ratio of CNT@RMF to TPP was adjusted to be 1:0.5, 1:1 and 1:1.5. For simplicity, the samples are denoted as PN-CNTs-1, PN-CNTs-2 and PN-CNTs-3, respectively.

For comparison, N-CNTs were prepared under the carbonization temperature of 800 °C using the same method without TPP.

1.2 **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. Powder X-ray diffraction (XRD) patterns were collected using a Y-2000X-ray Diffractometer using copper Kα radiation (λ=1.5406 Å) at 40 kV, 40 mA. The X-ray photoelectron spectroscopy (XPS) measurements were performed with an ESCA LAB 250 spectrometer using a focused monochromatic Al Kα line (1486.6 eV) X-ray beam with a diameter of 200 μm. The Raman measurements were performed on a Renishaw spectrometer at 532 nm on a Reishaw Microscope System RM2000. The nitrogen sorption measurements at 77 K were carried out by using a Micromeritics Tristar 2020 system with micropore analysis. Before the sorption tests, samples were degassed at 250 ^{o}C for 8 h under dynamic vacuum. 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/P0) of 0.99. Pore size distributions were fitted from Quenched Solid Density Functional Theory (QSDFT) based on the desorption branches.

1.3 Electrochemical characterization

All electrochemical experiments were carried out on a CHI 660D electrochemical workstation (CH Instruments, Inc.) at room temperature. 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 H_2O, Sigma-Aldrich) on a nickel foam (1×1 cm^2) and dried at 80°C for 24 h. As-made electrodes were pressed at a pressure of 10 MPa for 1min. The electrolyte was a 6.0 M KOH aqueous solution. In a three-electrode system, the electrode was the test electrode, platinum foil as the counter electrode, Ag/AgCl electrode as the

reference electrode. The cyclic voltammetry (CV) curves were obtained at various scan rates with voltage ranging from -1 V to 0 V. The chronopotentionmetry (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. Cycling life measurement was studied in the potential range of 0−1.0 V at 2.0 A g^{-1} for 8000 cycles.
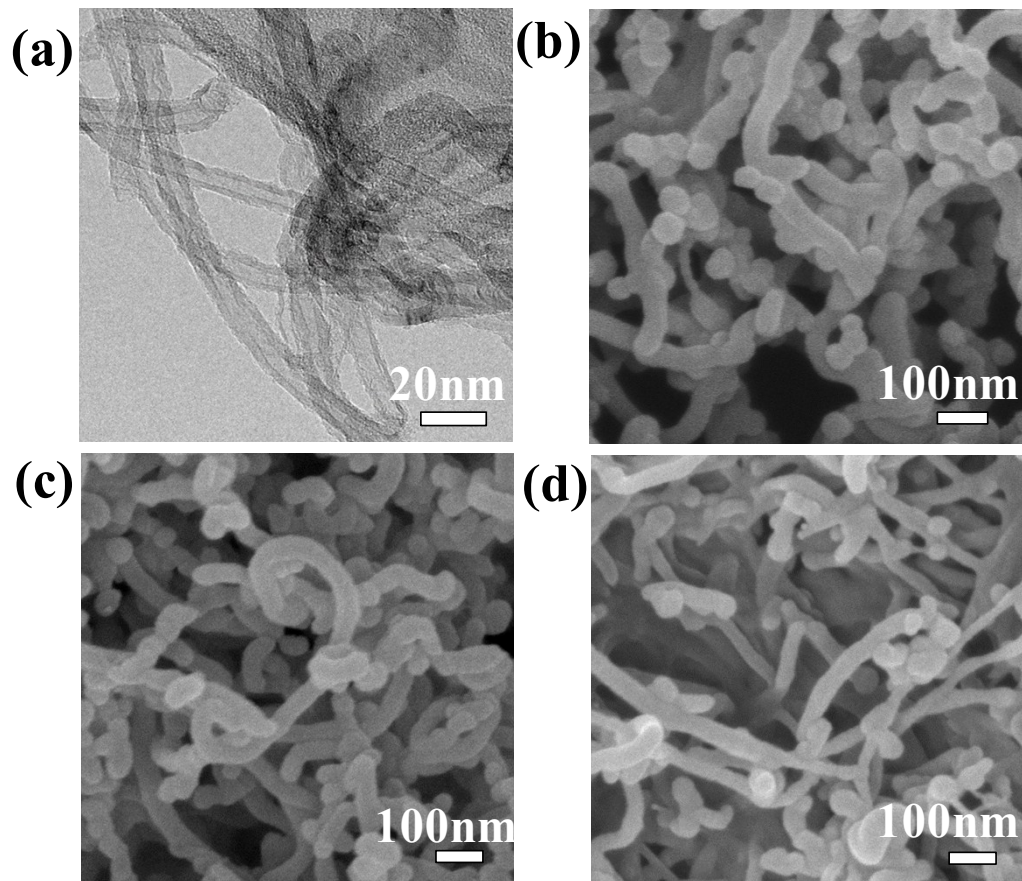
2. Figures

Figure S1 TEM images of (a) CNTs, SEM images of (b) PN-CNTs-1, (c) PN-CNTs-2 and (d)PN-CNTs-3.
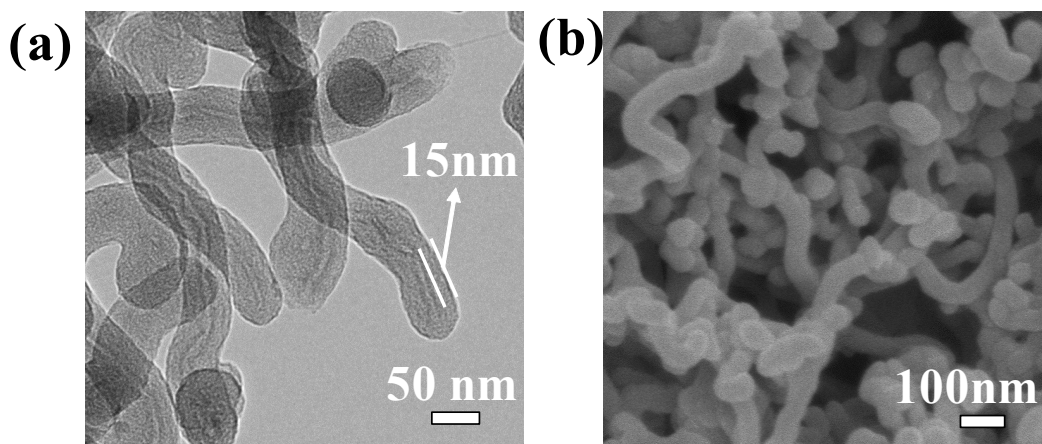

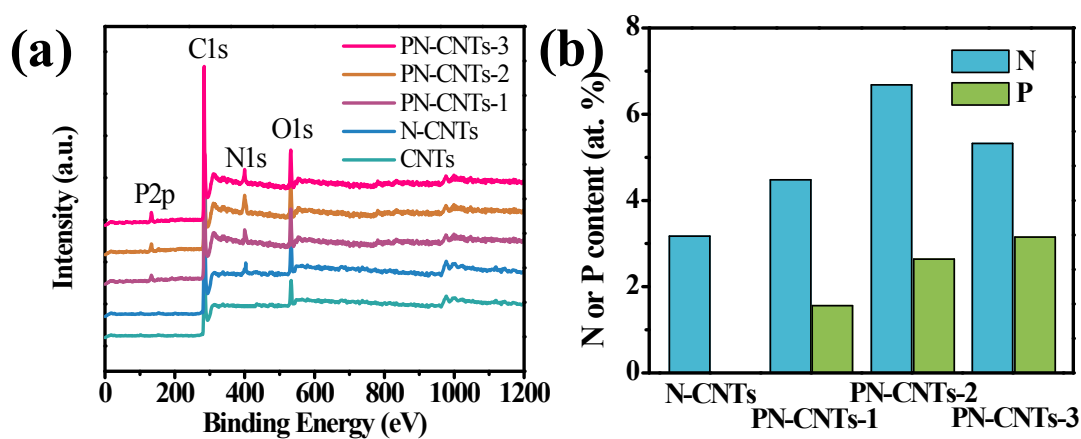**Figure S2** TEM images of (a) N-CNTs, SEM images of (b) N-CNTs.

Figure S3 (a) The wide XPS survey of CNTs, N-CNTs, PN-CNTs-1, PN-CNTs-2, and PN-CNTs-3. (b) The amount of nitrogen and phosphorus of N-CNTs, PN-CNTs-1, PN-CNTs-2, and PN-CNTs-3.
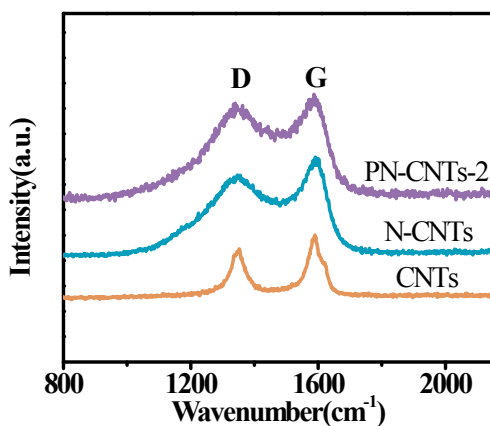

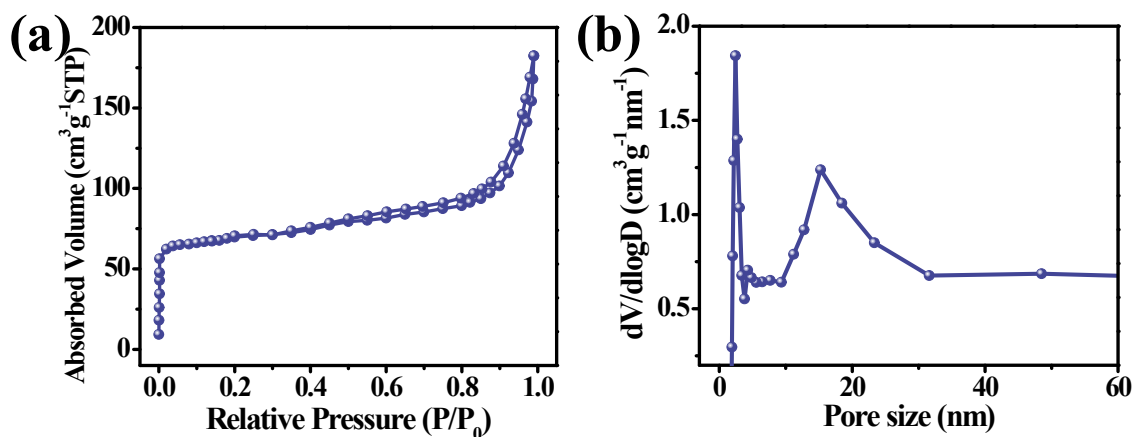**Figure S4** Raman spectra of the PN-CNTs-2, N-CNTs and CNTs.

Figure S5 (a) N_2 adsorption and desorption isotherms and (b) pore size distribution of CNT@RMF.
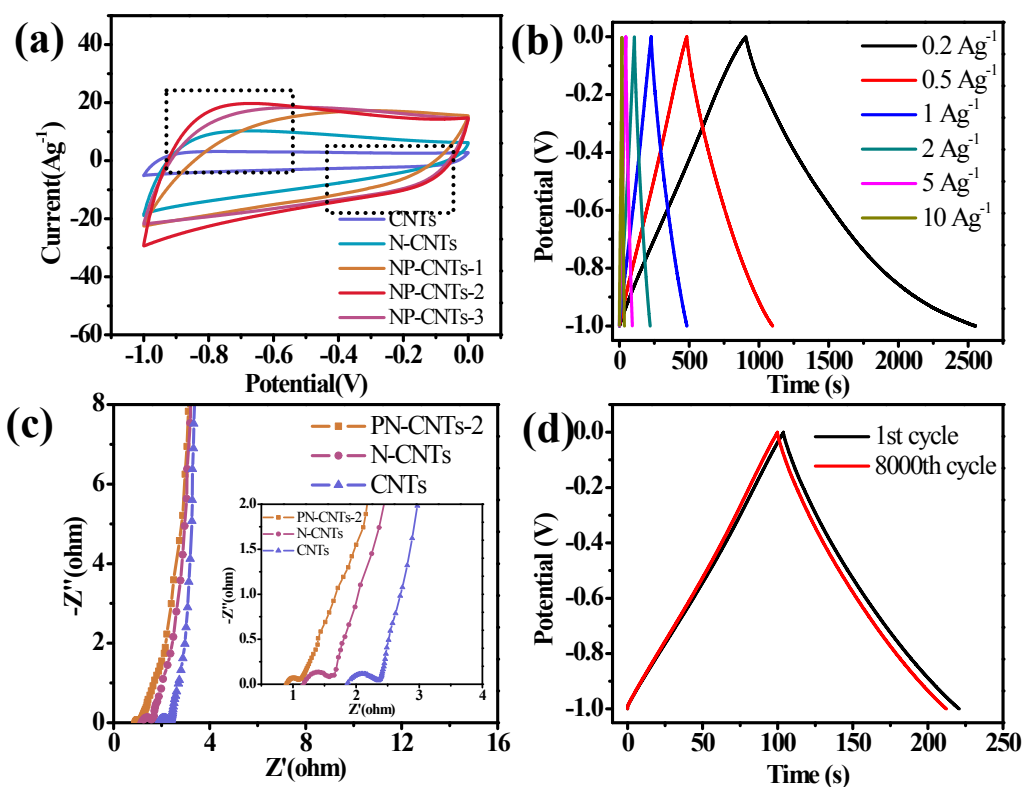
Figure S6 Electrochemical performances measured in a three-electrode system. (a) Cyclic voltammograms curves of all samples at 100 mV s^{-1}. (b) Galvanostatic charge−discharge curves of PN-CNTs-2 at different current densities (c) Nyquist plots of PN-CNTs-2, N-CNTs and CNTs in the frequency range of 100 kHz and 10 mHz. The inset in (c) is the magnified region. (d) Galvanostatic charge/discharge curves of PN-CNTs-2 before and after 8000 cycles measured at 2 A g^{-1}.
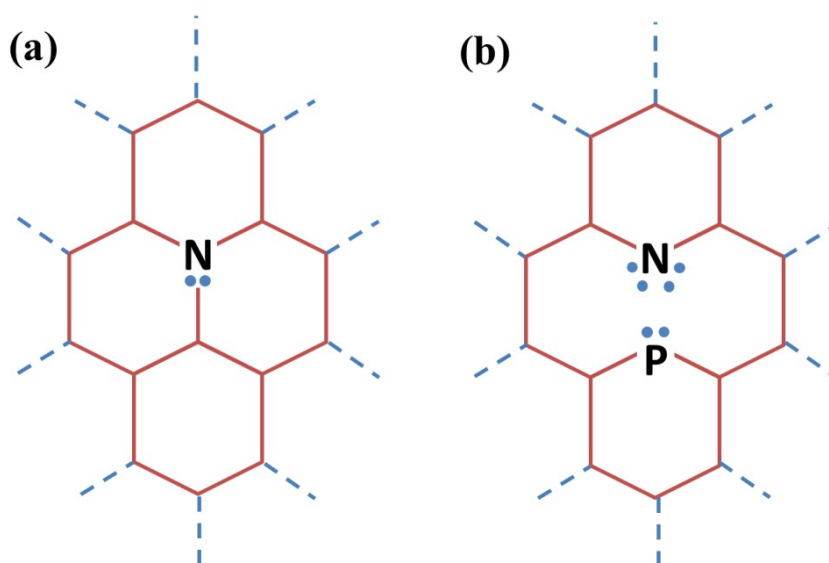
Figure S7 Schematic representation of the bonding environment of the N and P,N co-doped carbon.

3.Tables

Table S1 Fitting results summary of C, N and P core level XPS spectra of CNTs, N-CNTs and PN-CNTs.

Sample	C (at.%)	N (at.%)	P (at.%)	P/N
CNTs	96.79	---	---	---
N-CNTs	92.49	3.17	---	---
PN-CNTs-1	88.27	4.48	1.56	0.35
PN-CNTs-2	83.97	6.68	2.64	0.40
PN-CNTs-3	82.61	5.32	3.15	0.59

Table S2 Comparison of capacitance data reported for different P/N co-doped carbon-based materials.

Samples	Electrolyte	Scan Rate	Specific capacitance (F g^{-1})	Ref.
P/N dual doped mesoporous carbonderived from melamine and polyphosphoric acid	6 M KOH	5 mVs^{-1}	271 F g^{-1}	S1
N/Pcodoped thermally reduced graphene oxide derived from $(NH_4)_3PO_4$	6 M KOH	0.1Ag^{-1}	165 F g^{-1}	S2
N/P co-dopednonporous carbon nanofibers polyacrylonitrile and phosphoric acid	1 M H$_2$SO$_4$	0.5 Ag^{-1}	224.9 F g^{-1}	S3
N/P co-doped microporous carbonderived from ammonium phosphate	6 M KOH	0.1Ag^{-1}	183.8 F g^{-1}	S4
N/P co-dopedactivated carbon derived fromammonium biphosphate	7 M KOH	0.05 Ag^{-1}	227 F g^{-1}	S5
P-functionalized carbon nanotube derived from phosphoric acid	6 M KOH	0.1 Ag^{-1}	173 F g^{-1}	S6

References

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