

**Supporting Information (SI) for**

**Highlighting the role of nitrogen doping in enhancing CO<sub>2</sub> uptake  
onto carbon surface: A combined experimental and computational  
analysis**

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## ***Experimental and Computational Methods***

### **Synthesis of N-doped porous carbons**

The N-doped porous carbon was synthesized by the copolymerization of phenol, formaldehyde and melamine, following by carbonization and template removal according to our recent study.<sup>1</sup> Briefly, 1.8 g melamine, 0.6 g of phenol, 10mL formalin aqueous solution (37 wt%), 40  $\mu$ L 1mol L<sup>-1</sup> NaOH solution and 10mL deionized water were mixed and refluxed at 80°C to obtain the NPC precursor solution. Then, tetraethyl orthosilicate (TEOS) aqueous solution, containing 2.1 g of TEOS, 1g 0.1mol L<sup>-1</sup> HCl, 10 mL ethonal, and 10mL deionized water was added into above precursor solution and kept at 80 °C for another 30min. After cooling down to room temperature, the mixture was dried at 100 °C and subsequently carbonized under 900°C. Washing by 10%HF solution yield the resulted N-doped porous carbons. The porous carbon products with different melamine contents (0g, 0.6g, 1.2g, 1.8g) were denoted as PC, NPC-1, NPC-2, NPC-3, respectively.

### **Structural characterization and CO<sub>2</sub> adsorption test**

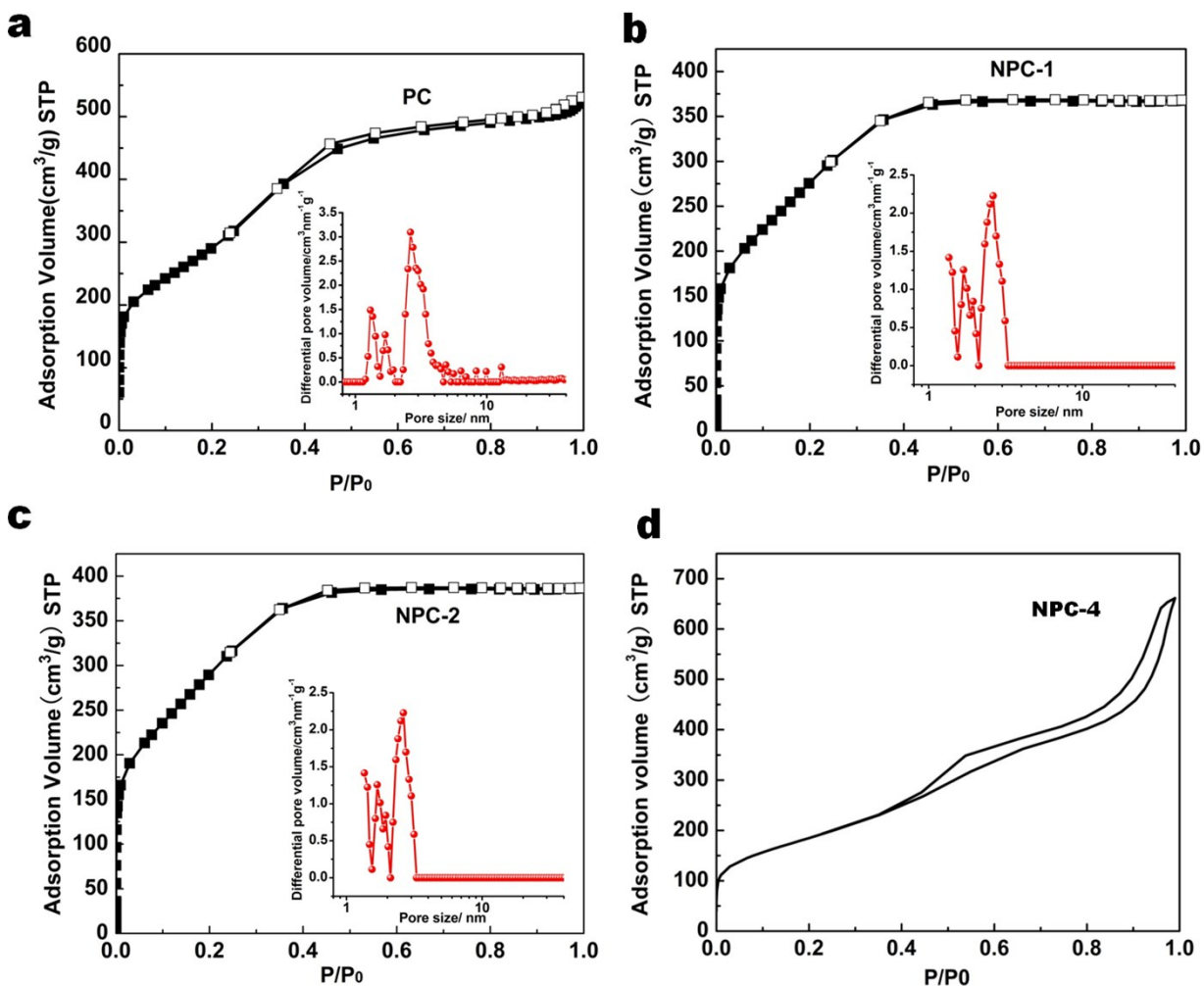
The morphology and microstructure of carbons were analyzed using scanning electron microscopy (JSM-7401F) and transmission electron microscopy (TEM, JEOL-2010), respectively. The pore structure was determined by N<sub>2</sub> adsorption at -196°C using ASAP 2020 sorption analyzer. X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI 5700 ESCA System using AlK $\alpha$  X-ray at 14 kV and 6 mA. Raman spectroscopy was examined on a Renishaw inVia Micro-Raman spectrometer (532 nm). The CO<sub>2</sub> adsorption isotherms of prepared samples were also measured using ASAP 2020 sorption analyzer at 0 and 25 °C with the pressure ranging from 0 to 800 mmHg.

### **Computational methods.**

Density functional theory (DFT) calculations were conducted to obtain the CO<sub>2</sub> adsorption patterns, adsorption positions and energy decomposition on various carbon surface models with or without N doping. Three theoretical cluster models of N-doped carbon surface containing different typical N-containing functional groups were developed according to the XPS characterization, and a pure carbon surface model was also constructed as a comparison. All the calculations were completed at BLYP/def2-SVP level using ORCA software.<sup>2</sup> Basis set superposition by means of geometrical correction<sup>3</sup> and dispersion correction<sup>4</sup> were taken into account. Since dispersion correction proved crucial when calculating the interaction between gas

molecule and carbon surface<sup>5</sup> and neglect of it could bring fatal error. Density fitting approximation was also used to accelerate the calculation without loss of accuracy.<sup>6-7</sup>

Noncovalent interactions analysis by means of the reduced density gradient<sup>8</sup> was carried out in Multiwfn<sup>9</sup> to claim the mechanism how N-doping could enhance CO<sub>2</sub> adsorption. The reduced density gradient isosurfaces ( $s = 0.6$  au) are colored on a blue-green-red scale according to values of  $\text{sign}(\lambda_2)\rho$  ranging from -0.04 to 0.02 au all through the paper. Large, negative values of  $\text{sign}(\lambda_2)\rho$  are indicative of attractive interactions (such as dipole–dipole or hydrogen bonding); while if  $\text{sign}(\lambda_2)\rho$  is large and positive, the interaction is nonbonding<sup>8</sup>. Values near zero indicate very weak, van der Waals interactions.<sup>8</sup> VMD software was employed for all the drawing throughout the paper.<sup>10</sup> Energy decompositions were carried by PSI4 software<sup>11</sup> at the level of SAPT0/jun-cc-PVDZ, which proves both reliable and computationally expedient.<sup>12</sup>



**Fig. S1.** (a) Nitrogen adsorption isotherm and corresponding DFT pore size distribution of PC. (b) Nitrogen adsorption isotherm and corresponding DFT pore size distribution of NPC-1; (c) Nitrogen adsorption isotherm and corresponding DFT pore size distribution of NPC-2. (d) Nitrogen adsorption isotherm and corresponding DFT pore size distribution of NPC-4 (melamine 2.4g).

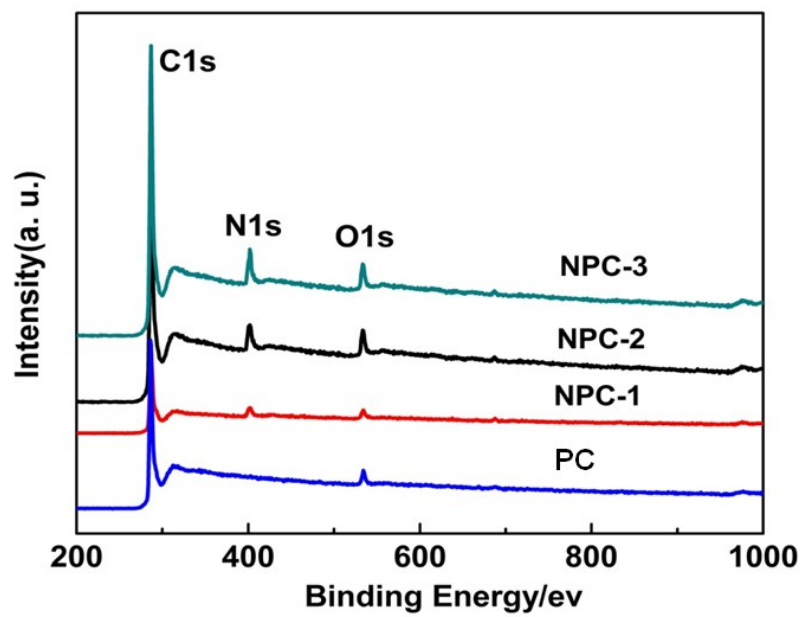
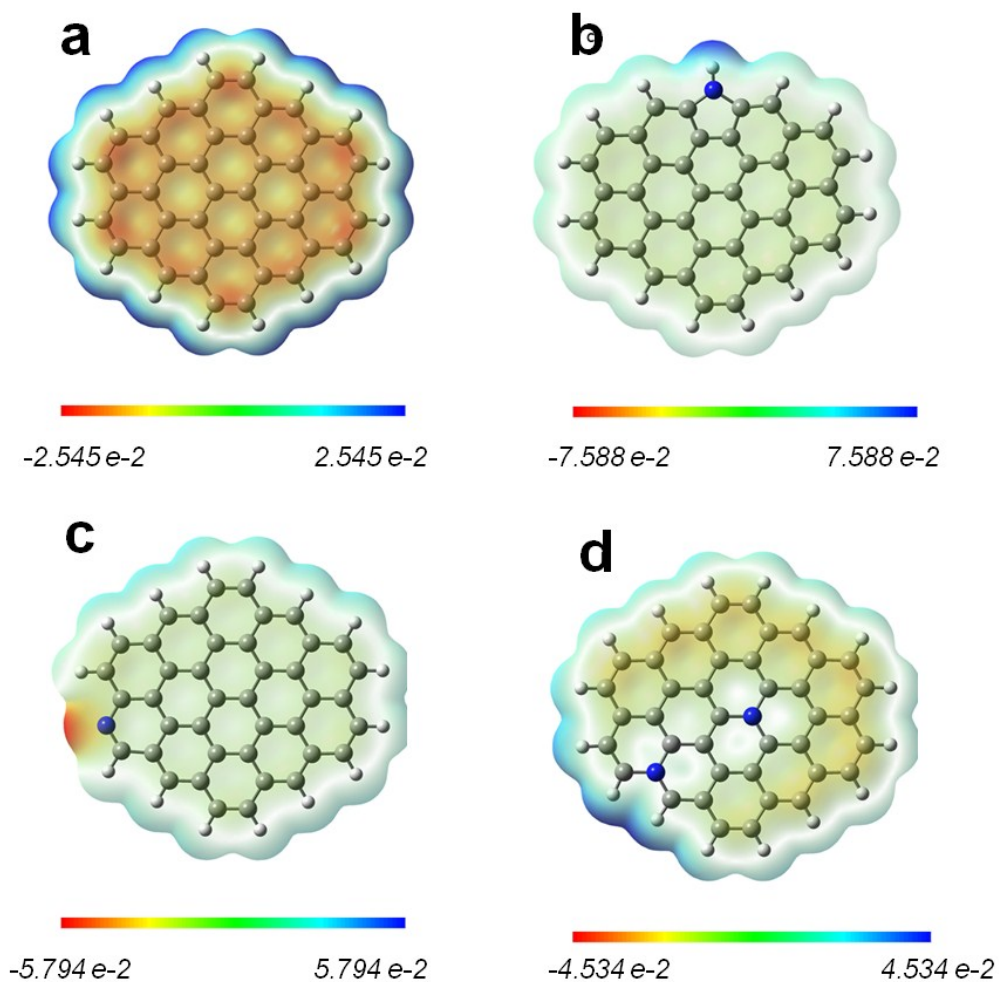
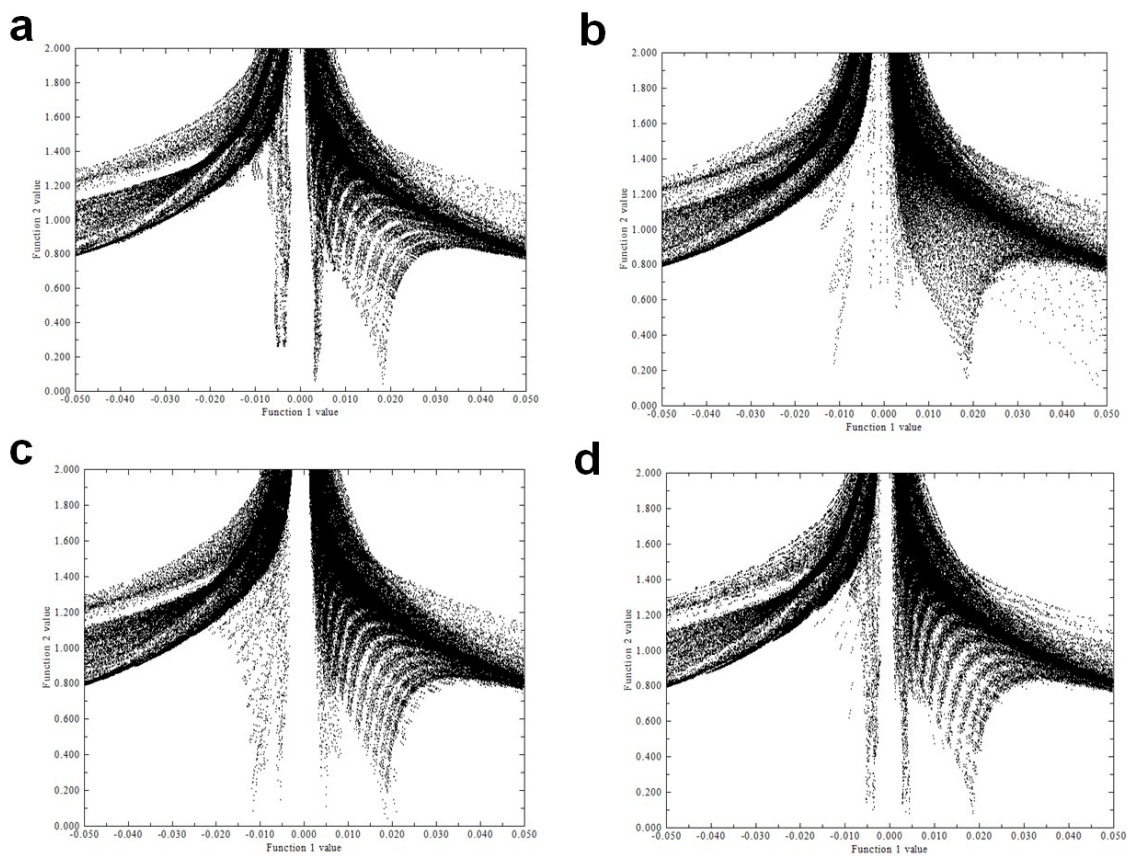


Fig. S2. XPS survey spectra of as-prepared NPC samples.



**Fig. S3.** Electrostatic potential maps on molecular surface of pure carbon surface and N-doped carbon surfaces. (a) pure carbon surface; (b) N-5 doped carbon surface; (c) N-6 doped carbon surface; (d) N-Q doped carbon surface. It's clear that when nitrogen atom is embedded into carbon surface, extremum points will show on the maps, which may induce extra  $\text{CO}_2$  adsorption sites or the polarization of carbon surface.



**Fig. S4.** Plots of sign ( $\lambda_2$ )  $\rho$  and reduced density gradient  $s$  for CO<sub>2</sub> adsorption on (a) basal plane of pure carbon surface; (b) edge position of N-5 doped carbon surface; (c) edge position of N-6 doped carbon surface; (d) basal plane of N-Q doped carbon surface. The data was obtained by evaluating BLYP/def2-SVP density and gradient values on grids.

**Table S1** Physicochemical characterization and CO<sub>2</sub> uptake capacities of prepared samples

<i>Samples</i>	<i>Melamine</i> (g)	<i>Pore parameters</i>		<i>XPS (at%)</i>			<i>C</i> <sub>CO2</sub> (mmol g <sup>-1</sup> ) <sup>d</sup>	<i>C</i> <sub>CO2</sub> (μmol m <sup>-2</sup> ) <sup>e</sup>
		<i>S</i> <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> ) <sup>a</sup>	<i>V</i> <sub>t</sub> (cm <sup>3</sup> g <sup>-1</sup> ) <sup>b</sup>	<i>C</i> <sup>c</sup>	<i>O</i> <sup>c</sup>	<i>N</i> <sup>c</sup>		
PC	0	1051	0.8	96.5	3.24	0.27	2.34	2.23
NPC-1	0.6	1042	0.56	91.9	3.78	4.25	3.59	3.45
NPC-2	1.2	1094	0.59	88.4	3.85	7.57	4.12	3.78
NPC-3	1.8	1013	0.55	86.1	3.66	10.2	4.32	4.27

a. Calculated by the BET model from the adsorption branches of the isotherms;

b. Single point pore volume calculated from adsorption data at  $P/P_0 = 0.982$ ;

c. Atom percentage of C, N and O elements obtained from XPS analysis;

d. Gravimetric CO<sub>2</sub> uptake amount under 0 °C and 1bar;

e. Areal CO<sub>2</sub> uptake obtained using gravimetric CO<sub>2</sub> uptake and the specific surface area.

## Notes and references

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