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## Facile Synthesis of Nitrogen-Doped Porous Carbon for Selective CO<sub>2</sub> Capture

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### Abstract

Solid-state post-combustion CO<sub>2</sub> sorbents have certain advantages over traditional aqueous amine systems, including reduced regeneration energy since vaporization of liquid water is avoided, tunable pore morphology, and greater chemical variability. We report here an ordered mesoporous nitrogen-doped carbon made by the co-assembly of a modified-pyrrole and triblock copolymer through a soft-templating method, which is facile, economic, and fast compared to the hard-template approach. A high surface area mesoporous carbon was achieved, which is comparable to the silica counterpart. This porous carbon, with a *Brunauer–Emmett–Teller* (BET) specific surface area of 804.5 m<sup>2</sup> g<sup>-1</sup>, exhibits large CO<sub>2</sub> capacities (298 K) of 1.0 and 3.1 mmol g<sup>-1</sup> at 0.1 and 1 bar, respectively, and excellent CO<sub>2</sub>/N<sub>2</sub> selectivity of 51.4. The porous carbon can be fully regenerated solely by inert gas purging without heating. It is stable for multiple adsorption/desorption cycles without reduction in CO<sub>2</sub> capacity. These desirable properties render the nitrogen-doped hierarchical porous carbon a promising material for post-combustion CO<sub>2</sub> capture.

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## 1. Introduction

The effect of increasing atmospheric CO<sub>2</sub> concentration on global climate change is recognized as one of the most important environmental issues facing society today [1]. The levels of CO<sub>2</sub> in the atmosphere have reached a monthly average of 397 ppmv at Mauna Loa observatory as of August 2014 [2], an increase of over 100 ppmv from the pre-industrial era. Although amine-based absorption is the current state-of-the-art technology for capturing CO<sub>2</sub>, it is not clear that absorption technologies alone will lead to the cost reductions required to achieve a gigaton-scale solution to CO<sub>2</sub> emissions. For this reason, adsorption technologies have been attracting increasing interests for research and development.

Adsorption-based technologies for CO<sub>2</sub> capture have several advantages over the traditional amine-based solvent absorption approaches [3]. For instance, within an adsorption-based approach water is absent, which decreases the energy requirements associated with regeneration since heating a large amount of water is the greatest energetic expense associated with CO<sub>2</sub> capture using solvent-based approaches. The heat of regeneration of a solvent-based separation process is  $C_p\Delta T + \Delta H$ , such that  $C_p$  is the heat capacity of the solvent and  $\Delta H$  is the heat of reaction required for breaking the chemical bond between CO<sub>2</sub> and the chemical species (e.g., amine) responsible for capturing CO<sub>2</sub>. The heat capacity of water is 4.18 J/gK, while that of sorbents is on the order of 1 J/gK. Another benefit of using solid sorbents is the ability to tune the structural parameters of the material, as well as perform chemical modifications to enhance CO<sub>2</sub> uptake. In addition, materials such as carbon possess favorable heat conduction properties. Mesoporous carbons are potential candidates for CO<sub>2</sub> capture due to their chemical inertness, low cost, high surface area, and tunable pore structures [4-6]. Their porous structures and high surface areas allow addition of chemical functionality by grafting or impregnation. Nitrogen functionalization plays an important role in surface chemistry to achieve enhanced CO<sub>2</sub> adsorption capacity [7].

This work mainly focuses on the facile synthesis of nitrogen-doped mesoporous carbon sorbent with high surface area and ordered pore structures for post-combustion CO<sub>2</sub> capture. Nitrogen-doped carbon was prepared by a soft-templating method. Pluronic P-123, a triblock copolymer, was used as building blocks for the soft template in aqueous solution. A pyrrole derivative with a hydrophilic side group was chosen as nitrogen containing monomer and was allowed to self-assemble onto the soft template followed by polymerization. Removal of the templates at elevated temperature resulted in highly ordered porous structures. The hierarchical structures with macroscopic interconnecting networks and hexagonal-packing mesoscopic pore channels were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. Pore analysis was performed using nitrogen as probe gas. The Brunauer–Emmett–Teller (BET) surface area and total pore volume were found to be 804 m<sup>2</sup>/g and 0.88 cm<sup>3</sup>/g, respectively. The CO<sub>2</sub> adsorption performance of the nitrogen-doped porous carbon was evaluated under both static equilibrium and dynamic conditions. At 298 K, the nitrogen-doped carbon showed CO<sub>2</sub> capacities of 1.0 and 3.1 mmol/g at 0.1 and 1 bar of CO<sub>2</sub>, respectively. A high CO<sub>2</sub>/N<sub>2</sub> selectivity of 51:1 was found. Furthermore, dynamic column breakthrough experiments were performed which gives consistent CO<sub>2</sub> capacity compared to static equilibrium data. The porous carbon was found to retain its CO<sub>2</sub> capacity over multiple adsorption/desorption cycles with the ease of CO<sub>2</sub> release and minimal regeneration energy requirement. All of these properties suggest its potential in practical column adsorption applications.

## 2. Experimental Methods

### 2.1 Material and Synthesis

All reagents were purchased from Sigma Aldrich without further purification. Triblock copolymer Pluronic P-123 is used as the soft template for the synthesis of mesoporous polypyrrole. Hydrochloric acid and ice water bath were used to control the solution pH and temperature, respectively. Ferric chloride was added to the aqueous solution to radically polymerize the pyrrole derivative over the soft template surfactant in a controlled manner.

In a typical synthesis, 0.598 g of Pluronic P-123 and 1.14 g of Ferric chloride was added to 15 ml Millipore water and 2.5 ml 12 M HCl in an ice water bath. The solution was vigorously stirred for 2 hours before the pyrrole derivative was added drop-wise to the solution matrix. After vigorous stirring for 20 minutes, the solution with ice water bath was allowed to age for 20 hours, followed by hydrothermal heating to 100 °C to complete the

polymerization of the pyrrole derivative. The hydrothermal product was then filtered and washed with de-ionized water repeatedly to remove excess ions. The polymer composite was then calcined at 800 °C for 2 hour in a horizontal tube furnace (25-mm diameter), with nitrogen flow of 75 sccm and working pressure of ~520 Torr. The polymer was heated at a ramp rate of 1°C/min from temperature before 600 °C and 5°C/min ramp for temperature above 600 °C with a 3 hours hold at 350 °C to slowly decompose the triblock copolymer surfactant to produce the final porous carbon.

## 2.2 Characterization Methods

Transmission electron microscopy (TEM) investigations were performed using a 200 kV TEM FEI Tecnai T20 instrument. Scanning electron microscopy (SEM) was performed using an FEI Magellan 400 XHR microscope with a 5 kV accelerating voltage and 25 pA current. TG analysis was carried out using a Mettler Toledo TGA- sDTA851 analyzer (Switzerland) from 25 to 800 °C under nitrogen a heating rate of 5 °C min<sup>-1</sup>. Freeze drying (FD) was performed using Labconco FreeZone 4.5L Benchtop Freeze Dry system.

Nitrogen and CO<sub>2</sub> sorption experiments were performed using an Autosorb iQ (Quantachrome) low-pressure gas sorption analyzer. The samples were outgassed at 0.001 torr and 200 °C for 12 hours prior to measurements. Nitrogen physisorption was carried out using 99.999% N<sub>2</sub> at 77 K. Pore size distributions (PSD) were obtained using quenched solid-state density functional theory (QSDFT) calculations with carbon model of slit, spherical and cylindrical pores. Surface areas were obtained by the Brunauer-Emmett-Teller (BET) method within the pressure range of  $p/p_0 = 0.05 - 0.35$ . The same outgassing procedure was adapted for the CO<sub>2</sub> adsorption measurements. CO<sub>2</sub> adsorption was performed at 25 °C and the temperature was controlled by a circulating bath.

## 2.3 Dynamic Column Adsorption/Desorption

The dynamic CO<sub>2</sub> capacity was evaluated using a custom-built dynamic gas breakthrough system. The schematic of the dynamic column breakthrough apparatus is shown in Fig. 1. A mixed gas of 90 vol% N<sub>2</sub> and 10 vol% CO<sub>2</sub> was obtained by regulating the flow rates of each gas with mass flow controllers. The total flow rate of the mixed gas was kept at 30 cm<sup>3</sup>/min. The packed-bed column was a vertical stainless steel tube with an inner diameter of 0.40 cm. The sorbent sample was held on a porous stainless steel filter, which was cut to fit tightly inside the stainless steel tube. The typical sample size is within the range of 20 - 30 mg. The column is heated using controlled Thermolyne heating tape. The sorbent sample was heat treated at 130 °C in a helium stream for 2 hours prior to analysis. The effluent gas was analyzed using an Extrel Max300-LG mass spectrometer.

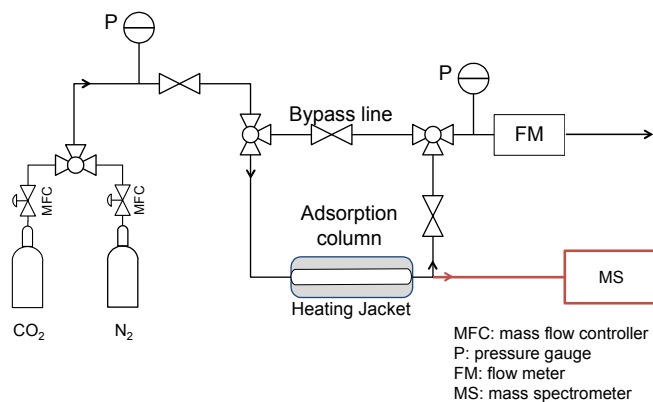


Fig. 1. Schematic of the dynamic column breakthrough apparatus.

### 3. Results and discussion

#### 3.1 SEM and TEM analysis

The micron-scale interconnecting macroscopic structures of the nitrogen-doped porous carbon can be observed from the SEM image in Fig. 2a, while the well-ordered mesoporous structures can be confirmed from the TEM images in Fig. 2b and 2c. The corresponding fast Fourier diffractograms (Fig. 2b and 2c insets) indicate that the porous carbon has a high degree of periodicity viewed from the [110] and [001] directions, further confirming the 2D hexagonal mesostructure. The macroporous structure was formed through an emulsion polymerization process where porous polymer network was made. The mesopore channels were originated from the removal of the block copolymer template during the carbonization step. Furthermore, these channels are of uniform width from the TEM images indicating the successful formation of micellar rod arrays in the assembly solution. It is worth noting that this hierarchical morphology is beneficial for the applications of CO<sub>2</sub> capture, since the macroscopic networks facilitate CO<sub>2</sub> diffusion by reducing the mass transfer resistance and the small pores provide thermal dynamic driving force for CO<sub>2</sub> adsorption.

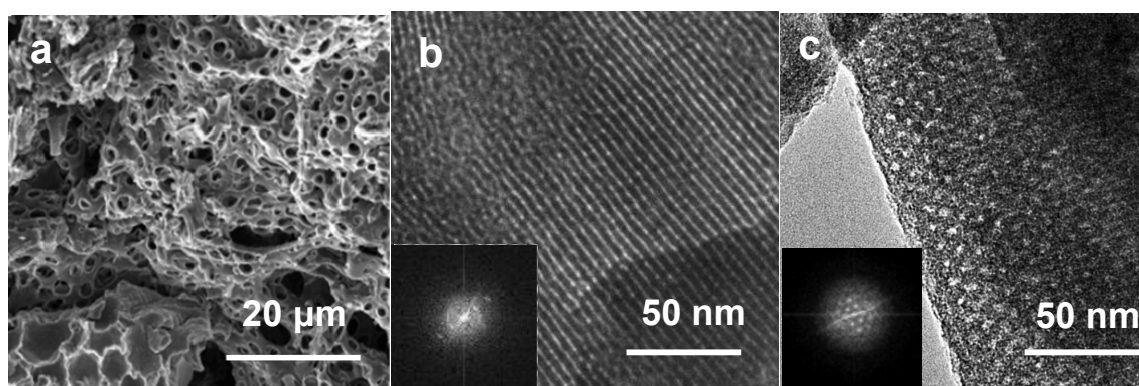


Fig. 2. a) SEM b) c) TEM images (insets: Fourier diffractogram) of the nitrogen-doped porous carbon.

#### 3.2 Gas adsorption analysis

The porous structures of the porous carbon sample were further analyzed by gas adsorption/desorption techniques. N<sub>2</sub> and CO<sub>2</sub> were selected as a probe gas. N<sub>2</sub> adsorption and desorption were performed at 77 K while CO<sub>2</sub> adsorption was carried out at 273 K. A combination of the N<sub>2</sub> and CO<sub>2</sub> sorption data provides information on the pore characteristics ranging from mesopore (2 nm < d < 50 nm) to ultramicropore (d < 0.8 nm). The N<sub>2</sub> sorption isotherms are shown in Fig. 3a, where the solid and open circles represent adsorption and desorption uptake of N<sub>2</sub>, respectively. The isotherm can be classified as a type IV isotherm according to the IUPAC recommendations [8]. The steep uptake at low relative pressures reveals the microporous features (d < 2 nm) while the hysteresis indicates the existence of mesopores. The apparent specific surface area of the mesoporous carbon was 804.5 m<sup>2</sup> g<sup>-1</sup>, which was calculated using the Brunauer–Emmett–Teller (BET) method based upon the N<sub>2</sub> adsorption isotherm at relative pressures of 0.05 – 0.3. A total pore volume of 0.88 cm<sup>3</sup> g<sup>-1</sup> was estimated from the nitrogen uptake at the relative pressure of 0.995. Fig. 3b shows Pore size distributions (PSDs) obtained by the non-local density functional theory (NLDFT). From the PSD calculated from the nitrogen isotherms, a major peak can be seen at ~5 nm, corresponding to the mesoporous channels originated from the removal of the block copolymer template. Furthermore, the microporous features were designed through thermal cleavage of the side group of the pyrrole derivative. These features can be observed from the CO<sub>2</sub> PSD, with three major peaks at 0.35, 0.48 and 0.79 nm. The cumulative

ultramicropore ( $d < 0.8$  nm) volume is  $0.12 \text{ cm}^3 \text{ g}^{-1}$ . It is worth noting that the ultramicropores play an important role in  $\text{CO}_2$  capture as they largely correspond with the  $\text{CO}_2$  adsorption capacity in carbon materials [9-11].

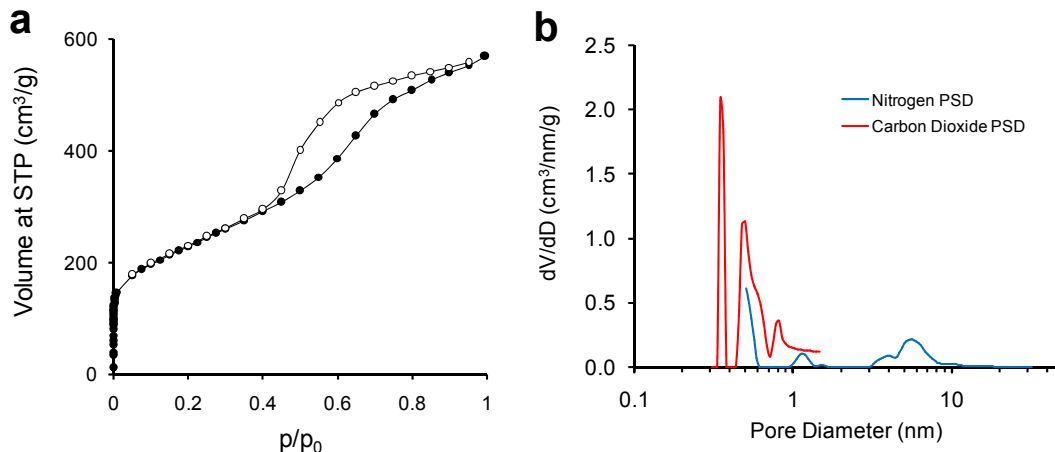


Fig. 3. a)  $\text{N}_2$  adsorption (solid dots) and desorption (open dots) isotherms at 77 K; b) Pore size distributions predicted by the non-local density functional theory (NLDFT) based upon the  $\text{N}_2$  and  $\text{CO}_2$  isotherm data.

### 3.3 X-ray photoelectron spectroscopy (XPS) analysis

The nature of the nitrogen species on the surface of the porous carbons was further investigated by XPS. The  $\text{N} 1s$  spectra of the porous carbons prepared are shown in Fig. 4. Three intense peaks at 398.0, 399.5 and 400.8 eV can be distinguished, which corresponds to pyridinic nitrogen, pyrrolic nitrogen and quaternary nitrogen, respectively. The quaternary nitrogen is the most stable nitrogen species under pyrolysis conditions and it represents 69% of all nitrogen species in the porous carbon [12].

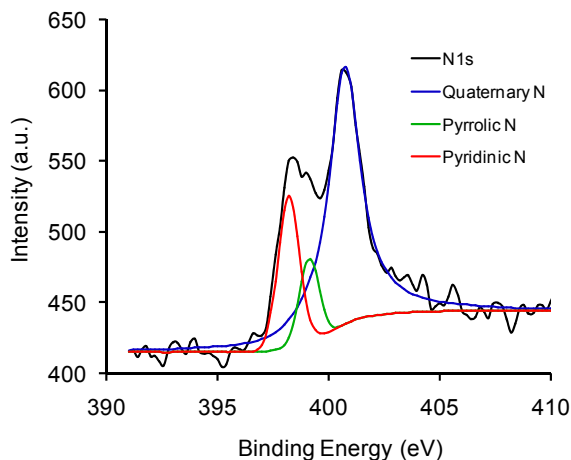


Fig. 4. X-ray photoelectron spectroscopy (XPS) of the porous carbon, indicating three types of nitrogen functionalities.

### 3.4 CO<sub>2</sub>/N<sub>2</sub> testing under equilibrium conditions

The equilibrium CO<sub>2</sub> isotherms at 273, 298 and 323 K and N<sub>2</sub> isotherm at 298 K were measured by volumetric method and plotted in Fig. 5a. At 298 K, the porous carbon exhibits a high CO<sub>2</sub> capacity of 3.13 mmol/g at 1 bar, which is superior to commercial activated carbons with surface area of 2000 – 3000 m<sup>2</sup>/g showing CO<sub>2</sub> capacities ranging from 2.1 to 2.5 mmol/g under the same conditions [13]. Moreover, at 0.1 bar, which is a pressure more relevant to the applications of post-combustion capture, the porous carbon shows a promising capacity of 0.94 mmol/g, compared to other previously reported mesoporous carbons [5,6]. Generally, the CO<sub>2</sub> capacities decrease as temperature increases, suggesting the exothermic nature of the CO<sub>2</sub> adsorption process. Comparatively, N<sub>2</sub> adsorption at 298 K and 1 bar was found to be 0.36 mmol/g, which is far smaller than that of CO<sub>2</sub> adsorption under identical conditions. The initial slopes of the CO<sub>2</sub> and N<sub>2</sub> adsorption isotherms at 298 K were calculated, which are 33.4 and 0.65 mmol/g/bar for CO<sub>2</sub> and N<sub>2</sub>, respectively. The ratio of these slopes was then calculated to estimate the CO<sub>2</sub>/N<sub>2</sub> selectivity, which is 51.4:1. The high CO<sub>2</sub> initial slope could be a result from the thermodynamic driving force for CO<sub>2</sub> adsorption provided cooperatively by microporosity and nitrogen functionality.

The strength of the interaction between CO<sub>2</sub> and the porous carbon can be further evaluated by the isosteric heat of adsorption, which was calculated by the Clausius-Clapeyron equation based upon the CO<sub>2</sub> adsorption isotherms at 273, 298 and 323 K. The isosteric heat of adsorption ranges from 37.4 kJ/mol to 24.1 kJ/mol in a corresponding CO<sub>2</sub> adsorption range of 0.01 – 2 mmol/g (Fig. 5b). The high isosteric heat of adsorption at low CO<sub>2</sub> loading originates from the strong pole-pole interactions between the quadrupole of the CO<sub>2</sub> molecules and the polar nitrogen groups [14]. As the CO<sub>2</sub> loading increases, the adsorbed CO<sub>2</sub> molecules occupy the active surface sites therefore weakening the interactions between the surface sites and gas-phase CO<sub>2</sub>. Hence, the isosteric heat of adsorption decreases as CO<sub>2</sub> loading increases and eventually flattens out at around 24 kJ/mol.

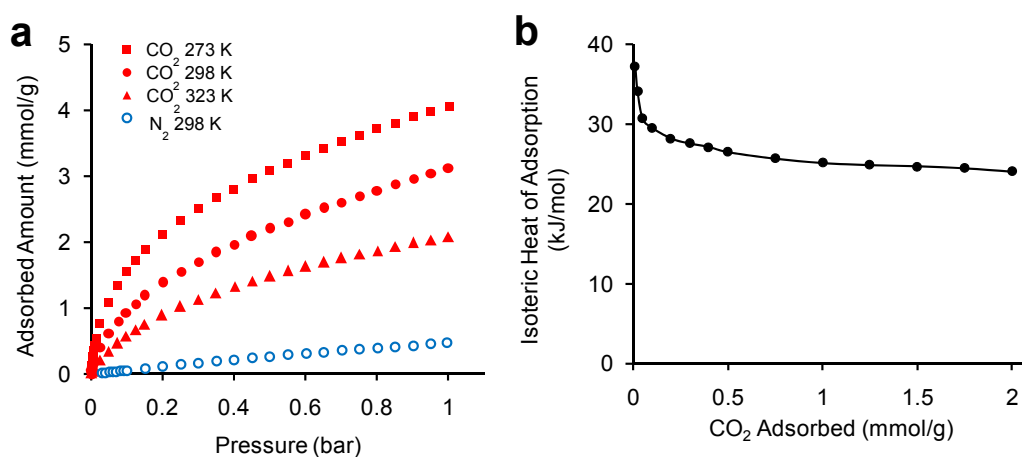


Fig. 5. a) Equilibrium adsorption isotherms of CO<sub>2</sub> at 273, 298 and 323 K and N<sub>2</sub> at 298 K; b) CO<sub>2</sub> isosteric heat of adsorption as a function of CO<sub>2</sub> adsorbed.

### 3.5 Dynamic column separation of CO<sub>2</sub>/N<sub>2</sub>

In addition to adsorption performance based upon pure-gas isotherms, to assess the potential of applying the sorbent in practical processes, more realistic conditions are required, *i.e.*, competitive CO<sub>2</sub> adsorption with N<sub>2</sub> in a dynamic system. Furthermore, regenerability and stability over multiple cycles are also critical in practical applications. Therefore, dynamic column breakthrough experiments were carried out. In a typical experiment, a mixed gas stream of 10% (v/v) CO<sub>2</sub> with balance N<sub>2</sub> was used to approximately simulate a post-combustion flue gas

(Fig. 1). The dynamic CO<sub>2</sub> capacity was calculated by the CO<sub>2</sub> mass balance based upon the integration of the CO<sub>2</sub> breakthrough curves subtracted by a blank experiment. The resulting CO<sub>2</sub> capacity is 0.96 mmol/g at 298 K, which matches well with that from the equilibrium measurements using pure CO<sub>2</sub> at 298 K and 0.1 bar (0.93 mmol/g) taking experimental error into account. This implies that CO<sub>2</sub> preferentially adsorbs onto the porous carbon over N<sub>2</sub>, which further confirms the high CO<sub>2</sub>/N<sub>2</sub> selectivity of the material. Furthermore, the slope of the sorbent breakthrough curve resembles that of the blank breakthrough curve, which means the CO<sub>2</sub> gas adsorbed instantaneously upon contact with the sorbent. This fast adsorption kinetics is probably due to the interconnected hierarchical structure that facilitates gas diffusion and adsorption.

The reversibility of CO<sub>2</sub> adsorption was tested by the dynamic column breakthrough method. To a sample saturated with CO<sub>2</sub>, pure N<sub>2</sub> was purged at 298 K until no CO<sub>2</sub> was detected from the effluent after 30 min. Subsequent CO<sub>2</sub> adsorption suggests full recovery of the CO<sub>2</sub> capacity of the sample. It is important to note that this mild condition for CO<sub>2</sub> release is advantageous since it imposes minimum energy penalty associated with sorbent regeneration, compared to sorbents that require thermal energy input for regeneration such as amine-functionalized materials [7,15]. In addition, 10 cycles of adsorption and desorption were performed and the resulting capacity for each cycle is plotted in Fig. 6. It can be seen that the CO<sub>2</sub> capacity of the porous carbon retains over 10 cycles except for variations due to experimental error. Hence, the porous carbon presented here can be easily and fully regenerated over multiple cycles without noticeable reduction in CO<sub>2</sub> adsorption performance.

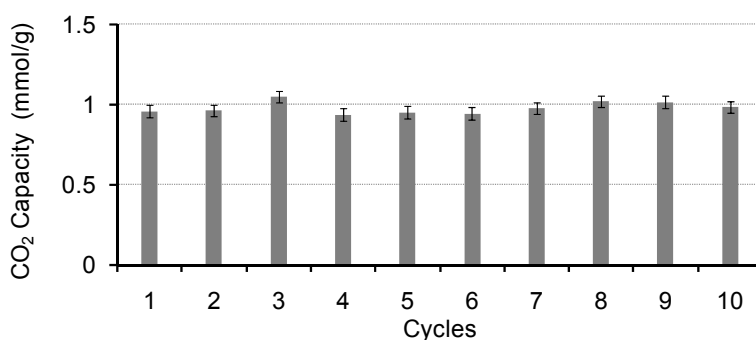


Fig. 6. Multicycle adsorption of CO<sub>2</sub> from 90%/10% CO<sub>2</sub>/N<sub>2</sub> mixture.

#### 4. Conclusion

Nitrogen-doped porous carbon was prepared by facile assembly of pyrrole derivative and block copolymer in aqueous solution followed by high-temperature pyrolysis. The removal of block copolymer creates hierarchical structures with macroscopic interconnecting networks and highly ordered mesoscopic channels, with a total surface area of 804.5 m<sup>2</sup> g<sup>-1</sup>. The resulting sorbent displayed promising CO<sub>2</sub> capacities at 298 K with excellent CO<sub>2</sub>/N<sub>2</sub> selectivity. Furthermore, dynamic column breakthrough experiments were performed which gives consistent CO<sub>2</sub> capacity compared to static equilibrium data, suggesting its potential in practical column adsorption applications. The porous carbon was shown to be stable over multiple adsorption/desorption cycles with the ease of CO<sub>2</sub> release and minimal regeneration energy requirement.

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## References

- [1] Intergovernmental Panel on Climate Change (IPCC). Special report on renewable energy sources and climate change mitigation, New York: Cambridge University Press; 2011.
- [2] Earth System Research Laboratory. Trends in atmospheric carbon dioxide. <http://www.esrl.noaa.gov/gmd/ccgg/trends/>, accessed on September 16<sup>th</sup>, 2014.
- [3] Wilcox J. Carbon Capture. New York: Springer Publishing; 2012.
- [4] Li W, Zhao D. An overview of the synthesis of ordered mesoporous materials. *Chem Commun* 2013;49:943-946.
- [5] Wei J, Zhou D, Sun Z, Deng Y, Xia Y, Zhao D. A controllable synthesis of rich nitrogen-doped ordered mesoporous carbon for CO<sub>2</sub> capture and supercapacitors. *Adv Funct Mater* 2013;23:2322-2328.
- [6] Hao GP, Li WC, Qian D, Wang GH, Zhang WP, Zhang T, Wang AQ, Schuth F, Bongard HJ, Lu AH. Structurally designed synthesis of mechanically stable poly(benzoxazine-co-resol)-based porous carbon monolith and their application as high-performance CO<sub>2</sub> capture sorbents. *J Am Chem Soc* 2011;133:11378-11388.
- [7] Chen Z, Deng S, Wei H, Wnag B, Huang J, Yu G. Activated carbons and amine-modified materials for carbon dioxide capture – a review. *Front Environ Sci Eng* 2013;7(3):326-340.
- [8] IUPAC recommendations. *Pure Appl Chem* 1994;66:1739.
- [9] Wei H, Deng S, Hu B, Chen Z, Wang B, Huang J, Yu G. Granular bamboo-derived activated carbon for high CO<sub>2</sub> adsorption: the dominant role of narrow micropores. *ChemSusChem* 2012;5:2354-2360.
- [10] Presser V, McDonough J, Yeon SH, Gogotsi Y. Effect of pore size on carbon dioxide sorption by carbide derived carbon. *Energy Environ Sci* 2011;4:3059-3066.
- [11] Sevilla M, Parra JB, Fuertes AB. Assessment of the role of micropore size and N-doping in CO<sub>2</sub> capture by porous carbons. *ACS Appl Mater Interfaces* 2013;5:6360-6368.
- [12] Jiang H, Su Y, Zhu Y, Shen J, Yang X, Feng Q, Li C. Hierarchical interconnected macro-/mesoporous co-containing N-doped carbon for efficient oxygen reduction reactions. *J Mater Chem A* 2013;1:12074-12081.
- [13] Himeno S, Komatsu T, Fujita S. High-pressure adsorption equilibria of methane and carbon dioxide on several activated carbons. *J Chem Eng Data* 2005;50:369-376.
- [14] Sevilla M, Valle-Vigon P, Fuertes AB. N-doped polypyrrole-based porous carbons for CO<sub>2</sub> capture. *Adv Funct Mater* 2011;21:2781-2787.
- [15] Choi S, Drese JH, Jones CW. Adsorbent materials for carbon dioxide capture from large anthropogenic point sources. *ChemSusChem* 2009, 2, 796-854.