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# Superior CO<sub>2</sub> uptake of N-doped activated carbon through hydrogen-bonding interaction

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## SUPPORTING INFORMATION

### **Superior CO<sub>2</sub> Uptake on N-doped Activated Carbon through Hydrogen-Bonding Interaction**

*Wei Xing, \* Chao Liu, Ziyan Zhou, Lei Zhang, Jin Zhou, Shuping Zhuo, \* Zifeng Yan, \* Hong Gao, Guiqiang Wang, Shi Zhang Qiao\**

[\*] Prof. W. Xing, Mr. C. Liu, Prof. Z. Zhou, Dr. J. Zhou, Prof. S. Zhuo, Prof. G. Wang

School of Chemical Engineering, Shandong University of Technology  
Zibo 255049 (P. R. China)

E-mails: xingwei@sdut.edu.cn, zhuosp@sdut.edu.cn

Dr. L. Zhang, Dr. H. Gao

State Key Laboratory of Catalysis

Dalian Institute of Chemical Physics, Chinese Academy of Science, 457 Zhongshan Road, Dalian 116023 (P. R. China)

Prof. Z. F. Yan

State Key Laboratory of Heavy Oil Processing

Key Laboratory of Catalysis, CNPC

School of Chemical Engineering, China University of Petroleum, 66, Changjiang West Road

Qingdao 266580 (P. R. China)

Email: zfyancat@upc.edu.cn

Prof. S. Z. Qiao

School of Chemical Engineering

The University of Adelaide, SA5005 (Australia)

Email: s.qiao@adelaide.edu.au

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**Table S1** Surface area and pore-structure parameters of the activated carbons

Sample	$S_{\text{BET}}^{[a]}$ ( $\text{m}^2/\text{g}$ )	$V_{\text{Micro}}^{[b]}$ ( $\text{cm}^3/\text{g}$ )	$V_{\text{total}}^{[c]}$ ( $\text{cm}^3/\text{g}$ )	Pore Size $^{[d]}$ (nm)
SK-0.3-700	579	0.23	0.29	2.34
SK-0.5-600	710	0.29	0.44	2.52
SK-0.5-700	1060	0.44	0.52	2.49
SK-0.5-800	1134	0.46	0.68	2.40
SK-0.5-900	1193	0.48	0.71	2.38
SK-1-700	1316	0.55	0.63	2.60
SK-2-700	1395	0.56	0.86	2.47
SK-3-700	2040	0.82	0.89	2.17
SK-4-700	2792	0.92	1.04	2.14

<sup>[a]</sup> BET specific surface area. <sup>[b]</sup> Micropore volume calculated by modern NLDT method. <sup>[c]</sup> Single point total pore volume measured at  $p/p^0 = 0.995$ . <sup>[d]</sup> Pore size =  $4V_{\text{total}}/S_{\text{BET}}$ .

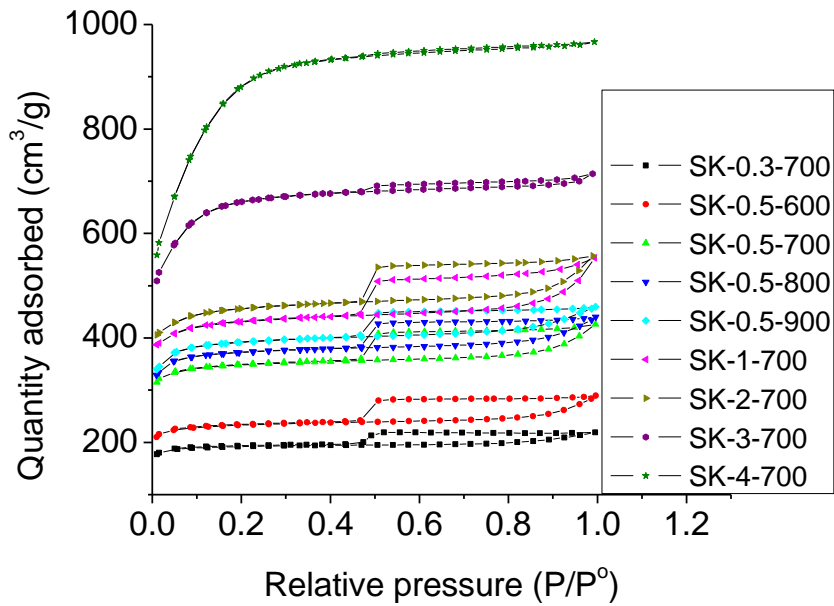
**Table S2** Surface composition of the activated carbons

sample	Concentration (mmol/g)					
	Total N	Pyridine	$\text{PhNH}_2\text{--C=NH}$	Pyrrole	Quaternary N	Oxynitride
SK-0.3-700	0.31	0.048	0.072	0.106	0.06	0.024
SK-0.5-600	0.25	0.038	0.058	0.089	0.056	0.009
SK-0.5-700	0.2	0.034	0.056	0.072	0.033	0.005
SK-0.5-800	0.11	0.007	0.03	0.035	0.022	0.016
SK-0.5-900	0.08	0.018	0.016	0.013	0.008	0.025
SK-4-700	0.13	0.029	0.005	0.004	0.082	0.01

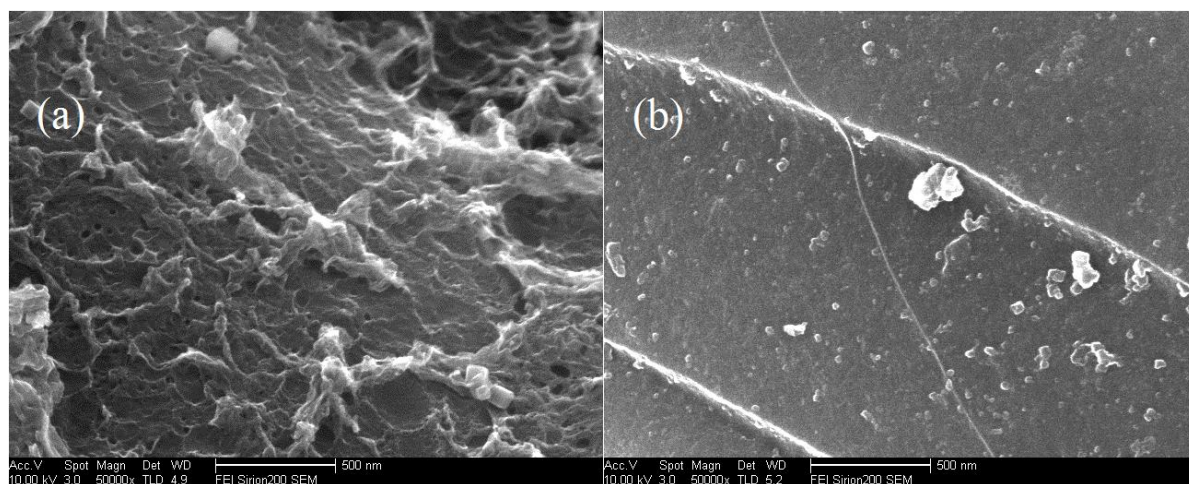
**Table S3** The total energies for NCSM-CO<sub>2</sub> and CSM-CO<sub>2</sub> complexes <sup>[a]</sup>

Species	$E_{\text{zero}}$ (a.u.)	$E_{\text{total}}$ (a.u.)	$\Delta E_i$ (kJ/mol)	Species	$E_{\text{zero}}$ (a.u.)	$E_{\text{total}}$ (a.u.)	$\Delta E_i$ (kJ/mol)
NCSM	0.326922	-1384.8532479	---	CSM	0.392071	-1230.3673953	---
NCSM -CO <sub>2</sub> -1	0.338920	-1573.4464803	7.46	CSM-CO <sub>2</sub> -1	0.403779	-1418.9583021	1.35
NCSM -CO <sub>2</sub> -2	0.338858	-1573.4458879	5.90	CSM-CO <sub>2</sub> -2	0.403665	-1418.9583340	1.43
NCSM -CO <sub>2</sub> -3	0.338844	-1573.4465088	7.53	CSM-CO <sub>2</sub> -3	0.403710	-1418.9580147	0.60
NCSM -CO <sub>2</sub> -4	0.338789	-1573.4459003	5.93	CSM-CO <sub>2</sub> -4	0.403790	-1418.9584483	1.73
NCSM -CO <sub>2</sub> -5	0.338903	-1573.4468563	8.44	CSM-CO <sub>2</sub> -5	0.403716	-1418.9582739	1.28
NCSM -CO <sub>2</sub> -6	0.338757	-1573.4457918	5.65	CSM-CO <sub>2</sub> -6	0.403642	-1418.9580932	0.80
NCSM -CO <sub>2</sub> -7	0.339117	-1573.4480562	11.59	CSM-CO <sub>2</sub> -7	---	---	---
NCSM -CO <sub>2</sub> -8	0.339101	-1573.4475194	10.18	CSM-CO <sub>2</sub> -8	0.403608	-1418.9584041	1.62

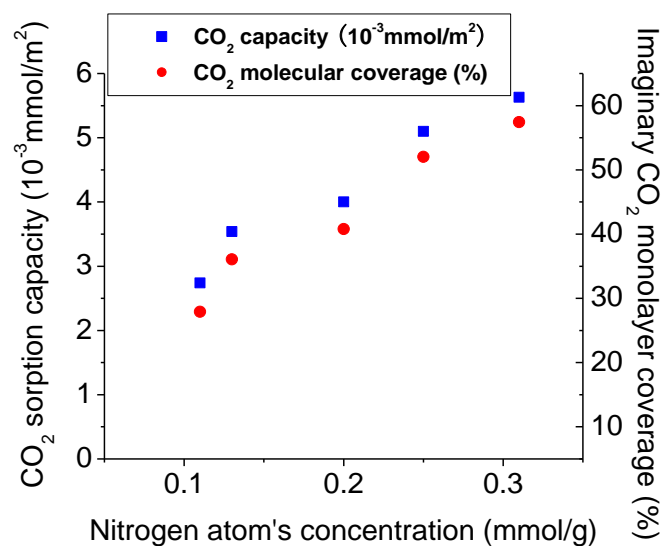
<sup>[a]</sup>  $E(\text{CO}_2)$  : -188.5903926 a.u.;  $\Delta E_i = [E_{\text{total}}(\text{M}) + E(\text{CO}_2)] - E_{\text{total}}(\text{M-CO}_2-i)$ , where M represents NCSM or CSM, and  $i$  represents 1,2,3,4,5,6,7,8;  $\Delta E_i$  is equal to hydrogen bond energy.



**Figure S1** N<sub>2</sub> adsorption isotherms for all the carbons investigated



**Figure S2** SEM images of (a) SK-0.5-700 and (b) SK-4-700



**Figure S3** The plot of CO<sub>2</sub> adsorption capacity per unit surface area and imaginary CO<sub>2</sub> monolayer coverage on the surface of carbon versus the nitrogen content of the carbons

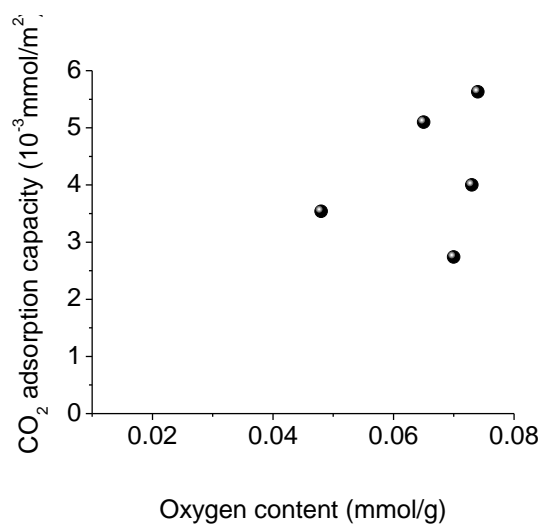
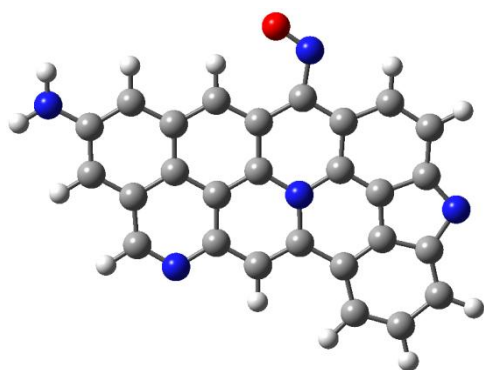
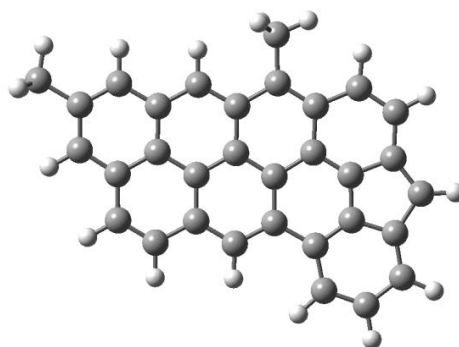


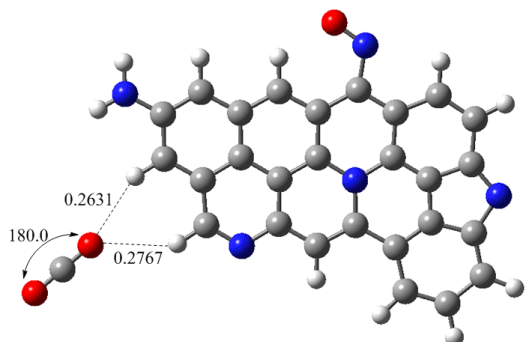
Figure S4 A plot of CO<sub>2</sub> adsorption capacities vs. oxygen contents of the carbons



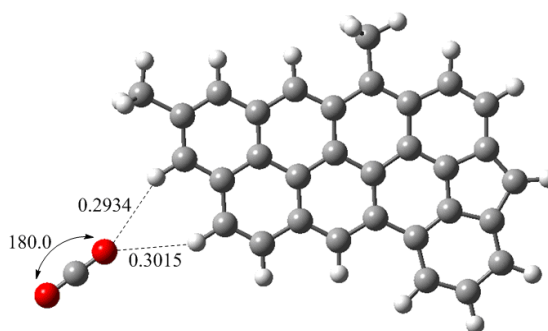
NCSM:  $E = -1384.8532479$  a.u.



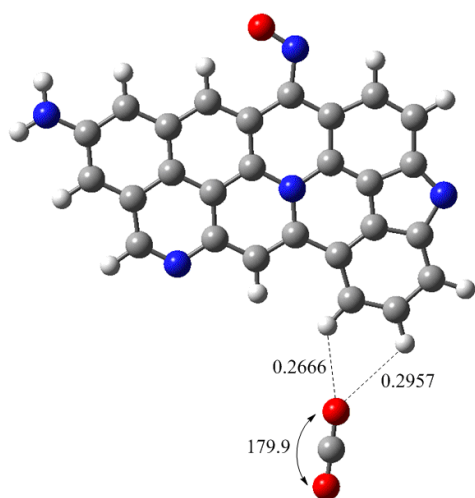
CSM:  $E = -1230.3673953$  a.u.



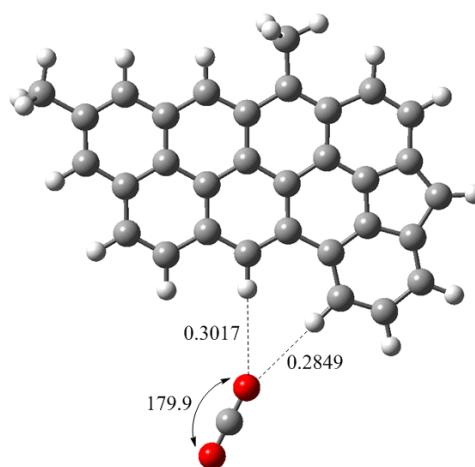
NCSM-CO<sub>2</sub>-1:  $E = -1573.4464803$  a.u.



CSM-CO<sub>2</sub>-1:  $E = -1418.9583021$  a.u.

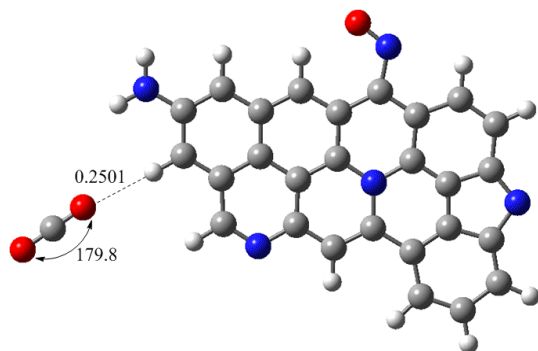


NCSM-CO<sub>2</sub>-2:  $E = -1573.4458879$  a.u.

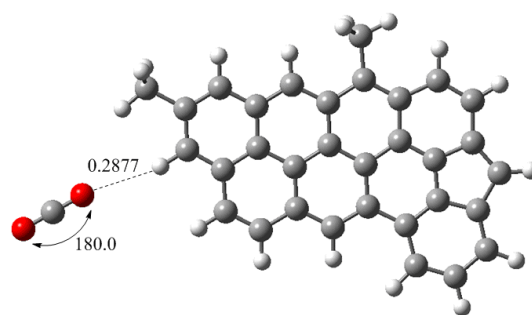


CSM-CO<sub>2</sub>-2:  $E = -1418.9583340$  a.u.

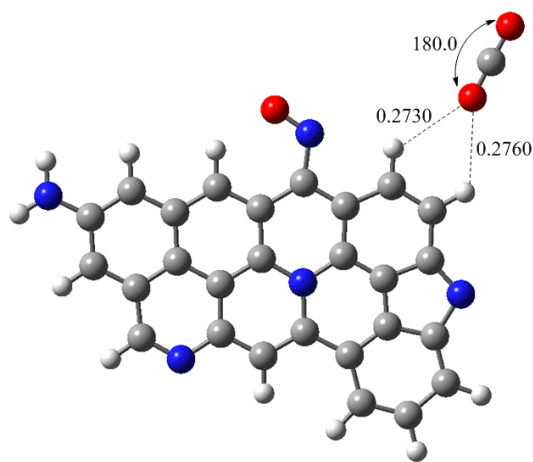




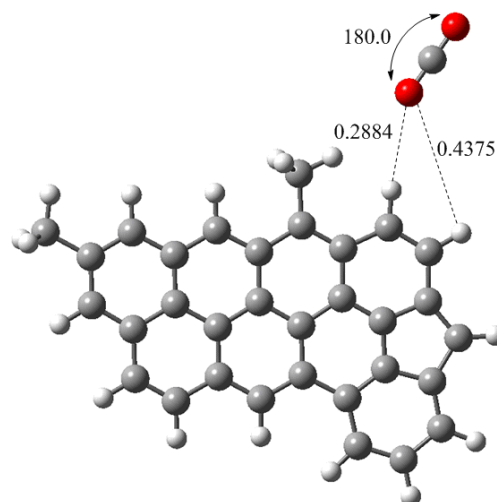
NCSM-CO<sub>2</sub>-3: E= -1573.4465088 a.u.



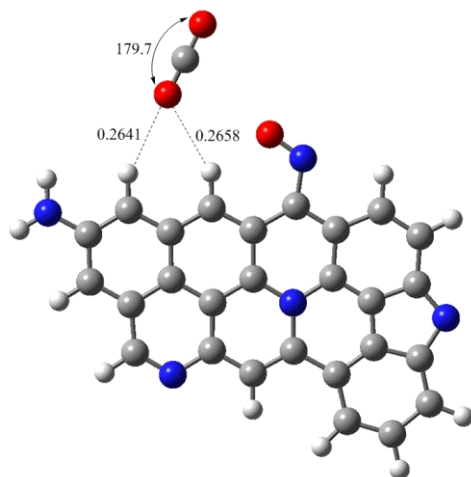
CSM-CO<sub>2</sub>-3: E=-1418.9580147 a.u.



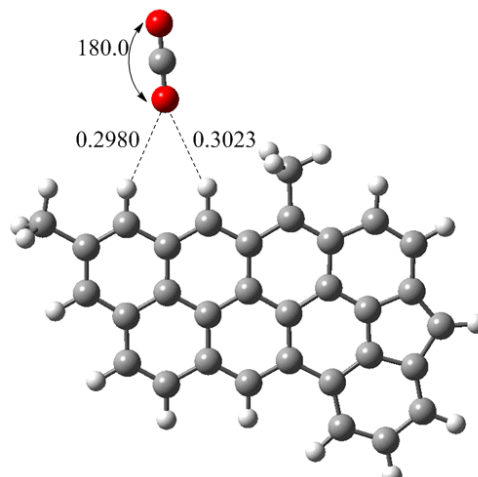
NCSM-CO<sub>2</sub>-4: E=-1573.4459003 a.u.



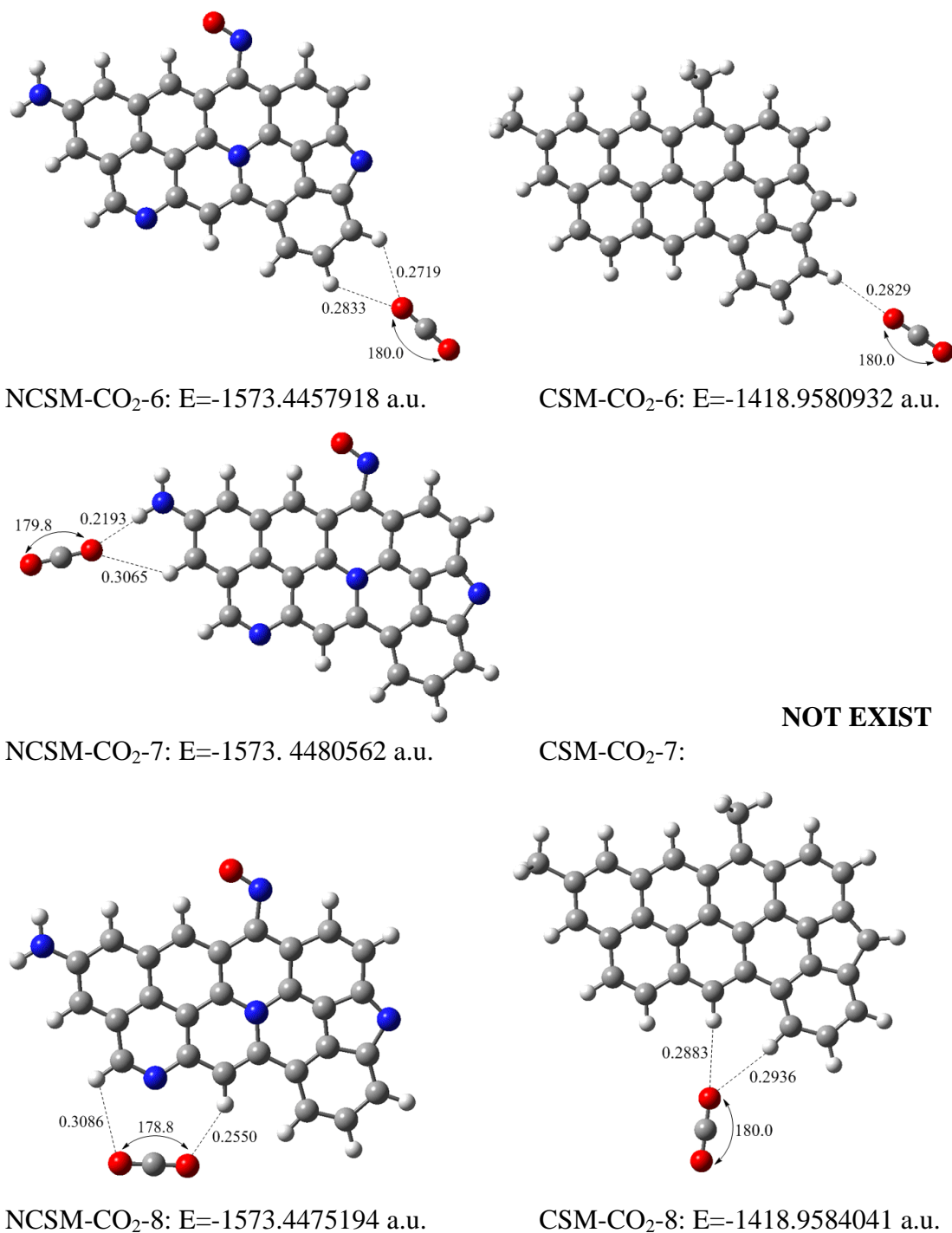
CSM-CO<sub>2</sub>-4: E=-1418.9584483 a.u.



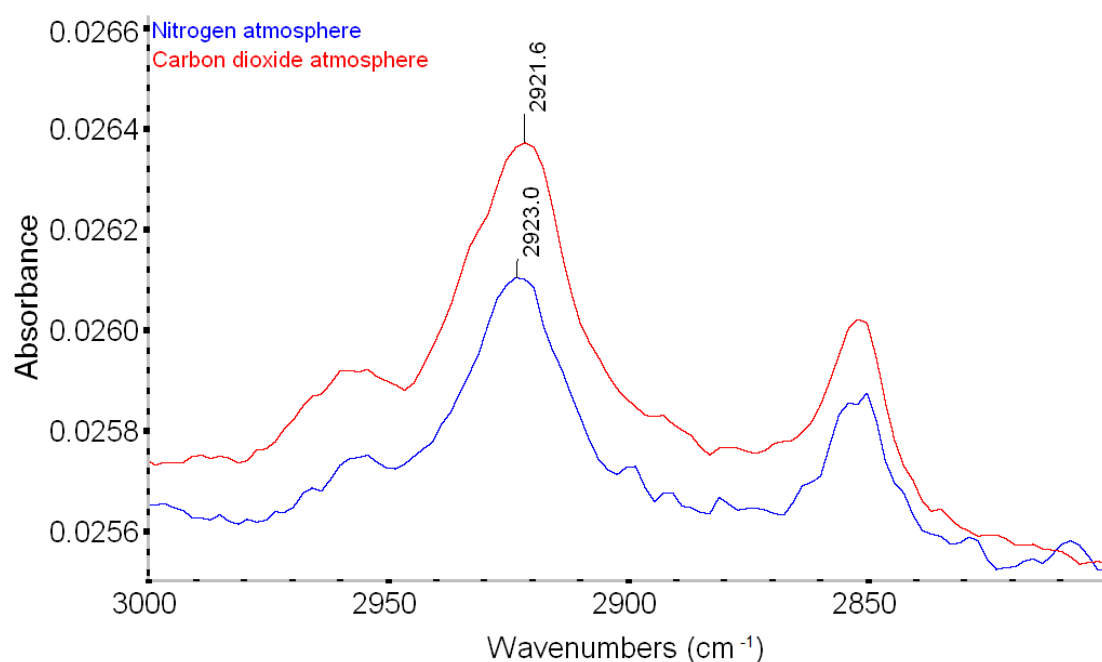
NCSM-CO<sub>2</sub>-5: E=-1573.4468563 a.u.



CSM-CO<sub>2</sub>-5: E=-1418.9582739 a.u.

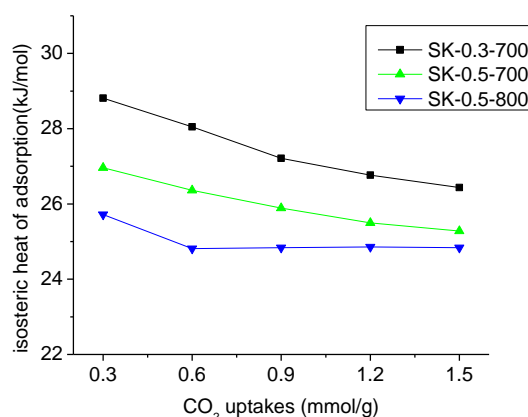


**Figure S5** Geometric configurations and total energies for NCSM, CSM, NCSM-CO<sub>2</sub> complexes and CSM-CO<sub>2</sub> complexes simulated by Gaussian03 package <sup>[1]</sup>. (red ball: oxygen atom; blue ball: nitrogen atom; grey ball: carbon atom; small grey ball: hydrogen atom). The units for bond length and bond angle are nm and degree, respectively.



**Figure S6** FT-IR spectra of the activated carbon measured under different atmosphere

The infrared spectra of SK-0.3-700 were recorded under N<sub>2</sub> and CO<sub>2</sub> atmosphere, respectively, using a Nicolet 5700 infrared spectrometer with an accuracy of 0.1 cm<sup>-1</sup>. Under N<sub>2</sub> atmosphere, the peak at 2923.0 cm<sup>-1</sup> was attributed to the C-H anti-symmetric stretching vibration. When the atmosphere was switched to CO<sub>2</sub>, this peak was broadened and red-shifted to 2921.6 cm<sup>-1</sup>. It is reported that hydrogen-bonding interactions can weaken the C-H bond energy, which results in the peak widening and red-shift of corresponding peak in FT-TR spectra.<sup>[2, 3]</sup> This phenomenon proved that hydrogen-bonding interactions do exist between carbon surface and CO<sub>2</sub> molecules, which is well fitted with the quantum chemical calculations conducted in this work.



**Figure S7** Isosteric heats of CO<sub>2</sub> adsorption on activated carbons at different CO<sub>2</sub> uptakes

The isosteric heats of adsorption were calculated according to Clausius-Clapeyron equation:

$$\ln\left(\frac{p_1}{p_2}\right) = Q_{st} \times \frac{T_2 - T_1}{R \times T_1 \times T_2} \quad (1)$$

where  $Q_{st}$  is the isosteric heats of adsorption,  $T_i$  represents a temperature at which an isotherm  $i$  is measured,  $p_i$  represents a pressure at which a specific equilibrium adsorption amount is reached at  $T_i$ ,  $R$  is gas constant ( $8.314 \text{ J/(K mol}^{-1}\text{)}$ ). As is shown in Figure S7, the isosteric heats of CO<sub>2</sub> adsorption on the carbons are between 24 to 30 kJ/mol. The isosteric heat of adsorption of SK-0.3-700 (with N content of 0.31 mmol/g) is higher than that of SK-0.5-800 (with N content of 0.11 mmol/g) by 1.5~3 kJ/mol, which roughly agrees with the calculated binding energy difference (about 6.5 kJ/mol) between NCSM-CO<sub>2</sub> and CSM-CO<sub>2</sub> complexes. This energy difference indicates that N-doping on carbon surface will increase the isosteric heat of CO<sub>2</sub> adsorption by about 6.5 kJ/mol.

The binding energies for NCSM-CO<sub>2</sub> or CSM-CO<sub>2</sub> complexes are calculated based on interactions between a ideal graphene-like model and CO<sub>2</sub> molecules. In contrast, CO<sub>2</sub> adsorption on micropore surface is apparently different from what is depicted by this ideal interacting model. As is well known, micropores have strong adsorption potential, resulting in high heat of gas adsorption on micropores. That is to say, the binding energies for NCSM-CO<sub>2</sub> or CSM-CO<sub>2</sub> complexes can not reflect the absolute value of adsorption heat on micropores, but somehow reflect the effect of N-doping on heat of gas adsorption.

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