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#### Broader context

# Porous carbon nanosheets with precisely tunable thickness and selective CO<sub>2</sub> adsorption properties<sup>†</sup>

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We report the wet-chemistry synthesis of a new type of porous carbon nanosheet whose thickness can be precisely controlled over the nanometer length scale. This feature is distinct from conventional porous carbons that are composed of micron-sized or larger skeletons, and whose structure is less controlled. The synthesis uses graphene oxide (GO) as the shape-directing agent and asparagine as the bridging molecule that connects the GO and *in situ* grown polymers by electrostatic interaction between the molecules. The assembly of the nanosheets can produce macroscopic structures, i.e., hierarchically porous carbon monoliths which have a mechanical strength of up to 28.9 MPa, the highest reported for the analogues. The synthesis provides precise control of porous carbons over both microscopic and macroscopic structures at the same time. In all syntheses the graphene content used was in the range 0.5-2.6 wt%, which is significantly lower than that of common surfactants used in the synthesis of porous materials. This indicates the strong shape-directing function of GO. In addition, the overall thickness of the nanosheets can be tuned from 20 to 200 nm according to a fitted linear correlation between the carbon precursor/GO mass ratio and the coating thickness. The porous carbon nanosheets show impressive  $CO_2$  adsorption capacity under equilibrium, good separation ability of  $CO_2$  from  $N_2$ under dynamic conditions, and easy regeneration. The highest CO2 adsorption capacities can reach 5.67 and 3.54 CO<sub>2</sub> molecules per nm<sup>3</sup> pore volume and per nm<sup>2</sup> surface area at 25 °C and  $\sim$ 1 bar.

The control of anthropogenic  $CO_2$  emissions is a crucial matter in view of the significant role that this gas plays in global climate change. In recent years, great efforts have been directed towards the  $CO_2$  capture and storage. Compared with the liquid-phase absorption process, the use of porous solids, especially porous carbons, as sorbents for capturing  $CO_2$  has shown great promise due to the low cost, high availability, large surface area, an easy-to-design pore structure, hydrophobicity and low energy requirements for regeneration. Here we present a novel route for the preparation of porous carbon nanosheets (PCNs) whose thickness can be precisely controlled over the nanometer length scale from 20 to 200 nm. Benefitting from the short diffusion paths and high microporosity, the PCNs exhibit high sorption capacity, fast sorption kinetics and a good  $CO_2$ -N<sub>2</sub> selectivity.

## 1 Introduction

Nowadays, carbon capture has great environmental and societal implications. The efficient removal of  $CO_2$  from gas mixtures could benefit greatly from the next generation of adsorbents either liquid or solid. For gas mixtures with high  $CO_2$  partial

pressures like natural gas, aqueous amines are industrially used as  $CO_2$  scrubbing agents, while for gas mixtures with very low  $CO_2$  partial pressures, solid adsorbents are often used. Among widely available carbon capture processes, the quick removal of  $CO_2$  from a dilute hydrated gas in environments such as spacecraft, submarines, and mines is the most energy- and costintensive aspect of carbon capture.<sup>1,2</sup> This is the incentive for the development of efficient porous materials, which include carbons,<sup>3-9</sup> hybrid crystalline solids (*e.g.*, metallic organic framework related materials),<sup>10-15</sup> zeolites,<sup>16-19</sup> *etc*.

However, most of these porous materials commonly face two main limitations. First, they have a large crystallite size in all dimensions and it therefore takes a long time for the  $CO_2$ molecules to transfer into and out of the inner microporous network. This leads to the starvation of  $CO_2$  for the inner pores and further a low utilization of the overall surfaces and porosities. To address this issue, approaches including the

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<sup>†</sup> Electronic supplementary information (ESI) available: The zeta potential changes and experimental phenomena recorded during the synthesis, FE-SEM images of PCN-9.9 and the control sample including samples prepared in the absence of a GO-template and commercial activated carbons, N<sub>2</sub> adsorption isotherms and micropore size distribution, CO<sub>2</sub> adsorption isotherm at 0 °C, XPS spectra, EDX mapping of PCN-17, and regeneration cycling of CO<sub>2</sub> separation from a stream of CO<sub>2</sub>-H<sub>2</sub>O-N<sub>2</sub> of 14/3/83 and 9/3/88 v% at 25 °C over the sample of PCN-17. See DOI: 10.1039/c3ee41906a

#### Paper

construction of a hierarchical pore system,20-29 adding mesoporosity<sup>30-36</sup> and reducing the dimensions of crystallites to the nanoscale37,38 have been widely used by researchers. For example, we and other groups have reported various kinds of carbon materials with micron size spherical building blocks and either micro-macroporous or micro-meso-macroporous pore systems, which show a high capacity in CO<sub>2</sub> adsorption.<sup>21,23,27-29</sup> Second, their moisture-resistant ability as well as mechanical strength (attrition resistance) needs to be improved, especially in dynamically consecutive cycles for the separation of CO<sub>2</sub> from hydrated gas streams. Since porous materials with polar surfaces showing high CO2 affinities commonly deliver even higher affinities for water, this may further lead to not only the deterioration of CO2 adsorption capacity but also structural collapse.<sup>39,40</sup> Generally, carbon materials show hydrophobic properties. If a high mechanical strength can also be achieved, porous carbons would be good CO<sub>2</sub> adsorbers because of their long-term structural stability under dynamically consecutive cycles.

Recently, the development of hierarchical structures through the assembly of graphene (oxide) has also been extensively explored and significant progress has been made.<sup>41–47</sup> Although the open pore structures arising from the stacking of one-atom thick sheets can theoretically deliver fast sorption kinetics, the adsorption potential for effective trapping CO<sub>2</sub> is too weak, which often leads to a low adsorption capacity. Therefore, before their potential application in CO<sub>2</sub> adsorption, CO<sub>2</sub>-philic species must be introduced by additional functionalization (*e.g.*, surface grafting, deposition, *etc.*).<sup>48–50</sup> These treatments often involve multiple steps, a special drying process (freeze or supercritical condition) and a high consumption of graphene (graphene content >90 wt% in the final products).

Here in a departure from these strategies we report a graphene-directed molecular assembly of porous carbon nanosheets with precisely tunable thickness and selective CO<sub>2</sub> adsorption properties. The synthesis uses a graphene oxide (GO, with an oxygenated and charged surface) sheet as the shape-directing agent, and the amino acid asparagine as the bridging molecule that connects the GO and the in situ grown polymers by electrostatic interaction between the molecules (see Fig. 1). The assembly of the nanosheets produces macroscopic structures, i.e. hierarchically porous carbon monoliths. It must be noted that the GO is not the main component of the product but has the role of directing the structure and orientation of the porous carbon formed on it. In all the syntheses, the GO content was in the range 1.1-6.2 wt%, corresponding to graphene contents of 0.5-2.6 wt%. The content is significantly less than that of the common structural directing agents, e.g. the mesostructure directing agent, triblock copolymer F127 that requires a mass content of up to ca. 20-40%, 24,26 indicating the substantial directing role of GO. In addition, the porous carbon nanosheets are also distinct from the common straightforward graphene-based materials with a graphene content of higher than 90%.51-53

The overall thickness of the porous carbon nanosheets can be precisely tuned to be in the range 20–200 nm, which is 2–3 orders smaller than the skeletons of most available porous



**Fig. 1** Schematic of the formation of the PCNs. (a) The negatively charged GO sheet; the picture (right) shows its Tyndall phenomenon. (b) Positively charged amino acids, equally dispersed at the molecular-level on both surfaces of the GO. (c) *In situ* co-polymerization of pre-adsorbed asparagine, resorcinol and formal-dehyde. (d) The polymer layer transformed into a microporous carbon layer during pyrolysis in Ar.

activated carbons,54-56 carbons, such as synthetic carbons,<sup>24,26,57,58</sup> etc. This enables fast CO<sub>2</sub> sorption kinetics, and a high utilization degree of the overall porosity and surface area. Furthermore, the combination of graphene sandwiched between the two microporous carbon sheets shows an unprecedented high mechanical strength of up to 28.9 MPa. In addition, the large amount of microporosity with pore size 6  $\pm$  1 Å is particularly suitable as a "CO2 reservoir".59,60 Because of this unique structure, the porous carbon nanosheets display overall adsorption and separation advantages as demonstrated in the following.

### 2 Experimental sections

#### 2.1 Chemicals and materials

Resorcinol (denoted R, 99.5%) was purchased from Tianjin Kermel Chemical Reagent Co., Ltd. Asparagine (99.5%) was purchased from Fluka. Formalin (37 wt%) was supplied by Sinopharm Chemical Reagent Co., Ltd. GO colloids used in this work were prepared following a modified Hummers method.<sup>61</sup> The as-obtained concentrated GO was dispersed in deionized water under the aid of sonication at a power of 100 W for 4 h (KQ-100TDB, Kun Shan Ultrasonic Instruments Co., Ltd, China). The diluted GO colloids were then centrifuged to remove the unexfoliated fraction. The supernatant homogeneous GO colloids (dark yellow-brown), showing a liquid crystal behavior, were collected for subsequent use. Before use, the concentration of the GO colloids was determined by the weight difference of an amount of GO colloids before and after drying. Unless otherwise specified, all chemicals were used as received.

#### 2.2 Synthesis of porous carbon nanosheets

The synthesis of porous carbon nanosheets (PCNs) is illustrated in Fig. 1. Typically, 0.23 g asparagine was first dissolved in 26 mL GO colloids (1.8 mg mL<sup>-1</sup>) under magnetic stirring at 25 °C. After completely dissolving, 0.75 g R was added to the above solution and stirred for *ca*. 5 min until the reaction solution was again homogeneous. Subsequently, 1.106 g formalin (37 wt%) containing formaldehyde (denoted F) was quickly injected into the solution. The color of the reaction solution became darker, and the reaction mixture was stirred at 25 °C for another 5–10 min. The homogeneous solution was then sealed and transferred to an oven at 90 °C. It gelled and solidified within 45 min. This gel was cured for an additional 17 h.

The gel was dried at room temperature (at least for 24 h) and 50 °C until no further visible weight loss, followed by pyrolysis at 800 °C for 2 h under a nitrogen atmosphere to obtain porous carbon nanosheets (denoted PCN-*x*, where *x* represents the thickness of the carbon layer on each side of the graphene. For example, in the above synthesis, the coating was measured to be *ca.* 17 nm, and was thus denoted PCN-17). In the subsequent text the resorcinol-formaldehyde is referred to as the carbon precursor (CP). By varying the mass ratio of CP/GO, different PCNs were prepared. In all syntheses, the mass ratio of asparagine:GO was set to 4.91 : 1 and R:F as 1.83 : 1.

#### 2.3 Structure characterization

Scanning electron microscope (SEM) investigations for the PCNs were carried out with a NOVA NanoSEM 450 instrument. The EDX mapping was also done on this instrument equipped with an energy dispersive X-ray analyzer. The SEM images for samples prepared in the absence of GO were taken on a Hitachi S-4800. Nitrogen sorption isotherms were measured with a Micromeritics TriStar 3000 physisorption analyzer. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface areas ( $S_{BET}$ ). Total pore volumes ( $V_{total}$ ) were calculated from the amount of nitrogen adsorbed at a relative pressure,  $P/P_0$ , of 0.97. Micropore volumes ( $V_{\text{micro}}$ ) were calculated using the t-plot method. The micropore size was analyzed by low pressure N<sub>2</sub> sorption which was calculated by a QSDFT (Quenched Solid State Functional Theory) model using a Quantachrome Autosorb iQ physisorption analyzer. The mechanical properties of the samples were tested under uniaxial compression using a 2 kN intelligent strength tester (model DL III, Dalian Research & Design Institute of Chemical Industry). The compressive strength is the maximum stress supported by the samples during the test, *i.e.*, the stress at which macroscopic failure occurs. Tests were performed at a strain rate of 1 mm min<sup>-1</sup>. All measurements were recorded at ca. 25 °C and 60% relative humidity. Samples were cylinders carefully machined to have perfectly parallel bases and a length/ diameter ratio of 1. No precautions were taken to prevent moisture adsorption by the carbon monoliths.

#### 2.4 CO<sub>2</sub> adsorption and separation measurements

Equilibrium gas adsorption measurements: the gas adsorption isotherms of the PCNs were measured using a Micromeritics ASAP 2020 static volumetric analyzer at the required temperature. Prior to each adsorption experiment, the sample was degassed for 8 h at 200 °C ensuring that the residual pressure fell below 0.05 mbar and then cooled down to the required temperature, followed by the introduction of pure  $CO_2$  into the system. The gas adsorption capacity in terms of adsorbed volume under standard temperature and pressure (STP) was then recorded.

#### 2.5 Dynamic gas separation measurements

The separation of  $CO_2$  from a  $CO_2$ -H<sub>2</sub>O-N<sub>2</sub> mixture was performed in a fixed-bed flow sorber (a stainless steel tube with an inner diameter of 9 mm and a length of 100 mm, sample of *ca.* 330 mg) operated at *ca.* 1 bar and 25 °C, which was controlled by a pressure controller and a thermostatic water bath. The sorbent bed was first heated to 200 °C in Ar at a flow rate of 100 mL min<sup>-1</sup> and held for 30 min. Breakthrough experiments were carried out by switching abruptly from Ar to a gas mixture of  $CO_2$ -H<sub>2</sub>O-N<sub>2</sub> with the  $CO_2$  concentration of 4–14 v% at a flow rate of 7 mL min<sup>-1</sup>. The treated gas from the sorber was monitored online using an Agilent 7890A gas chromatograph with a TCD detector.

## 3 Results and discussion

As shown in Fig. 1, the electrostatic interaction between the GO and the guest species, and the *in situ* grown polymers has occurred sequentially. GO with a heavily oxygenated surface (Fig. 1a) was chosen as a shape-directing agent. Its negatively charged surface characteristic is confirmed by zeta potential analysis (ESI, Fig. S1a<sup>†</sup>), which is consistent with previous work.<sup>61</sup> Because of this electrostatic interaction, surface-engineering on such GO sheets is expected to produce new hybrid products that are short and lie normal to the plane, imparting new functionality.

Considering the negative charge of the GO, typical amphoteric compounds, asparagine with amine and carboxylic acid groups in one molecule, are selected as molecular linkers that would readily bridge the GO and the polymer (Fig. 1b). This can be realized by tuning its total surface charge by changing the pH of the reaction system. At a pH below its isoelectric point (pI = 5.41), asparagine carries a net positive charge, otherwise, it is negatively charged due to the loss or gain of protons. Thus, asparagine would carry positive charges when dissolved in the template colloids with a pH of 2.7 (Fig. S1b†). After its addition, the zeta potential of the reaction solution increases from -57.5 mV to -44.0 mV (Fig. S1c†), accompanied by a pH change from 2.7 to 3.7, and the system retains excellent colloidal stability. This indicates a strong electrostatic interaction between asparagine molecules and GO.

In particular, the GO leads to a molecular-level dispersion of positively charged asparagine molecules on both surfaces. The changes of zeta potential and pH are consistent with studies of the synthesis of colloidal silica layers, using cationic CTA<sup>+</sup> surfactants as linkers in the presence of GO.<sup>62,63</sup> However, our study shows that the use of this kind of cationic surfactants fails to achieve such hybrid carbons due to insufficient interaction between the linkers and the carbon precursors. Clearly, the

pre-loaded amphoteric amino acids can substantially bridge the two sides, in parallel with uniform nucleation and *in situ* co-polymerization with resorcinol and formaldehyde on the surface of the substrate. Consequently, it ensures a smooth and uniform growth of the carbon precursor on both surfaces of a GO sheet (Fig. 1c). Such co-polymerization could be completed in a remarkably effective, simple and controllable manner (*e.g.* 90 °C,  $\leq$ 45 min, or even at room temperature) (Fig. S2†). During high temperature pyrolysis in Ar, as the GO is reduced to graphene the polymer layers are transformed into microporous carbon coatings (Fig. 1d).

Field-emission scanning electron micrographs (FE-SEM) of our PCNs show a layer structure with lateral dimensions ranging from hundreds of nanometers to several micrometers with the graphene sandwiched between two uniformly thick carbon layers (Fig. 2). With thinner carbon coatings ( $\leq 20$  nm), it is difficult to see such a sandwich-like structure due to the flexible nature of the thinner building blocks (Fig. 2a and b and S3†). Observations suggest a strong interface between the graphene sheets and carbon coatings. Fig. 2b, d, f and S3† correspond to PCNs prepared under gradually increasing mass ratios of carbon precursor to GO (CP/GO). As shown, the average thicknesses of the carbon coatings are measured to be  $9.9 \pm 1$ ,  $17 \pm 2$ ,  $71 \pm 3$  and  $82 \pm 3$  nm, at CP/GO values of 15.1:1,



**Fig. 2** FE-SEM images with low and high magnification of the obtained porous carbon nanosheets with different thicknesses: (a and b) PCN-17, (c and d) PCN-71, and (e and f) PCN-82. The marked coating thickness on the top of (b), (d), and (f) is the average thickness based on the measurements.

25.3 : 1, 86.5 : 1 and 100 : 1, respectively. Here, the obtained PCN samples are denoted as PCN-*x*, where *x* represents the thickness of each side of the carbon layer. Note that such hybrid carbon sheets exhibit a smooth surface, different from that of reported pure graphene assemblies that commonly show endless ripples, wrinkles and open edges,<sup>41,42,44,45</sup> and are distinct from the synthetic carbons,<sup>24,25</sup> prepared in the absence of GO, displaying large spherical units with an average diameter of  $3 \pm 1 \mu m$  (Fig. S4a and b†). These results clearly demonstrate the strong shape and structure directing role of GO during the formation processes.

The high resolution transmission electron microscope (HR-TEM) image of PCN-17 reveals the interconnected micropores (Fig. 3a). Further, by fitting the coating thickness vs. mass ratio of CP/GO, a perfect linear relationship between the two variables was established, showing a high correlation coefficient of 0.9997 (Fig. 3b). This enables one to alter the coating thickness (each side) continuously over a wide range of 10-100 nm by changing the mass ratio of the reactants. This confirms the precise nanoscale control of the carbon coating on both surfaces of the central graphene. A further comparison with relevant benchmark materials either prepared from a fundamental study (polymer-based synthetic carbons, Fig. S4a and b<sup>†</sup>) or from industry (commercially activated carbons, Fig. S4c and d<sup>†</sup>) shows that the PCNs have a dramatically shortened path length through which CO2 molecules have to travel, even as small as 10 nm. Such a tunable and shortened path may play a critical role in enhancing the diffusion kinetics of the molecules.

The large amount of porosity in the nanometer scale for our samples is confirmed by N<sub>2</sub> sorption isotherms (Fig. 3c) and structural parameters (Table S1<sup>†</sup>). The adsorption isotherms of PCN-17 and PCN-71 are type I, reflecting the micropore structures, while the adsorption isotherm of PCN-9.9 is essentially a pseudo-type II, showing inter-particle capillary condensation. The significant N<sub>2</sub> uptake at the relative pressure  $P/P_0$  <



**Fig. 3** Structure analysis. (a) HR-TEM image of PCN-17. (b) The relationship between the CP/GO mass ratio and the thickness of the microporous carbon coatings. (c) The N<sub>2</sub> sorption isotherms for samples with different coating thicknesses. The isotherm of sample PCN-71 is vertically offset by 50 cm<sup>3</sup> g<sup>-1</sup>, STP. (d) The compressive strength of PCNs with different coating thicknesses.

0.1 confirms the high microporosity. The micropore size of the representative sample PCN-17 was tested to be *ca.* 6 Å based on DFT (Fig. S5†), which is ~2 times as large as the kinetic diameter of  $CO_2$  (3.3 Å). The large amount of micropores with the size of 6 Å is responsible for the strong adsorption of  $CO_2$  molecules and thus has been proven to be selective for  $CO_2$  adsorption.<sup>64</sup>

Besides imparting a large microporosity to the surrounding carbon layers, the graphene sheet interlayer delivers superior mechanical performance. The PCNs show an unprecedented compressive strength with a value of up to 28.9 MPa (Fig. 3d), exceeding those of most reported porous carbon macrostructures, including graphene aerogels (0.03–0.3 MPa),<sup>65</sup> structured mesoporous carbon monoliths<sup>66,67</sup> and state-of-the-art molded activated carbons (0.2–22 MPa).<sup>68–70</sup> The excellent mechanical properties allow the PCNs to be directly engineered in the form of monoliths, which are much more convenient to handle compared to powdered samples. Furthermore, the PCNs also inherit the good thermal stability of carbonaceous materials. As seen in Fig. S6,† the TG result shows a good thermal stability of PCN-17 at temperature below 500 °C in air.

As demonstrated above, the PCNs are in the form of nanoscale building blocks with a large accessible surface area. This is the result of an integration of a thin sheet structure and microporous amorphous carbons. The short diffusion lengths of the layered building blocks greatly alleviate the CO<sub>2</sub> starvation of the inner micropores<sup>37,38,71</sup> that the porous materials composed of micron-sized building blocks usually suffer from. The precisely tunable thickness on the nanometer scale provides considerable flexibility in constructing the macroscopic assemblies. As shown in Fig. S7,† monolithic polymers and carbons can be prepared using different CP/GO ratios. Considering these advanced properties and advantages together, such novel carbon nanosheets are therefore tested for CO<sub>2</sub> adsorption.

The equilibrium CO<sub>2</sub> adsorption isotherms at 25 °C and 0 °C of samples with different thicknesses were tested, as shown in Fig. 4 and S8.<sup>†</sup> At 25 °C and 1 bar, the maximum CO<sub>2</sub> uptake of PCN-9.9, PCN-17, and PCN-71 is 2.02, 2.36, and 2.88 mmol  $g^{-1}$ , respectively (Fig. 4a). These values are significantly higher than or at least comparable with those of reported porous carbon and graphene materials.72-74 More detailed comparisons are shown in Table S2<sup>†</sup>.<sup>75-77</sup> The probable reason is that the interaction of PCN samples with CO<sub>2</sub> molecules is strong due to (a) the large amount of microporosity with the pore size of ca. 6 Å and (b) the polar surface caused by the residual heteroatom-containing (e.g. O, N) species (Fig. S9<sup>†</sup>) derived from the decomposition of O/N-containing precursors. The surface nitrogen and oxygen contents measured from XPS spectra in PCN-17 and PCN-71 are given in Table S3.<sup>†</sup> Determination of the surface chemical binding states has been undertaken by high resolution spectral analysis of C1s, O1s and N1s. As seen in Fig. S10,† the spectrum of O1s contains multiple components due to the coexistence of different chemical states of O. It can be deconvoluted into two peaks: the peaks at binding energies of 532.0 and 533.1 eV can be attributed to the C-O-C or C-OH and O-C=O bonds, respectively, while the curve fittings of the N1s spectra of the two samples yield three main components with binding energies of



**Fig. 4** CO<sub>2</sub> adsorption evaluation of the PCNs. (a and b) CO<sub>2</sub> adsorption isotherms for high and low CO<sub>2</sub> partial pressures at 25 °C, where the solid line represents a Toth model fit to the CO<sub>2</sub> isotherms. (c) The number of CO<sub>2</sub> molecules adsorbed per nm<sup>3</sup> pore volume and (d) per nm<sup>2</sup> surface area for PCNs with different thicknesses.

398.0, 400.7, and 401.9 eV, which can be assigned to pyridinic nitrogen, pyrrolic nitrogen, and quaternary nitrogen, respectively. These properties together enable the porous carbon nanosheets as a kind of effective material for the capture of  $CO_2$  due to their high  $CO_2$  adsorption capacity and the need for no additional shaping process.

Remarkably, samples PCN-9.9, PCN-17, and PCN-71 can accordingly trap 2.75, 4.63, and 5.67 CO2 molecules per nm3 pore volume (Fig. 4c), which demonstrates the high efficiency of the microporous carbon coatings as a "CO<sub>2</sub> reservoir". Correspondingly, PCNs can accommodate 3.54, 2.54, and 2.92 CO<sub>2</sub> molecules per nm<sup>2</sup> surface area (Fig. 4d). This again confirms the high utilization degree of the overall porosity and surface area of our PCNs. In particular, CO<sub>2</sub> uptakes of these series of PCNs at a relatively low pressure of only 0.04 bar are in the range of 0.33–0.41 mmol  $g^{-1}$  (Fig. 4b), which outperforms those of the widely used activated carbons including Norit R1 Extra, BPL, Maxsorb, etc.3 This is of significance to broaden their potential applications in the separation of CO<sub>2</sub> from dilute gases such as flue gas, methanol cracked gas, enclosed space gas, etc. Besides this, we have also considered to increase the surface area and pore volume by physical activation, in order to test whether a high CO<sub>2</sub> uptake can be achieved. For example, the sample PCN-17 was activated by steam for 30 min. The obtained sample (denoted as PCN-17-act30) shows more developed porosities with a surface area of 1086  $m^2 g^{-1}$  and a pore volume of 0.64 cm<sup>3</sup> g<sup>-1</sup> (Fig. S11a<sup>†</sup>). The activation leads to an enhanced  $CO_2$  uptake from 2.36 to 2.75 mmol g<sup>-1</sup> at 25 °C and 1 bar (Fig. S11b<sup>†</sup>).

Kinetically, we test the CO<sub>2</sub> adsorption rate of PCNs and reference activated carbons (AC-620 and AC-920 have surface areas of 620 m<sup>2</sup> g<sup>-1</sup> and 920 m<sup>2</sup> g<sup>-1</sup>, respectively) using a thermal analyzer based on gravimetric methods (Fig. S12†). The adsorption of CO<sub>2</sub> at 25 °C proceeds rapidly for the first few

minutes, and then reaches equilibrium. Particularly, at the start, *e.g.* within 5 min, the traping of  $CO_2$  over the PCNs is quicker than the reference ACs (Fig. S12b<sup>†</sup>). More interesting, the equilibrium sorption capacity of our PCNs is clearly higher than the reference ACs, whose surface areas are larger than the PCNs. This again reveals a high efficiency of our PCNs in  $CO_2$  capture.

The steepness of the rise in the isotherm, especially at low pressure, indicates a relatively strong CO<sub>2</sub> binding interaction for the PCNs. Indeed, by fitting the CO<sub>2</sub> adsorption isotherms measured at 0 °C and 25 °C and applying a variant of the Clausius-Clapeyron equation, the isosteric heats of adsorption  $(Q_{\rm st})$  were calculated to lie in the ranges of 18–39, 44–92, and 31–58 kJ mol<sup>-1</sup> for graphene, PCN-17, and PCN-71, respectively (Fig. 5a and see ESI for calculation details<sup> $\dagger$ </sup>). The higher  $Q_{st}$  in the initial stage of adsorption leads to a preferential adsorption of CO<sub>2</sub> over N<sub>2</sub>, which can be interpreted as strong quadrupolar interactions of CO<sub>2</sub> molecules with the heterogeneous micropore walls (e.g., O/N-doped) at low pressure for the PCNs.<sup>78,79</sup> As for graphene, when the  $CO_2$  loading is up to 0.02 mmol  $g^{-1}$ , intermolecular interactions between CO<sub>2</sub>-CO<sub>2</sub> begin to appear, due to the neighboring arrangement of CO<sub>2</sub> on the open surface of graphene as illustrated in Fig. 5b.

As demonstrated above, the PCNs perform very well thermodynamically for the adsorption of pure CO<sub>2</sub> under dry conditions. Further, dynamic "breakthrough" separation experiments were carried out under conditions that mimic a flue gas and/or an environment in an enclosed space with little air exchange, which commonly contains CO2 of 4-14 v% or even lower in a hydrated N<sub>2</sub> stream. To separate CO<sub>2</sub> from such a dilute hydrated gas, porous materials with a polar surface and high microporosity, showing high CO2 affinities, need to be used. However, such characteristics often endow the materials with even higher affinities to moisture. For example, the bestperforming zeolites (X type) can adsorb 2.5 mmol  $g^{-1}$  CO<sub>2</sub> at 0.06 bar and 50 °C under dry conditions (single-component CO<sub>2</sub> equilibrium adsorption); unfortunately the CO<sub>2</sub> adsorption capacities decreased substantially from 2.5 to 0.1 mmol  $g^{-1}$ , as the H<sub>2</sub>O concentration increased from 0.8 to 16.1 wt%.80 A similar phenomenon (at a relative humidity of 70%, a 84% drop of its natural CO<sub>2</sub> capacity) is observed for Mg-MOF-74, state-ofthe-art MOF at 1 bar and 298 K.81

Remarkably, as demonstrated by the "breakthrough curves" (Fig. 6a–c), our PCN-17 can dynamically separate the  $CO_2$  from



**Fig. 5**  $CO_2$  adsorption evaluation of the PCNs. (a) Isosteric heat of adsorption at different  $CO_2$  loadings. (b) Illustration of the interactions between  $CO_2$  and sorbents, or  $CO_2$ – $CO_2$ .

 $CO_2-N_2$  streams that are water saturated at 25 °C, with  $CO_2$  concentrations of 14 v%, 9 v% and even as low as 4%. The calculated  $CO_2$  uptakes are 0.81, 0.58 and 0.28 mmol g<sup>-1</sup>, respectively. These values are ideally consistent with the pure  $CO_2$  adsorption data at partial pressures of 0.14, 0.09 and 0.04 bar, indicating its extraordinary moisture resistance. These dynamic data provide clear evidence that PCN-17 is extremely selective for adsorbing  $CO_2$  over  $N_2$ , which represents a significant step forward in rationally designing a material for dilute  $CO_2$  separation under humid conditions.

The cycling experiments using CO<sub>2</sub>-H<sub>2</sub>O-N<sub>2</sub> of 4/3/93 v% also verified the selective and reversible CO2 adsorption capacity of PCN-17 (Fig. 6d). A sample saturated with CO<sub>2</sub> was subjected to an Ar purge flow of 15 mL min<sup>-1</sup> at 50 °C. After approximately 30 min, no CO<sub>2</sub> was detected in the effluent. Successive regenerations reveal that the sample retains more than 97% of its intrinsic capacity after such mild regeneration. The 3% loss of  $CO_2$  capacity may be due to the strongly adsorbed CO<sub>2</sub> on highly active sites. This can be explained by the high  $Q_{\rm st}$  at the ultra-low CO<sub>2</sub> uptake. As the regeneration temperature increases to 100 °C, the residual CO<sub>2</sub> (ca. 3%) can also be recovered. Further cycles do not lead to a reduction of the capacity. Consecutive regeneration cycles for the separation of CO2 from CO2-H2O-N2 of 14/3/83 v% and 9/3/88 v% are also highly stable and efficient (Fig. S13<sup>†</sup>). Furthermore, the dynamical adsorption-desorption test for sample PCN-17 was carried out for 200 cycles in total under a gas stream of CO2-N2 of 14/86 v% (Fig. S14<sup>†</sup>). It also shows a very stable regeneration performance. These tests signify that PCN-17 provides highperformance separation under mild conditions for regeneration, which is highly desirable for practical applications.82,83

Besides the good performances in CO<sub>2</sub> capture, our PCNs also show great potential in hydrogen storage, which represents an important energy topic.<sup>84,85</sup> The preliminary result (Fig. S15<sup>†</sup>) reveals a superior H<sub>2</sub> storage performance of PCN-9.9 (surface area: 350 m<sup>2</sup> g<sup>-1</sup>, pore volume: 0.45 cm<sup>3</sup> g<sup>-1</sup>) at 77 K and 1 bar. Its storage capacity is high up to 2.28 wt% (19.62 H<sub>2</sub>



**Fig. 6** CO<sub>2</sub> separation evaluation of PCN-17 in dynamic breakthrough tests. (a)– (c) Breakthrough curves, using CO<sub>2</sub>–H<sub>2</sub>O–N<sub>2</sub> of 14/3/83, 9/3/88 and 4/3/93 v%, respectively. (d) Cycling of CO<sub>2</sub> separation from a stream of CO<sub>2</sub>–H<sub>2</sub>O–N<sub>2</sub> of 4/3/93 v% at 25 °C, following a regeneration by an Ar purge at 50 °C.

molecules per nm<sup>2</sup> surface area), which is more than double that of reported mesoporous carbon (H<sub>2</sub> storage: 0.98 wt%, corresponding to 3.00 H<sub>2</sub> molecules per nm<sup>2</sup> surface area),<sup>86</sup> and even comparable to microporous activated carbons with highly developed pores (H<sub>2</sub> storage: 2.49 wt%, corresponding to 2.35H<sub>2</sub> molecules per nm<sup>2</sup> surface area)<sup>87</sup> under identical conditions. Thus the potential application of porous carbon nanosheets in other energy fields can be expected.

## 4 Conclusion

New porous carbon nanosheet materials, whose thickness can be precisely controlled over the nanometer length scale, have been produced by wet-chemistry synthesis using graphene oxides as the shape-directing agent. This feature is distinct from conventional porous carbons that are composed of a micronsized or larger skeleton. The assembly of the nanosheets produces hierarchically porous carbon monoliths which are mechanically robust compared to porous carbon monoliths reported in the literature.65 By creating such precisely controlled materials with short diffusion paths and high microporosity, instead of larger pores (little contribution to CO<sub>2</sub> capacity), these PCNs greatly accelerate CO2 adsorption kinetics, increasing the utilization degree of the overall porosity and surface area. The typical product, as characterized using various techniques, is highly effective and stable in selectively adsorbing CO<sub>2</sub> from a dilute hydrated gas. This may have a major impact on the continuous advance in new materials for CO2 separation under more harsh conditions. Thus, we believe our fundamentally new approach will provide avenues for the rational design of novel porous carbon materials with associated advantages and great potential applications in gas separation and storage.

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## Notes and references

- 1 J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477–1504.
- 2 A. Samanta, A. Zhao, G. K. H. Shimizu, P. Sarkar and R. Gupta, *Ind. Eng. Chem. Res.*, 2012, **51**, 1438–1463.
- 3 S. Himeno, T. Komatsu and S. Fujita, *J. Chem. Eng. Data*, 2005, **50**, 369–376.
- 4 G.-P. Hao, W.-C. Li and A.-H. Lu, J. Mater. Chem., 2011, 21, 6447–6451.
- 5 X. Zhu, P. C. Hillesheim, S. M. Mahurin, C. Wang, C. Tian,
  S. Brown, H. Luo, G. M. Veith, K. S. Han, E. W. Hagaman,
  H. Liu and S. Dai, *ChemSusChem*, 2012, 5, 1912–1917.

- 6 L. Zhao, Z. Bacsik, N. Hedin, W. Wei, Y. Sun, M. Antonietti and M.-M. Titirici, *ChemSusChem*, 2010, **3**, 840–845.
- 7 W. Xing, C. Liu, Z. Zhou, L. Zhang, J. Zhou, S. Zhuo, Z. Yan,
   H. Gao, G. Wang and S. Qiao, *Energy Environ. Sci.*, 2012, 5,
   7323–7327.
- 8 M. Sevilla and A. B. Fuertes, *Energy Environ. Sci.*, 2011, 4, 1765–1771.
- 9 Z. Wu, N. Hao, G. Xiao, L. Liu, P. Webley and D. Zhao, *Phys. Chem. Chem. Phys.*, 2011, **13**, 2495–2503.
- 10 D. Britt, H. Furukawa, B. Wang, T. G. Glover and O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.*, 2009, **106**, 20637–20640.
- 11 T. Ben, H. Ren, S. Ma, D. Cao, J. Lan, X. Jing, W. Wang, J. Xu, F. Deng, J. M. Simmons, S. Qiu and G. Zhu, *Angew. Chem.*, *Int. Ed.*, 2009, **48**, 9457–9460.
- 12 S. Horike, S. Shimomura and S. Kitagawa, *Nat. Chem.*, 2009, 1, 695–704.
- 13 D. M. D'Alessandro, B. Smit and J. R. Long, *Angew. Chem., Int. Ed.*, 2010, **49**, 6058–6082.
- 14 A. Phan, C. J. Doonan, F. J. Uriberomo, C. B. Knobler, M. O'Keeffe and O. M. Yaghi, Acc. Chem. Res., 2010, 43, 58–67.
- 15 J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.*, 2012, **112**, 869–932.
- 16 S. Cavenati, C. A. Grande and A. E. Rodrigues, J. Chem. Eng. Data, 2004, 49, 1095–1101.
- 17 Y. Wang and M. D. LeVan, *J. Chem. Eng. Data*, 2009, **54**, 2839–2844.
- 18 S. Choi, J. H. Drese and C. W. Jones, *ChemSusChem*, 2009, 2, 796–854.
- 19 F. Akhtar, Q. Liu, N. Hedin and L. Bergström, *Energy Environ.* Sci., 2012, 5, 7664–7673.
- 20 H.-B. Yao, H.-Y. Fang, X.-H. Wang and S.-H. Yu, *Chem. Soc. Rev.*, 2011, **40**, 3764–3785.
- 21 Y. Li, Z.-Y. Fu and B.-L. Su, *Adv. Funct. Mater.*, 2012, **22**, 4634–4667.
- 22 G.-P. Hao, W.-C. Li, D. Qian, G.-H. Wang, W.-P. Zhang,
   T. Zhang, A.-Q. Wang, F. Schüth, H.-J. Bongard and
   A.-H. Lu, J. Am. Chem. Soc., 2011, 133, 11378–11388.
- 23 G.-P. Hao, W.-C. Li, D. Qian and A.-H. Lu, *Adv. Mater.*, 2010, 22, 853–857.
- 24 G.-P. Hao, W.-C. Li, S. Wang, G.-H. Wang, L. Qi and A.-H. Lu, *Carbon*, 2011, **49**, 3762–3772.
- 25 Y. Huang, H. Cai, D. Feng, D. Gu, Y. Deng, B. Tu, H. Wang,
   P. A. Webley and D. Zhao, *Chem. Commun.*, 2008, 2641–2643.
- 26 Y. Wan and D. Zhao, Chem. Rev., 2007, 107, 2821-2860.
- 27 M. Nandi, K. Okada, A. Dutta, A. Bhaumik, J. Maruyama,
   D. Derks and H. Uyama, *Chem. Commun.*, 2012, 48, 10283– 10285.
- 28 M. Zhong, S. Natesakhawat, J. P. Baltrus, D. Luebke, H. Nulwala, K. Matyjaszewski and T. Kowalewski, *Chem. Commun.*, 2012, 48, 11516–11518.
- 29 J. Patiño, M. Gutíerrez, D. Carriazo, C. O. Ania, J. B. Parra, M. L. Ferrer and F. del Monte, *Energy Environ. Sci.*, 2012, 5, 8699–8707.
- 30 C. D. Liang, Z. J. Li and S. Dai, Angew. Chem., Int. Ed., 2008, 47, 3696–3717.

- 31 A. Stein, Z. Y. Wang and M. A. Fierke, *Adv. Mater.*, 2009, 21, 265–293.
- 32 J. Park, Z. U. Wang, L.-B. Sun, Y.-P. Chen and H.-C. Zhou, *J. Am. Chem. Soc.*, 2012, **134**, 20110–20116.
- 33 Y. Zhao, J. Zhang, B. Han, J. Song, J. Li and Q. Wang, *Angew. Chem., Int. Ed.*, 2011, **50**, 636–639.
- 34 R. Y. Ryoo, S. H. Joo, M. Kruk and M. Jaroniec, *Adv. Mater.*, 2001, **13**, 677–681.
- 35 T.-Y. Ma, H. Li, Q.-F. Deng, L. Liu, T.-Z. Ren and Z.-Y. Yuan, *Chem. Mater.*, 2012, **24**, 2253–2255.
- 36 W. Li and D. Zhao, Chem. Commun., 2013, 49, 943-946.
- 37 A. Carné, C. Carbonell, I. Imaz and D. Maspoch, *Chem. Soc. Rev.*, 2011, 40, 291–305.
- 38 J. Zhang, L. Sun, F. Xu, F. Li, H.-Y. Zhou, Y.-L. Liu, Z. Gabelica and C. Schick, *Chem. Commun.*, 2012, 48, 759–761.
- 39 S. Keskin, T. M. van Heest and D. S. Sholl, *ChemSusChem*, 2010, **3**, 879–891.
- 40 R. Dawson, L. A. Stevens, T. C. Drage, C. E. Snape, M. W. Smith, D. J. Adams and A. I. Cooper, *J. Am. Chem. Soc.*, 2012, **134**, 10741–10744.
- 41 X. Huang, K. Qian, J. Yang, J. Zhang, L. Li, C. Yu and D. Zhao, *Adv. Mater.*, 2012, **24**, 4419–4423.
- 42 D. C. Wei and Y. Q. Liu, Adv. Mater., 2010, 22, 3225–3241.
- 43 H.-P. Cong, X.-C. Ren, P. Wang and S.-H. Yu, *ACS Nano*, 2012, 6, 2693–2703.
- 44 S. Yin, Y. Zhang, J. Kong, C. Zou, C. Li, X. Lu, J. Ma, F. C. Boey and X. Chen, *ACS Nano*, 2011, 5, 3831–3838.
- 45 Z. Tang, S. Shen, J. Zhuang and X. Wang, *Angew. Chem., Int. Ed.*, 2010, **49**, 4603–4607.
- 46 H.-P. Cong, J.-J. He, Y. Lu and S.-H. Yu, *Small*, 2010, **6**, 169–173.
- 47 Z.-P. Chen, W.-C. Ren, L.-B. Gao, B.-L. Liu, S.-F. Pei and H.-M. Cheng, *Nat. Mater.*, 2011, **10**, 424–428.
- 48 H. Bai, C. Li and G. Shi, Adv. Mater., 2011, 23, 1089-1115.
- 49 F. Börrnert, J. Kunstmann, A. Bachmatiuk, M. Pötschke, M. Shiraishi, M. Meyyappan, B. Büchner, R. Roche and G. Cuniberti, *Adv. Mater.*, 2011, 23, 4471–4490.
- 50 V. Chandra, S. Yu, S. Kim, Y. Yoon, D. Kim, A. Kwon, M. Meyyappan and K. Kim, *Chem. Commun.*, 2012, 48, 735– 737.
- 51 H. Bai, C. Li, X. Wang and G. Shi, *J. Phys. Chem. C*, 2011, **115**, 5545–5551.
- 52 L. Sun and G. Shi, J. Mater. Chem., 2012, 22, 12810-12816.
- 53 Z.-S. Wu, Y. Sun, Y.-Z. Tan, S. Yang, X. Feng and K. Müllen, *J. Am. Chem. Soc.*, 2012, **134**, 19532–19535.
- 54 M. Sevilla and A. B. Fuertes, *Energy Environ. Sci.*, 2011, 4, 1765–1771.
- 55 J. Wang, A. Heerwig, M. R. Lohe, M. Oschatz, L. Borchardt and S. Kaskel, *J. Mater. Chem.*, 2012, **22**, 13911–13913.
- 56 J. A. Thote, K. S. Iyer, R. Chatti, N. K. Labhsetwar, R. B. Biniwale and S. S. Rayalu, *Carbon*, 2010, 48, 396–402.
- 57 D. Carriazo, M. C. Serrano, M. C. Gutierrez, M. L. Ferrer and F. del Monte, *Chem. Soc. Rev.*, 2012, **41**, 4996–5014.
- 58 D. Carriazo, M. C. Gutiérrez, M. L. Ferrer and F. del Monte, *Chem. Mater.*, 2010, **22**, 6146–6152.
- 59 R. Banerjee, H. Furukawa, D. Britt, C. Knobler, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, **131**, 3875–3877.

- 60 B. Wang, A. P. Côté, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Nature*, 2008, 453, 207–211.
- 61 D. Li, M. B. Müller, S. Gilje, R. B. Kaner and G. G. Wallace, *Nat. Nanotechnol.*, 2008, 3, 101–105.
- 62 Z.-M. Wang, W. Wang, N. Coombs, N. Soheilnia and G. A. Ozin, ACS Nano, 2010, 4, 7437–7450.
- 63 S. Yang, X. Feng, L. Wang, K. Tang, J. Maier and K. Müllen, *Angew. Chem., Int. Ed.*, 2010, **49**, 4795–4799.
- 64 A. Vishnyakov, P. I. Ravikovitch and A. V. Neimark, *Langmuir*, 1999, **15**, 8736–8742.
- 65 X. Zhang, Z. Sui, B. Xu, S. Yue, Y. Luo, W. Zhan and B. Liu, J. Mater. Chem., 2011, 21, 6494–6497.
- 66 Y. Huang, H. Cai, D. Feng, D. Gu, Y. Deng, B. Tu, H. Wang,
  P. A. Webley and D. Zhao, *Chem. Commun.*, 2008, 2641–2643.
- 67 X. Wang, K. N. Bozhilov and P. Feng, *Chem. Mater.*, 2006, **18**, 6373–6381.
- 68 D. Lozano-Castelló, M. Jordá-Beneyto, D. Cazorla-Amorós, A. Linares-Solano, J. F. Burger, H. J. M. ter Brake and H. J. Holland, *Carbon*, 2010, 48, 123–131.
- 69 D. Lozano-Castelló, D. Cazorla-Amorós, A. Linares-Solano and D. F. Quinn, *Carbon*, 2002, **40**, 2817–2825.
- 70 A. K. Kercher and D. C. Nagle, Carbon, 2003, 41, 3-13.
- 71 D. Tanaka, A. Henke, K. Albrecht, M. Moeller, K. Nakagawa,S. Kitagawa and J. Groll, *Nat. Chem.*, 2010, 2, 410–416.
- 72 Q. Yang, C. Zhong and J. Chen, *J. Phys. Chem. C*, 2008, **112**, 1562–1569.
- 73 D. Saha and S. Deng, J. Colloid Interface Sci., 2010, 345, 402-409.
- 74 G. Chandrasekar, W.-J. Son and W.-S. Ahn, *J Porous Mater.*, 2009, **16**, 545–551.
- 75 J. An, S. J. Geib and N. L. Rosi, J. Am. Chem. Soc., 2010, 132, 38–39.
- 76 Q. Lin, T. Wu, S.-T. Zheng, X. Bu and P. Feng, J. Am. Chem. Soc., 2012, 134, 784–787.
- 77 Q. Lin, T. Wu, S.-T. Zheng, X. Bu and P. Feng, J. Am. Chem. Soc., 2012, 134, 784–787.
- 78 R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, P. G. Boyd, S. Alavi and T. K. Woo, *Science*, 2010, **330**, 650–653.
- 79 H. Kim, Y. Kim, M. Yoon, S. Lim, S. M. Park, G. Seo and K. Kim, J. Am. Chem. Soc., 2010, 132, 12200–12202.
- 80 F. Brandani and D. M. Ruthven, *Ind. Eng. Chem. Res.*, 2004, 43, 8339–8344.
- 81 A. C. Kizzie, A. G. Wong-Foy and A. J. Matzger, *Langmuir*, 2011, 27, 6368–6373.
- 82 M. Wriedt, J. P. Sculley, A. A. Yakovenko, Y. Ma, G. J. Halder,
  P. B. Balbuena and H.-C. Zhou, *Angew. Chem., Int. Ed.*, 2012,
  51, 9804–9808.
- 83 J. Liu, Y. Wang, A. I. Benin, P. Jakubczak, R. R. Willis and M. D. LeVan, *Langmuir*, 2010, 26, 14301–14307.
- 84 Z. Tang, H. Chen, X. Chen, L. Wu and X. Yu, J. Am. Chem. Soc., 2012, 134, 5464–5467.
- 85 Z. Tang, X. Chen, H. Chen, L. Wu and X. Yu, Angew. Chem., Int. Ed., 2013, 52, 5832–5835.
- 86 K. Xia, Q. Gao, C. Wu, S. Song and M. Ruan, *Carbon*, 2007, 45, 1989–1996.
- 87 H. Wang, Q. Gao and J. Hu, J. Am. Chem. Soc., 2009, 131, 7016–7022.