Supporting Information

Highly Selective CO_2 Capturing on N-doped porous carbon produced by Chemical Activation of Polypyrrole Functionalized Graphene Sheets

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EXPERIMENTAL SECTION

Materials. Graphite (300 mesh, Alfa Aesar), sodium nitrate (Aldrich), potassium permanganate (Aldrich), hydrogen peroxide (30% wt, Aldrich), sulfuric acid, hydrochloric acid, hydrazine (80%, Aldrich) ammonium persulphate (Aldrich), pyrrole (Aldrich), potassium hydroxide (90%, flakes, Sigma-Aldrich), CO_2 (99.999%, Aldrich), and N_2 (99.999%, Aldrich).

Synthesis of PGC and a-PGC. Graphene oxide (GO) was synthesized by Hummers method through oxidation of graphite [1]. The required amount of graphene oxide (25, 50 and 75wt. %) and pyrrole were dispersed in 100 ml water at 0°C in a sonication bath. A pre-cooled solution of ammonium per sulphate (APS), weight ratio (pyrrole/APS= ¼), was added to a GO-pyrrole solution at 0-5 ^{o}C with constant stirring [2]. After 10 h of polymerization, the product was washed with a large amount of water and redispersed in 100 ml distilled water. At 90^{o}C, the required amount of hydrazine hydrate was added and reduction was allowed to proceed for 12 h. Synthesis of polypyrrole was carried out in the same way in the absence of graphene oxide. The products were vacuum dried at 40 °C for 24 h.

The activation of PGC was achieved using a 7M potassium hydroxide solution [3-4]. 150 mg of PGC was dispersed in 10 ml of 7M KOH and stirred at room temperature for 24 hours. The product was filtered using Millipore filter paper (0.22 μm) and dried in an oven at 70 ^{o}C. Chemical activation was carried out for 1 hour in a tubular furnace under a N_2 gas flow (100 sccm) at 400-700 ^{o}C temperature (heating rate 3^{o}C/min). After activation the product was washed with an 8% HCl solution to neutralize KOH and dried under vacuum at 70 ^{o}C for 24 hours.

Materials Characterization. X-ray diffraction patterns (XRD) were recorded on a Riguka, Japan, RINT 2500 V X-ray diffraction-meter using Cu K_α irradiation (λ = 1.5406 Å). Fourier transformed infrared (FT-IR) spectra were recorded in KBr pellets with a Bruker FTIR. Raman spectra were carried out using a Senterra Raman Scope system with a 532nm wavelength incident laser light and power 20 mW. Scanning electron microscopy (SEM) images of the product were taken on a field emission scanning electron microscope (FESEM, JEOL, FEG-XL 30S). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) analyses were made with a JEM-2200F (Cs corrected TEM (NCNT)) electron microscope with an accelerating voltage of 200 kV. XPS analyses were performed with an ESCALAB-220I-XL (THERMO-ELECTRON, VG Company) device. Photoemission was stimulated by a nonmonochromatized Mg K_α source (1253.6 eV) for all samples.

Gas Adsorption Measurements. Gas adsorption measurements were carried out using a Belsorp mini II (Japan) device. Before each measurement the samples were heat treated at 100 ^{O}C in vacuum for 24 hours. BET surface area and pore size was calculated from N_2 adsorption–desorption isotherms measured at 77K. CO_2 adsorption isotherms were measured at 298 K and up to 1 bar pressure.

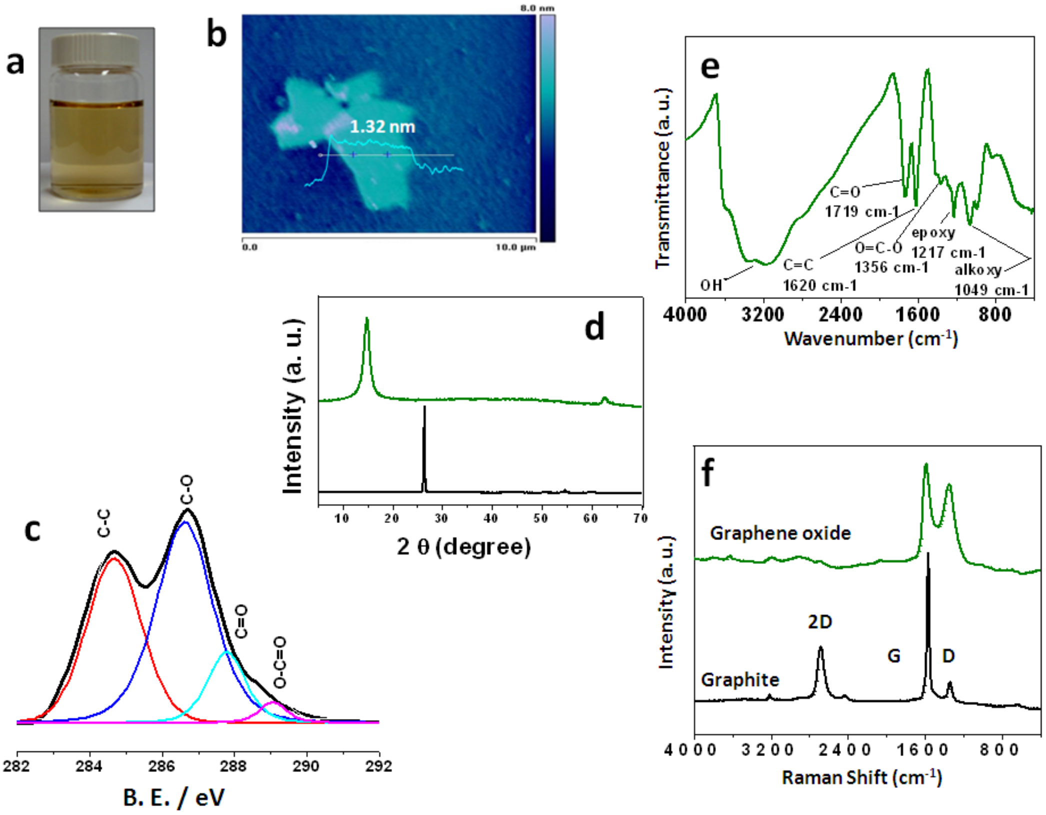

Figure S1. (a) Aqueous solution of graphene of concentration 0.5 mg/ ml. (c) XPS spectra of graphene. (b) AFM image of graphene oxide on mica sheet.Graphene oxide for C1s shows binding energy for oxygenated and nonoxygenated carbon. (d) Powder X-ray diffraction pattern shows low angle shift of 002 peak of graphite due to intercalation of functional groups. (e) FTIR spectra shows the presence of carbonyl C=O (1719 cm-1), aromatic C=C (1620 cm-1), carboxyl O=C-O (1356 cm-1), epoxy C-O (1217 cm-1), and alkoxy C-O (1049 cm-1) functional groups. (f) Raman spectra show broad D and G bands as compared to those of the graphite. These characterizations suggest formation of graphene oxide, in good agreement with the previous reports [1-3].

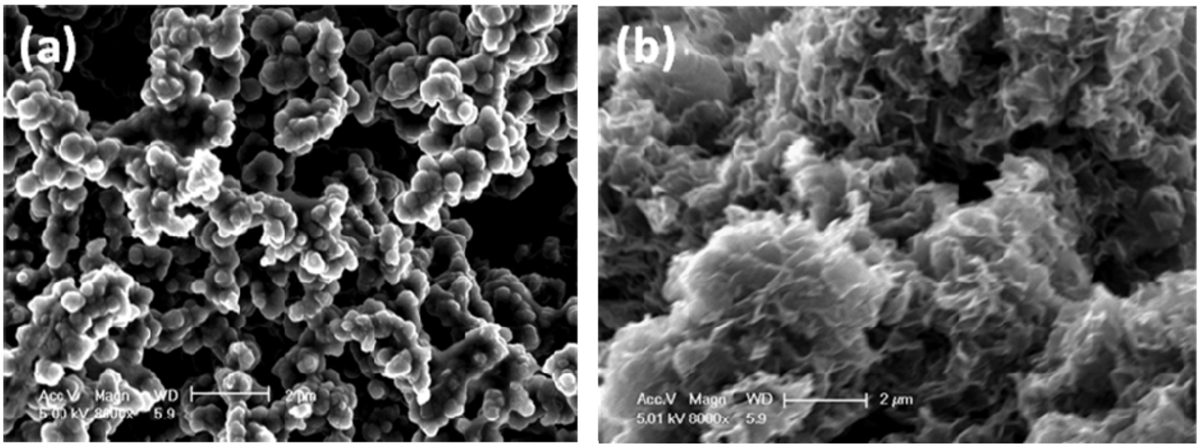

Fig. S2. SEM image of polypyrrole (a) and RGO (b).

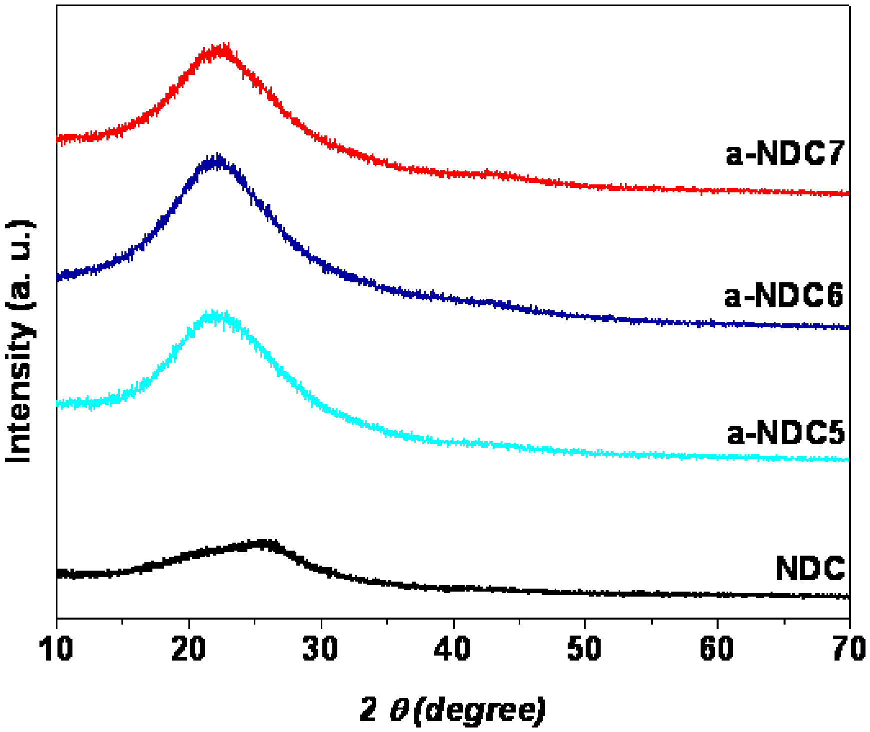

Figure S3. Powder X-ray diffraction pattern of adsorbents before and after chemical activation, showing the formation of amorphous phase.

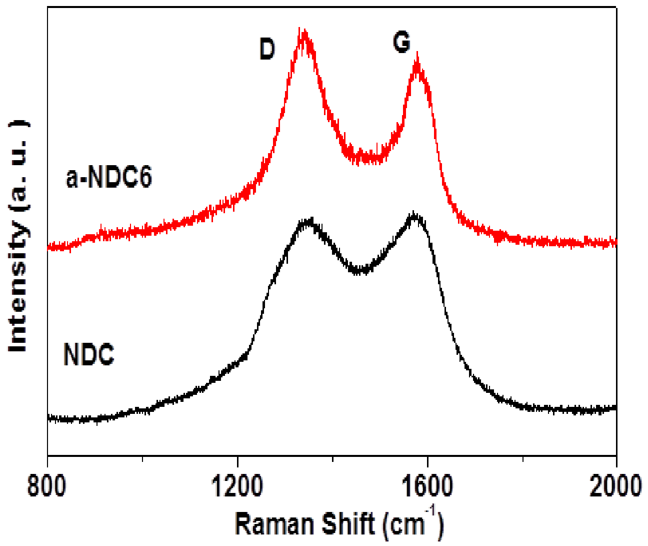

Figure S4. Raman spectra of NDC and a-NDC6.

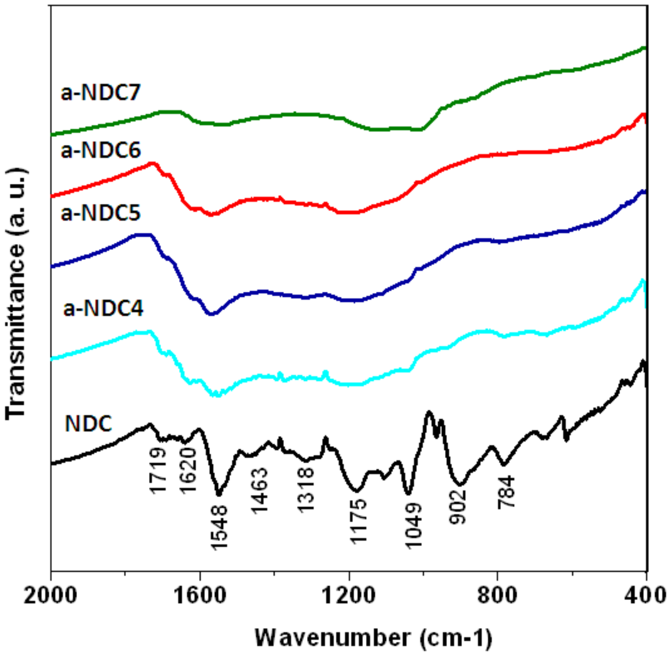

Figure S5. FTIR spectra of NDC and a-NDC (400, 500, 600 and 600 degree C).

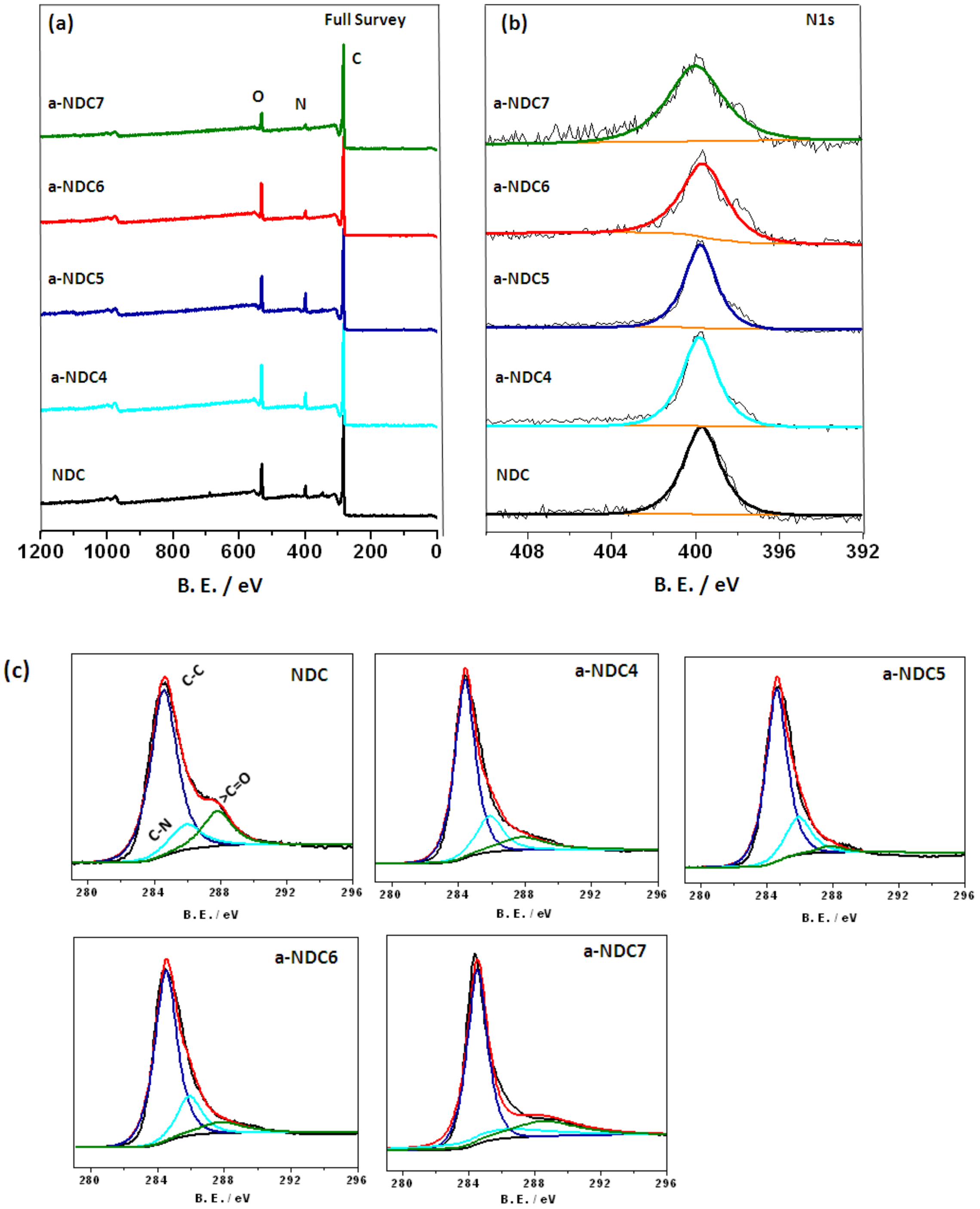

Figure S6. XPS spectra of adsorbents (a) Full Survey (b) Survey for N and (c) survey for C.

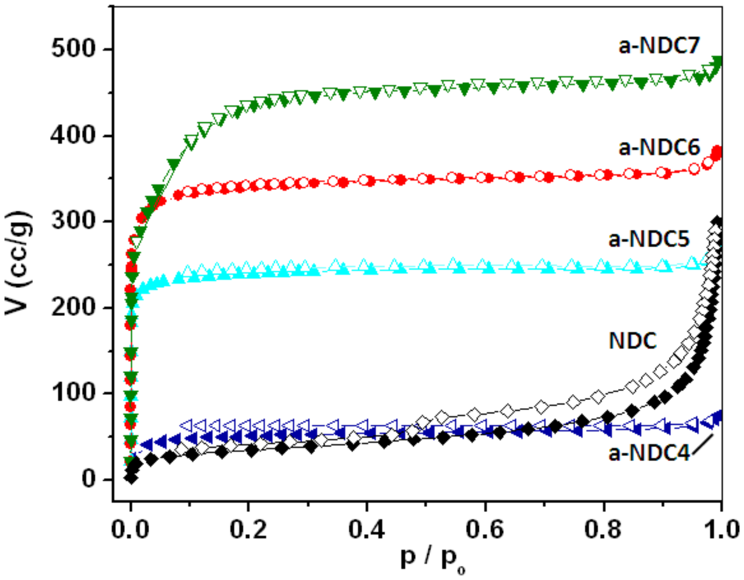

Figure S7. N_2 adsorption – desorption for NDC and a- NDC.

TableS1. Physical properties and chemical composition of the adsorbent (T: Activation temperature, SSA: specific surface area, V: pore volume, d: pores size).

Activation Temp. (°C)	BET Method			MP Method		Atomic %		
	SSA (m^2/g)	V (cm^3/g)	d (nm)	V (cm^3/g)	d (nm)	C (atom %)	O (atom %)	N (atom %)
-	122	0.45	14.72	0.01	0.7	64.6	24	7.5
400	193	0.11	2.33	0.09	0.7	77.2	14.6	7.3
500	952	0.41	1.73	0.41	0.6	81.2	11.3	7.0
600	1360	0.59	1.72	0.57	0.6	82.5	12.0	4.8
700	1588	0.75	1.88	0.73	0.8	91.1	6.2	2.7

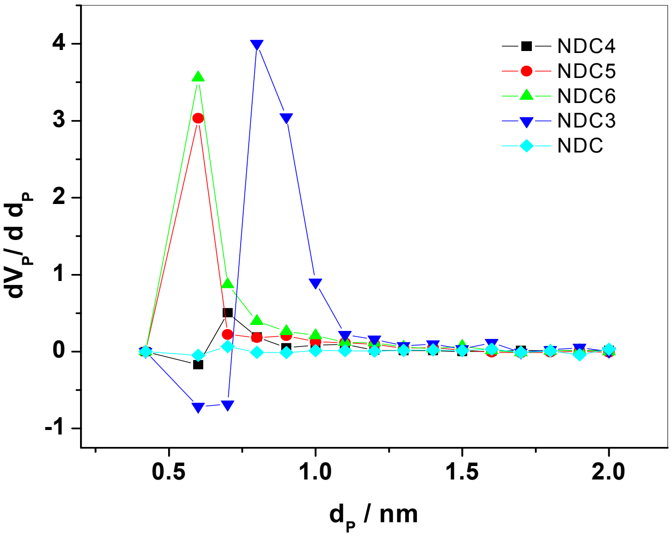

Figure S8. Pore volume distribution calculated by the MP method

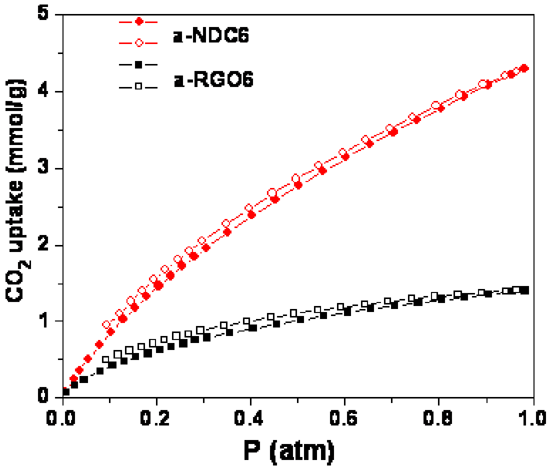

Figure S9. CO_2 adsorption isotherms for a-RGO6 and a-NDC6 at 298^{O}K (filled symbols –adsorption and open symbols - desorption).

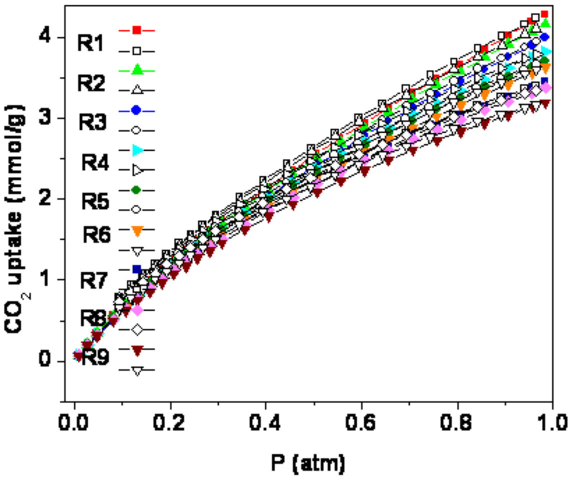

Figure S10. Cyclic adsorption of CO_2 for a-NDC6 at 298K via vacuum desorption.

Selectivity of CO_2 over N_2 was calculated using Henry's Law. The initial slopes were calculated from CO_2 and N_2 adsorption isotherms as reported earlier [5].

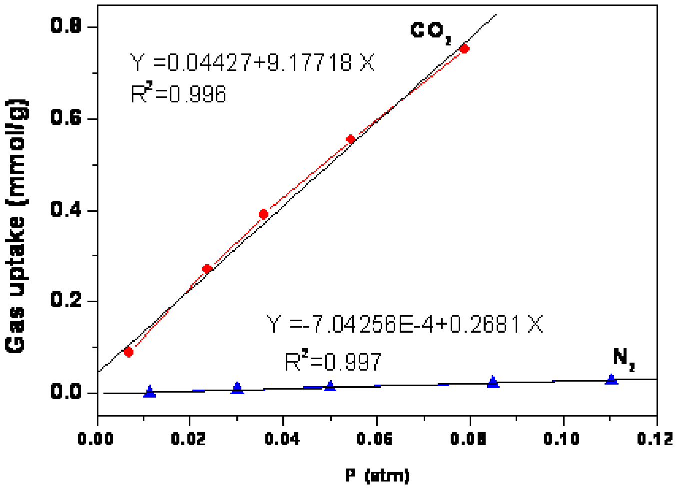

Figure S11. Initial slopes calculation from CO_2 and N_2 adsorption isotherms at 298K for a-NDC6.

References

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