Cost-Efficient Strategy for Sustainable Cross-Linked Microporous Carbon Bead with Satisfactory CO₂ Capture Capacity

Binbin Chang*,† Li Sun, Weiwei Shi,‡ Shouren Zhang,† and Baocheng Yang*,†

1Henan Provincial Key Laboratory of Nanocomposites and Applications, Institute of Nanostructured Functional Materials, Huanghe Science and Technology College, Zhengzhou, Henan 450006, China
2Huanghe Science and Technology College, Zhengzhou, Henan 450006, China

ABSTRACT: Cross-linked microporous carbon beads (MCBs) were successfully synthesized via a green, convenient, and cost-efficient strategy derived from a renewable sugar source. Such an approach avoids the time-consuming procedure and the use of corrosive chemical activating agents and toxic solvents and only involves a simple carbonization process, which makes it to be applicable for rapid and large-scale industrial production of MCB materials. The obtained MCBs possessed well-defined microporous structure, narrow pore size, and high surface area. Particularly, the microporosity of the resultant MCBs could be easily tailored to arise primary pores of size 0.5–0.9 nm by adjusting the carbonization temperature and reaction time, which remarkably favor the CO₂ capture. The optimal sample of MCBs-9-5 carbonized at 900 °C for 5 h was characterized by high microporosity (80% of the surface area from micropores), especially ultrahigh narrow microporosity (53% of pore volume from micropores of size <1 nm), which endowed it a great satisfactory CO₂ uptake of 4.25 mmol g⁻¹ at 25 °C and 1 bar. Significantly, a prominent CO₂/N₂ selectivity and superior recyclability of MCBs-9-5 were also achieved. Combined with the simple fabrication, the satisfactory adsorption capacity, and high selectivity, MCBs-9-5 should be a promising adsorbent for CO₂ capture and separation.

1. INTRODUCTION

Carbon dioxide (CO₂), as a primary greenhouse gas, has increased dramatically in the last recent decades owing to the large-scale burning of fossil fuels to meet the energy requirement of world, which results in global warming and anthropogenic climate change, such as the continuous rise of water level in sea, the increasing number of ocean storms, and so on.3 Thus, it is urgent and significant for reducing atmospheric CO₂ concentrations to develop efficient CO₂ capture and sequestration. Up to now, many technologies have been employed to separate and capture CO₂, for example, chemical/physical adsorption, membrane separation, solution adsorption, and cryogenic separation. Among these strategies, adsorption using porous solid adsorbents is the most promising technology because of their unique advantages over other methods such as low cost, low energy consumption, easy handling, and ease of applications. The key of the adsorption technology is developing a high-performance CO₂ adsorbent. Porous solid materials used for the CO₂ capture mainly involve porous carbons, zeolites, amine-modified mesoporous silica, metal–organic frameworks, porous organic polymers, graphene-based composite adsorbents, and so on.1–8 Porous carbons, especially activated carbons, are regarded as one of the most potential candidates for CO₂ adsorption owing to their high surface area, large pore volume, easy-to-tunable and developed porosity, low preparation cost, stable physicochemical properties, and low energy consumption for regeneration. However, traditional activated carbons exhibit a relatively low CO₂ adsorption capacity of typically ca. 2–3 mmol g⁻¹ under room temperature at 1 bar.1,9

One efficient way of improving CO₂ capture capacity is to introduce basic sites into the skeleton of carbon materials, as the basic sites are believed to promote the interaction between CO₂ molecules and carbon surface. For this purpose, many efficient approaches have been developed to design nitrogen-doped porous carbons, including postmodiﬁcation of amine on the carbon surface and incorporation of nitrogen groups into carbon skeleton.10,11 Fan et al. synthesized nitrogen-doped microporous carbons by a K₂CO₃ chemical activation strategy using chitosan as a carbon precursor, which exhibited a high CO₂ uptake of 3.86 mmol g⁻¹ at 25 °C and 1 bar.12 Wang et al. reported N-doped porous carbon hollow spheres with a CO₂ adsorption capacity of 2.96 mmol g⁻¹ (25 °C, 1 bar) by using a melamine–formaldehyde nanosphere as a hard template and a
resorcinol−formaldehyde resin as a carbon precursor.\textsuperscript{13} Unfortunately, designing nitrogen-doping materials usually involves poisonous, expensive, and corrosive raw materials, which can bring unexpected damage for the environment and equipment, restricting their practical applications.\textsuperscript{14} Another way to enhance the CO\textsubscript{2} capture capacity is to design microporous carbons especially containing rich and narrow micropores with a pore size of <1 nm.\textsuperscript{15,16} Wahby et al. synthesized petroleum pitch-derived carbon molecular sieves with developed microporosity with a narrow micropore size of 0.35−0.7 nm by the KOH chemical activation method, which showed an excellent CO\textsubscript{2} uptake of 8.6 mmol g\textsuperscript{−1} (0 °C, 1 bar).\textsuperscript{17} Sevilla et al. prepared microporous biomass-based carbon materials via KOH chemical activation of hydrothermal carbons derived from mixtures of algae and glucose, which possessed a large number of narrow micropores (<1 nm) and exhibited a satisfactory CO\textsubscript{2} adsorption capacity of 4.8 mmol g\textsuperscript{−1} (25 °C, 1 bar).\textsuperscript{18} These results demonstrate that microporous carbon with a large proportion of narrow micropore size of <1 nm can efficiently improve the CO\textsubscript{2} capture capacity. However, the synthesis of well-defined microporous carbons usually adopts the chemical activation route using KOH, NaOH, H\textsubscript{3}PO\textsubscript{4}, and ZnCl\textsubscript{2} as chemical activating agents, which is a time-consuming, step-tedious, and costly process.\textsuperscript{19−22} Meanwhile, these synthetic strategies suffer some other drawbacks, such as corrosion of the equipment, high energy consumption, and so on. Therefore, from the viewpoint of practical applications, it still remains a big challenge to design a more favorable ultramicroporous carbon sorbent for CO\textsubscript{2} capture not only with high performance but also with environmental friendliness and cost-effectiveness.

Herein, we develop a green and cost-efficient strategy for preparing cross-linking microporous carbon bead with large numbers of narrow micropores (<1 nm). Compared with other reported methods, this strategy only involves a simple heat treatment procedure and avoids the use of chemical activating agents and toxic organic solvents; meanwhile, it chooses inexpensive and renewable starch sugar as a carbon source, which exhibits an important potential for fast and large-scale preparation of microporous carbons to meet practical industrial applications. The evolution of microporosity with different calcination temperatures and reaction times was investigated.

Figure 1. N\textsubscript{2} adsorption−desorption isotherms and pore size distribution of all as-obtained MCBs materials: (a,b) MCBs-x-3 and (c,d) MCBs-9-y.
The optimal sample with a high surface area of 1755.4 m$^2$ g$^{-1}$ and a large micropore surface area of 1444.9 m$^2$ g$^{-1}$ was obtained by directly carbonizing at 900 °C for 5 h. As a CO$_2$ adsorbent, the CO$_2$ capture capacity of the resultant materials is evaluated and the optimal sample exhibits considerable CO$_2$ adsorption capacities of 6.15 and 4.25 mmol g$^{-1}$ under 0 and 25 °C at 1 bar, respectively. Furthermore, such a CO$_2$ adsorbent also shows an outstanding recyclability and CO$_2$/N$_2$ selectivity adsorption property.

2. RESULTS AND DISCUSSION

2.1. Material Characterizations. Cross-linked microporous carbon beads (MCBs) were synthesized via an air-assisted activated strategy without adding chemical activating agents and toxic organic solvents, and the possible fabrication mechanism of MCB materials is displayed in Scheme 1. Glucose-based carbon sphere precursors were the colloidal complex mixture of organic compounds with an extremely low carbonization degree. In the beginning stage, these CS precursors were easy to pyrolyze at high temperature to bring a microporous structure with the release of small molecules. Meanwhile, the colloidal glucose-based precursors were converted into cross-linked carbon beads, and the diameter of the bead reduced as a result of the structural shrinkage.

Subsequently, under the assistance of air, some of the carbons in the skeleton were burned by O$_2$ in the air to generate a promotive porosity and meanwhile released CO$_2$ during the process of carbon burning escaped through the spherical carbon substrate, which also produced more micropores and even enlarged pores. Moreover, some carbon substrates could react with CO$_2$ yielding CO whilst generate some fine micropores. Thus, the microporosity of MCB materials is greatly dependent on the calcinations temperature and reaction time. In brief, the porosity of the resulting MCB materials mainly derives from the incomplete burning of carbon taken in the reaction process. Different annealing temperatures and reaction times bring different degrees of carbon burning, resulting in the variation of porosity.

The influences of carbonization temperature and reaction time on the porosity of MCB materials were characterized by the N$_2$ sorption technology. Figure 1a,b shows the relationship of the porosity of MCB samples with carbonization temperature. It is clear that all samples present a typical type I isotherm of the microporous structure (Figure 1a), and these micropores should originate from the elimination of surface O- and H-groups during the carbonization process. Notably, although the isotherm of MCBs-10-3 can still be attributed to the type I curve, the adsorbed N$_2$ volume increases in a stepwise manner to the high-pressure region, indicating the increase in the percentage of mesopores in the total porosity of MCBs-10-3, which should be ascribed to the elimination of more volatile substance under high heat treatment temperature, resulting in the coalescence of some narrow micropores to form some larger micropores and even small mesopores (2–3 nm). Such results can be demonstrated by the pore size distribution in Figure 1b. For the MCBs-7-3 sample, the micropores mainly center in 0.80 and 1.25 nm, and micropores further develop to generate a multiscale microporosity in MCBs-8-3 and MCBs-9-3 samples with an extra micropore of ∼0.83 nm, and MCBs-9-3 should possess a superior microporosity than that of MCBs-8-3, which could be testified from the pore volume value. With continuously increasing annealing temperature to 1000 °C, most micropores of MCBs-10-3 enlarge to 1.25–1.58 nm and some micropores even further enlarge to mesopores of 2.05 nm, bringing the remarkable enhancement of mesoporosity (Table 1), which is consistent with the analytic result of isotherm. As shown in Figure S1a (Supporting Information), the proportion of micropores progressively enhances with the rise of temperature from 700 to 900 °C, in spite of the degree of growth in the micropore proportion was slow, whereas when the activation temperature rose to 1000 °C, the proportion of mesopores in the MCBs-10-3 sample sharply increased and accordingly the proportion of micropores in total pores noticeably declined. On the basis of these results, it was easy to draw such a conclusion that the carbonization temperature had a significant impact on the evolution of microporosity and pore proportion in MCB materials.

Activation time is another critical parameter for developing a superior porosity, and the results are displayed in Figure 1c,d. Obviously, all N$_2$ adsorption—desorption isotherms exhibit a typical type I isotherm, representing a typical microporous structure (Figure 1c). The increase of N$_2$ adsorbed quantity indicates the larger and larger surface area and pore volume, and the adsorbed N$_2$ volume gradually increases at the high-pressure region with the prolonging of activation time, suggesting the generation of enlarged micropores and even some mesopores. Figure 1d depicts the pore distribution curves of all MCBs-9-y samples, and it clearly shows the evolution
process of the micropore size with the increase of activation time. All MCBs-9-7 samples exhibit hierarchical narrow micropore size distributions of ~0.48, 0.68, and 0.85 nm as well as a relatively large micropore of ~1.25 nm. Noticeably, these hierarchical micropores further develop and optimize with the prolonging of reaction time, and as the reaction time progressively increases to 4 h, some new micropores of ~1.48 nm begin to generate. When the reaction time continuously prolongs to 6 h, such micropores of ~1.25 and 1.48 nm dominates the pore size, and even larger micropores of ~1.86 nm are generated in the MCBs-9-6 sample. Figure S1b analyzes the proportion of micro-/mesopores from the surface area and pore volume. Apparently, with the increase of reaction time from 1 to 3 h, the proportion of micropores retains a similar value of ~89% and then sharply declines as the reaction time increased from 4 to 6 h. A similar result can be drawn from the values of the micropore surface area and micropore volume (Table 1), and when the reaction time exceeds 4 h, $S_{\text{micro}}$ and $V_{\text{micro}}$ extremely slow increase and even reach a saturation value, whereas $S_{\text{meso}}$ and $V_{\text{meso}}$ gradually enhance, which brings the increase of the Brunauer–Emmett–Teller (BET) surface area and total pore volume. Figure S2 shows the comparison of pore structures of MCBs-9-5 and MCBs-9-5-r. In the absence of air, the MCBs-9-5-r sample has a BET surface area of 492.8 m$^2$ g$^{-1}$ mainly contributed by the micropore surface area of 439.5 m$^2$ g$^{-1}$ and these pores should be entirely originated from the pyrolysis of the CS precursor. From the comparison of the pore size distribution (Figure S2b), the MCBs-9-5-r sample owns an indistinct pore size distribution, indicative of the existence of small amount of pores, which is much poorer than the perfect multiscale micropore size distribution of the MCBs-9-5 sample. Such result further testifies the vital effect of air assisted on the generation of superior microporosity. Thus, these results suggest the formation of a multiscale microporous structure in the following stages: (i) the high-temperature pyrolysis of the carbonaceous precursor generated abundant micropores; (ii) with the assistant of air, these micropores further developed; (iii) some ultramicropores were enlarged and even produced mesopores by the combination of the partial carbon skeleton. Figure 2 depicts the micropore size distribution of all as-obtained MCB materials measured by CO$_2$ adsorption at 0 °C using the DFT method. Obviously, a multiscale micropore can be found in all samples, especially a superior hierarchical narrow micropore size (<0.7 nm) distribution. With the increase of calcination temperature, micropore sizes are gradually developed and enlarged and MCBs-9-3 exhibits a best micropore size in all MCBs-x-3 samples, especially the outstanding narrow micropore size distribution. Similarly, the micropore size shows a similar evolution with the prolonging of calcination time, and micropore sizes are gradually widened from narrow micropores (<0.7 nm) to fine micropores (0.7–1.0 nm) and even large micropores (>1.0 nm), which should be related to the further pyrolysis of the glucose-based precursor, resulting in the release of more volatile substance.

Figure S3a,b presents the wide-angle X-ray diffraction (XRD) patterns of all MCB materials with different calcination temperatures and times. All of the samples exhibited two similar broad and weak diffraction peaks at about $2\theta = 21.8$ and 43.5°, which correspond to (002) and (100) diffractions of the amorphous carbon skeleton, respectively, suggesting the low crystallinity of the resultant MCB materials. In addition, the intensity of diffraction peaks in XRD patterns gradually weakened from MCBs-9-1 to MCBs-9-6, which could be related to the gradual decrease in the microcrystallite zones of graphite in the MCB samples as the increase of reaction time. The Raman spectra of all MCBs-x-3 materials are displayed in Figure S4. Clearly, two strong peaks can be seen in these materials, which center at ~1334 and 1587 cm$^{-1}$. The peak located at about 1334 cm$^{-1}$ is assigned to the D-band, which should be ascribed to the vibration of carbon atoms with dangling bonds in planar terminations of the disordered graphite-like framework. The other peak centered at about 1587 cm$^{-1}$ is referred to the G-band, corresponding to the ideal graphite in-plane vibrations with E$_2g$ symmetry. Besides, the degree of graphitization can be further characterized by the ratio of relative intensities of D- and G-band peaks ($I_D/I_G$). The values of $I_D/I_G$ for MCBs-7-3, MCBs-8-3, MCBs-9-3, and MCBs-10-3 are 1.08, 0.99, 0.98, and 0.96, respectively, which indicate that the degree of graphitization enhances with the rise of carbonization temperature.

To evaluate the variation of surface functional groups, Fourier transform infrared (FTIR) spectra of the resultant samples are presented in Figure S5. In the CS precursor, the bands at 1710 and 1620 cm$^{-1}$ should be attributed to C=O and C=C stretching vibrations, respectively, and the results support the concept of aromatization of glucose during hydrothermal treatment. The bands centered at 1000–1300 cm$^{-1}$ are related to the C–OH stretching vibration and −OH bending vibration, which imply the existence of large numbers of residual hydroxy groups. The other adsorption bands at 1410–1510 and 2840–2930 cm$^{-1}$ correspond to the C–H bending vibration and stretching vibration, respectively. The broad adsorption band at 3450 cm$^{-1}$ should be ascribed to −OH bending vibration in the H$_2$O molecule. Such results suggest that the CS precursor should possess abundant oxygen-
containing and hydrogen-containing functional groups. Obviously, a similar FTIR spectrum can be found in MCB samples, in which only the C=O stretching vibration at ca. 1620 cm$^{-1}$ can be clearly found in MCB samples, and the characteristic adsorption bands of C=O and C−O disappear, which should be ascribed to the pyrolysis of precursors at high temperature, resulting in the elimination of surface oxygen-containing groups. In addition, it is clear that the adsorption bands of C−H (at 2840−2930 cm$^{-1}$) and −OH (at 3450 cm$^{-1}$) become indistinct and even disappeared with the rise of activation temperature, indicating that the activation temperature has a significant impact on the surface chemical property of MCB materials.

Figure 3. SEM images of as-prepared materials: (a) CS precursor; (b) MCBs-7-3; (c) MCBs-8-3; (d) MCBs-9-3; and (e) MCBs-10-3.

Figure 4. TEM images: (a,e) MCBs-7-3; (b,f) MCBs-8-3; (c,g) MCBs-9-3; and (d,h) MCBs-10-3.

Figure 5. CO$_2$ adsorption isotherms of all as-obtained MCB samples at 0 °C (a,b) and 25 °C (c,d).
To reveal the evolution of the morphology and pore structure, the as-obtained MCB samples were characterized by electron microscopy. As displayed in Figure 3a, glucose-based CS precursors present a cross-linked bead structure with an average diameter of ca. 400 nm. Obviously, such cross-linked beads are well-maintained after carbonizing the CS precursor in air atmosphere at different temperatures for 3 h (Figure 3), suggesting that the pyrolysis and air-assisted activation process do not destroy the initial structure of the CS precursor. However, the diameter size of cross-linked carbon beads reduces as a result of structural shrinkage, and MCBs-9-3 exhibits an average diameter of ~200 nm, and even MCBs-10-3 possesses a smaller size of ~150 nm because of a higher carbonization temperature. Figure S6 shows the scanning electron microscopy (SEM) images of as-prepared MCBs carbonized at 900 °C with different activation times. Similarly, all MCBs-9-y samples also retain the cross-linked bead structure, and importantly, these cross-linked carbon beads retain an almost identical diameter of ~200 nm, testifying that prolonging the activation time has no influence on the morphological structure. The evolutions of the morphology and structure are further verified by transmission electron microscopy (TEM) images. As shown in Figure 4, MCBs-x-3 materials clearly exhibit the progressive variation of the morphology and porous pore structure with the change of the carbonization temperature. Consistent with the SEM observation, all MCBs-x-3 materials present the cross-linked bead structure. Furthermore, from the high-magnification TEM images (Figure 4e–h), large numbers of nanopores are easily discernible on the surface of carbon beads. Meanwhile, it could be easily observed that these pores in MCBs-x-3 samples gradually enlarge as the increasing activation temperature. Similar results can be found from the TEM images of MCBs-9-y samples (Figure S7). Such results further confirm that the carbonization temperature and reaction time play a crucial role in the development of porosity of MCB materials.

2.2. CO2 Capture Performance. The CO2 adsorption capacities of all as-obtained materials are investigated at two representative temperatures (0 and 25 °C), and the adsorption isotherms are presented in Figure 5, and the related uptake capacities are listed in Table 2. As shown in Figure 5a, it can be observed that the MCBs-7-3 sample has a CO2 adsorption capacity of 3.79 mmol g⁻¹ at 0 °C and 1 bar. With the increasing activation temperature, the obtained MCBs-8-3 and MCBs-9-3 samples exhibit the enhanced CO2 capture capacities of 4.74 and 5.64 mmol g⁻¹, respectively; however, the further increase in the annealing temperature brings a negative effect on the CO2 adsorption capacity, and a declined CO2 uptake value of 5.39 mmol g⁻¹ is obtained over the MCBs-10-3 sample. Figure 5b displays the CO2 adsorption isotherms of MCBs-9-y series materials; it can be seen that CO2 uptakes are in the range of 4.85–6.15 mmol g⁻¹, and the CO2 adsorption capacities of MCBs-9-y materials are improved and then declined with the progressive prolonging of reaction time. Similarly, the same variation tendency of CO2 adsorption capacity over MCBs-x-3 and MCBs-9-y series materials tested at 25 °C can also be observed in Figure 5c,d, respectively. For all the as-prepared materials, the CO2 uptake enhances with the increase of CO2 pressure. Noticeably, at relatively low pressure, the CO2 uptakes of both MCBs-x-3 and MCBs-9-y series materials, especially MCBs-10-3 and MCBs-9-6 samples, are a little lower at higher activation temperature and longer reaction time, which should be related to the size effect because the micropore size of the obtained MCB materials further developed and enlarged gradually as the temperature and time increased, resulting in the decrease of the proportion of micropores (<1 nm).

The micropore surface area and micropore pore volume, especially micropores of size <1 nm, play a significant role in CO2 adsorption, and the relevant analysis results are displayed in Figure 6 and Figure S8, respectively. Apparently, even though MCBs-9-6 and MCBs-10-3 possess higher total surface area and larger total pore volume compared with those of MCBs-9-3, MCBs-9-4, and MCBs-9-5 materials, their CO2 uptakes are much lower than those of MCBs-9-3, MCBs-9-4, and MCBs-9-5, which should be attributed to their lower micropore (<1 nm) surface areas and micropore pore volumes. As displayed in Figures 6 and S7, the CO2 uptake (at 0 and 25 °C, 1 bar) is not determined by the total surface area and pore volume, but by the pore size, especially narrow micropores of <1 nm, which are more efficient than larger micropores and mesopores, creating stronger interactions between CO2 molecules and carbon adsorbents. Such results are consistent with the previous reported works.

On the basis of the above results, it can be clearly found that MCB materials display a good property for CO2 capture, exhibiting an excellent potential as CO2 adsorbents. The optimal sample of MCBs-9-5 shows the highest CO2 capture values of 6.15 mmol g⁻¹ (at 0 °C, 1 bar) and 4.25 mmol g⁻¹ (at 25 °C, 1 bar), which should mainly be related to the presence of large numbers of narrow micropores (<1 nm). To examine the influence of air activation, the MCBs-9-5 and MCBs-9-5-r samples were compared with regard to their CO2 adsorption capacities (Figure S9). Obviously, the CO2 uptakes of MCBs-9-5-r are only 3.72 mmol g⁻¹ (at 0 °C, 1 bar) and 2.79 mmol g⁻¹ (at 25 °C, 1 bar), which are much lower than those of the MCBs-9-5 sample. Table 3 lists the CO2 adsorption capacities of a variety of reported carbon-based adsorbents. Apparently, the CO2 adsorption capacity of the MCBs-9-5 material is comparable and even higher than other similar carbons and even some of the reported nitrogen-doped porous carbons and hierarchical porous carbons derived by chemical activation. For example, Wang et al. prepared a nitrogen-doped porous carbon hollow sphere with an ultrahigh nitrogen content of 15.9 wt %, which showed a CO2 uptake of 4.42 mmol g⁻¹ at 0 °C and 1 bar.58 Cai et al. reported poly(vinylidene chloride)-based carbon with ultrahigh microporosity prepared by KOH activation, which exhibited a lower CO2 adsorption capacity of 3.64 mmol g⁻¹ at 25 °C and 1 bar.41 Therefore, from these

Table 2. CO2 Uptake of the As-Obtained MCB Materials at Different Temperatures and Pressures

| sample    | 0 °C, 0.15 bar | 0 °C, 1 bar | 25 °C, 0.15 bar | 25 °C, 1 bar |
|-----------|---------------|------------|----------------|-------------|
| MCBs-7-3  | 1.75 (77)     | 3.79 (166.76) | 0.89 (39.16)  | 2.51 (110.44) |
| MCBs-8-3  | 1.86 (81.84)  | 4.74 (208.56) | 0.95 (41.8)   | 3.05 (134.2)  |
| MCBs-9-1  | 1.94 (85.36)  | 4.85 (213.4)  | 1.01 (44.44)  | 3.15 (138.6)  |
| MCBs-9-2  | 1.89 (83.16)  | 5.07 (223.08) | 0.99 (43.56)  | 3.29 (144.76) |
| MCBs-9-3  | 1.96 (86.24)  | 5.64 (248.16) | 1.03 (45.32)  | 3.58 (157.52) |
| MCBs-9-4  | 1.84 (80.96)  | 5.85 (257.4)  | 1.28 (56.32)  | 3.92 (172.48) |
| MCBs-9-5  | 1.78 (79.32)  | 6.15 (270.6)  | 1.35 (59.4)   | 4.25 (187)    |
| MCBs-9-6  | 1.72 (75.68)  | 5.32 (234.08) | 0.97 (42.68)  | 3.35 (147.4)  |
| MCBs-10-3 | 1.33 (58.52)  | 5.39 (237.16) | 0.98 (43.12)  | 3.38 (148.72) |
| MCBs-9-5-r| 1.86 (81.84)  | 3.72 (163.68) | 1.09 (47.96)  | 2.79 (122.76) |
comparisons, it is clear that the resultant MCBs-9-5 material via this green, cost-efficient, and free-chemical activating agent strategy achieves a satisfactory CO₂ capture capacity, which should be attributed to high surface area, optimal micro-/mesopore proportion, and developed microporosity, especially large microporosity dominated by pores of 0.5−0.9 nm.

2.3. CO₂/N₂ Selectivity. From the viewpoint of practical applications, superior adsorbents should possess a high selectivity against other gases in addition to high CO₂ uptake. To estimate the CO₂ separation performance of the optimal sample of MCBs-9-5 and the reference sample of MCBs-9-5-r, their CO₂ and N₂ isotherms at 0 and 25 °C are displayed in Figure 7a,b, respectively. Clearly, the adsorption capacity of N₂ is much lower than that of CO₂ at the same condition for both MCBs-9-5 and MCBs-9-5-r samples. At 25 °C and 1 bar, the MCBs-9-5 sample has a CO₂ uptake of 4.25 mmol g⁻¹ and a N₂ adsorption capacity of 0.24 mmol g⁻¹, which translates to an equilibrium CO₂/N₂ adsorption ratio of 18, and this adsorption ratio is far higher than the CO₂/N₂ adsorption ratio of 8 for the MCBs-9-5-r sample, suggesting the better selectivity of MCBs-

Table 3. Comparison of the CO₂ Adsorption Capacity Over Different Carbon-Based Adsorbents

| sample        | CO₂ uptake (mmol g⁻¹) | T (°C) | pressure (bar) | selectivity b | refs |
|---------------|-----------------------|--------|----------------|---------------|------|
| AC-2-635      | 5.90/3.86             | 0/25   | 1              | 21            | 9    |
| RFL-500       | 3.13                  | 25     | 1              | NA            | 11   |
| N′/TC-EMC     | 4.0                   | 25     | 1              | 14            | 35   |
| CP-Z-700      | 5.9/3.1               | 0/25   | 1              | NA            | 45   |
| TB-MOP        | 4.05/2.57             | 0/25   | 1              | 50.6          | 46   |
| MC-200D8H     | 2.73                  | 25     | 1              | 21.3          | 51   |
| AC            | 2.8/1.8               | 0/25   | 1              | 17            | 52   |
| Om-ph-MR      | 2.5/1.77              | 0/25   | 1              | NA            | 53   |
| PTEB          | 3.47                  | 0      | 1              | 25.9          | 54   |
| NSC           | 4.8/3.1               | 0/25   | 1              | NA            | 55   |
| commercial ACs| 2−3                   | 25     | 1              | NA            |      |
| MCBs-9-5      | 6.15/4.25             | 0/25   | 1              | 61            | this work |

a Adsorption temperature. b Adsorption selectivity of CO₂/N₂ calculated by IAST at 25 °C; NA represents not available.

Figure 7. CO₂ and N₂ adsorption isotherms of MCBs-9-5 (a) and MCBs-9-5-r (b) at 0 and 25 °C; IAST selectivity of CO₂/N₂ on MCBs-9-5 (c) and MCBs-9-5-r (d) at 0 and 25 °C.
9-5 for CO₂ from N₂ than that of MCBs-9-5-r. More importantly, the CO₂/N₂ adsorption ratio of 18 for MCBs-9-5 is much higher than that of conventional porous carbons (typical 5–11) and even comparable to those of nitrogen-doped carbons and microporous organic polymer-derived carbons.42–45

We also employ the ideal adsorbed solution theory (IAST) model to further evaluate the selectivity for CO₂ adsorption from the simulated postcombustion flue gas, which is an often used method to estimate the selectivity of solid adsorbents for any two gases in a binary gas mixture. The CO₂/N₂ ratio is 15/85 in the calculation, which represents the typical composition of the flue gas. The selectivity for CO₂ adsorption from the IAST model was derived from the following equation

\[ S = \frac{[p(CO_2)/q(CO_2)]}{[p(N_2)/q(N_2)]} \]

where \( S \) is the selectivity for CO₂, \( p \) is the uptake of adsorbed CO₂/N₂, \( q(CO_2) \) is 0.15, and \( q(N_2) \) is 0.85. The calculation results of IAST selectivity are presented in Figure 7c,d. MCBs-9-5 exhibits the CO₂ adsorption selectivity of 49 and 61 at 0 and 25 °C under 1 bar, respectively, which are higher than the CO₂ adsorption selectivity of 29 and 41 for MCBs-9-5-r. Importantly, the CO₂/N₂ selectivity of MCBs-9-5 is remarkably high compared with that of the other porous carbon-based sorbents and even comparable with that of nitrogen-rich porous carbons,46–49 as shown in Table 3. The good selectivity in combination with the satisfactory adsorption capacity makes the MCBs-9-5 material highly promising in the selective capture of CO₂ from gas mixtures containing N₂.

2.4. CO₂ Isosteric Heat of Adsorption (\( Q_{st} \)) and Regeneration of the Adsorbent. To further reveal the interaction between the CO₂ molecule/adsorbents and evaluate the energetic heterogeneity of surfaces of adsorbents, the isosteric heat of adsorption (\( Q_{st} \)) was calculated from the CO₂ adsorption isotherms measured at 0 and 25 °C. As depicted in Figure 8, the \( Q_a \) values for all as-obtained MCBs at low surface coverage are ranged from 23 to 38 kJ mol⁻¹. Obviously, the heat of adsorption gradually declines at the low CO₂ uptake and then reaches a near plateau with the increasing CO₂ uptake, manifesting the heterogeneity of interaction between CO₂ molecules and the surface of adsorbents, which could be ascribed to the continuous occupation of adsorption active sites with the growing CO₂ uptake. Moreover, it is worth of notice that the \( Q_a \) values of MCBs-x-3 samples gradually decline with the increase of activation temperature, indicating the weaker and weaker interactions between adsorbent surfaces and CO₂ molecule as the elevated activation temperature.50 Such result should be related to the poorer and poorer microporosity, especially the decreased narrow microporosity (<1 nm) with the rise of activation temperature, resulting in the weaker interaction. Similarly, the \( Q_a \) values of MCBs-9-y present a roughly similar variation trend, and the \( Q_a \) values gradually decrease with the prolonging of activation time, which could also be attributed to the variation of micropores’ proportion and size. For the MCBs-9-5-r sample, even though it has a higher \( Q_a \) value than those of other MCBs-9-y materials, its \( Q_a \) value continuously declines with the enhanced CO₂ uptake, suggesting the nonuniform and unstable CO₂ adsorption on the MCBs-9-5-r adsorbent surface, resulting in the poor regeneration and reversibility, which seriously restricts it to be an efficient CO₂ adsorbent.

Apart from the high CO₂ uptake capacity, the remarkable CO₂ adsorbents should possess easy regeneration ability for practical utilization. The regeneration test of the MCBs-9-5 material was conducted for five consecutive cycles at 0 and 25 °C. As shown in Figure S10, the CO₂ uptake remains almost constant in five cycles, which testifies that the obtained MCBs-9-5 material has satisfactory recyclability with relatively low energy requirement for regeneration.

3. CONCLUSIONS

In summary, a simple and cost-efficient strategy was successfully developed for the green synthesis of cross-linked MCBs derived from sustainable starch sugar. Inimitably, this approach avoids the use of chemical activating agents and only involves a simple curing process in an air atmosphere, which makes it convenient and rapid to achieve the preparation of MCBs in a large-scale industrial production. By tuning the carbonization temperature and reaction time, the microporosity, especially ultramicroporosity, of the resultant materials could be easily tailored to arise primarily from pores of size 0.4–0.9 nm, which greatly favors the postcombustion CO₂ adsorption. The optimal sample of MCBs-9-5 carbonized at 900 °C for 5 h under air atmosphere exhibits a satisfactory CO₂ uptake of 4.25 mmol g⁻¹ at room temperature under 1 bar, which should be related to its high proportion of micropores of <1 nm, high narrow micropore surface area, and large micropore volume. More importantly, the MCBs-9-5 material also possesses a superior recyclability for CO₂ capture and a high CO₂ adsorption selectivity against N₂ for CO₂/N₂ separation.

4. EXPERIMENTAL SECTION

4.1. Preparation of MCBs. The carbon bead precursor was synthesized by a convenient and controllable hydrothermal synthetic route using glucose as a carbon source.23 Typically, 6 g of glucose was dissolved in 60 mL of deionized water to obtain a clear solution, and then the solution was transferred...
into a Teflon-sealed autoclave and maintained at 180 °C for 8 h. The puce products were obtained by filtration, washed repeatedly by deionized water, and dried at 80 °C for more than 8 h. The obtained glucose-based carbon bead precursors were defined as the CS precursor.

A 1 g mass of dried CS precursors was placed in a 10 mL corundum crucible with a cover and then directly transferred into a muffle furnace at high temperatures (700, 800, 900, and 1000 °C) using crucible tongs. The samples were calcined for regular times (1, 2, 3, 4, 5, and 6 h) and then were taken out to cool to room temperature for obtaining cross-linked MCBs. The resultant samples were denoted as MCBs-x-y, where x = 7, 8, 9, and 10, referring to the calcination temperature of 700, 800, 900, and 1000 °C, respectively; y = 1, 2, 3, 4, 5, and 6, representing calcination time of 1–6 h, respectively. In the synthesis process, the air, especially O2 in the air, can be used in the calcination process of material preparation.

For comparison, the CS precursor was directly carbonized at 900 °C for 5 h under a N2 atmosphere, which was designated as MCBs-9-5.

### 4.2. Characterizations

**XRD patterns** were monitored by a Bruker D8 diffractometer using Cu Ka radiation (λ = 0.15418 nm) as an X-ray source. Nitrogen adsorption–desorption isotherms were carried out at −196 °C using a micromeritics ASAP 2020 HD88 analyzer. Before adsorption, the samples were out-gassed at 200 °C for 10 h. The specific surface area (S BET) was evaluated using the BET method, and the hierarchical pore size distributions were calculated according to the DFT method. The micropore was analyzed using the t-plot method, and the ratio of micro-/mesopore was calculated according to the t-plot method. The micropore size distributions were also analyzed by fitting the CO2 adsorption isotherm at 0 °C using the DFT model. The morphology was observed from a FEI Tecnai G2 20 TEM with an accelerating voltage of 200 kV and a SEM (Quanta 250 FEG). FTIR spectroscopy spectra of a sample in KBr wafer were recorded on a Nicolet Avatar 370 spectrometer.

### 4.3. Gas Adsorption Tests

Gas adsorption isotherms of CO2 and N2 were measured using a Micromeritics ASAP 2020 HD88 instrument. Highly pure gases CO2 (99.999%) and N2 (99.999%) were employed for the measures. The isotherms of CO2 and N2 at 0 and 25 °C were conducted in an ice-water bath and a water bath, respectively. Prior to each gas uptake measurement, the samples were degassed at 200 °C for 10 h to remove the guest molecules from pores. For the regeneration experiment, the recovered adsorbents were evacuated at room temperature for 10 min and then reused for next adsorption.

## ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b02056.

Evolution of micro-/mesopore proportion in MCB samples with the variation of calcination temperature and time; N2 adsorption–desorption isotherms and pore size distribution of MCBs-9-5 and MCBs-9-5-r; XRD patterns of all as-obtained MCB samples; Raman spectra of MCBs-x-3 samples; FTIR spectra of the CS precursor and MCBs-x-3; SEM images of the CS precursor and MCBs-9-y samples; TEM images of MCBs-9-y; analysis of dependence of CO2 capture capacity (at 0 °C and 1 bar) on surface area (a) and pore volume (b) for as-prepared MCB materials; CO2 adsorption isotherms of MCBs-9-5 and MCBs-9-5-r; and regeneration performance of MCBs-9-5 on CO2 adsorption at 0 and 25 °C (PDF)

## AUTHOR INFORMATION

**Corresponding Authors**

*E-mail: binbinchang@infm.hhstu.edu.cn (B.C.).
E-mail: baocengyang@yahoo.com (B.Y.).

**ORCID**

Binbin Chang: 0000-0001-6172-9952

**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The National Natural Science Foundation of China (51472102, 51602120, and 51702114), National Science Foundation of Henan Province (172102210381), National Science Foundation of Education Department of Henan Province (18A150011), and the National Undergraduate Training Program for Innovation of China (201711834002).

## REFERENCES

(1) Kenarsari, S. D.; Yang, D.; Jiang, G.; Zhang, S.; Wang, J.; Russell, A. G.; Wei, Q.; Fan, M. Review of recent advances in carbon dioxide separation and capture. *RSC Adv.*, 2013, 3, 22739–22773.

(2) D’Alessandro, D. M.; Smit, B.; Long, J. R. Carbon dioxide capture: prospects for new materials. *Angew. Chem., Int. Ed.* 2010, 49, 6058–6082.

(3) Zhang, X.-q.; Li, W.-c.; Lu, A.-h. Designed porous carbon materials for efficient CO2 adsorption and separation. *N. Carbon Mater.*, 2015, 30, 481–501.

(4) Dutcher, B.; Fan, M.; Russell, A. G. Amine-based CO2 capture technology development from the beginning of 2013–a review. *ACS Appl. Mater. Interfaces* 2015, 7, 2137–2148.

(5) Ashourirad, B.; Arab, P.; Islamoglu, T.; Cychoz, K. A.; Thomas, M.; El-Kaderi, H. M. A cost-effective synthesis of heteroatom-doped porous carbons as efficient CO2 sorbents. *J. Mater. Chem. A* 2016, 4, 14693–14702.

(6) Su, F.; Lu, C. CO2 capture from gas stream by zeolite 13X using a dual-column temperature/vacuum swing adsorption. *Energy Environ. Sci.* 2012, 5, 9021–9027.

(7) Ben, T.; Pei, C.; Zhang, D.; Xu, J.; Deng, F.; Jing, X.; Qiu, S. Gas storage in porous aromatic frameworks (PAFs). *Energy Environ. Sci.* 2011, 4, 3991–3999.

(8) Abdelmoaty, Y. H.; Tessema, T.-D.; Norouzi, N.; El-kadri, O. M.; Turner, J. B. M.; El-Kaderi, H. M. Effective approach for increasing the heteroatom doping levels of porous carbons for superior CO2 capture and separation performance. *ACS Appl. Mater. Interfaces* 2017, 9, 35802–35810.

(9) Park, D. H.; Lakhi, K. S.; Ramadas, K.; Kim, M.-K.; Talapaneni, S. N.; Joseph, S.; Ravon, U.; Al-Bahily, K.; Vinu, A. Energy efficient synthesis of ordered mesoporous carbon nitrides with a high nitrogen content and enhanced CO2 capture capacity. *Chem.—Eur. J.* 2017, 23, 10753–10757.

(10) Thote, J. A.; Iyer, K. S.; Chatti, R.; Labhsetwar, N. K.; Biniwate, R. B.; Rayalu, S. S. In situ nitrogen enriched carbon for carbon dioxide capture. *Carbon* 2010, 48, 396–402.

(11) Hao, G.-P.; Li, W.-C.; Qian, D.; Lu, A.-H. Rapid synthesis of nitrogen-doped porous carbon monolith for CO2 capture. *Adv. Mater.* 2010, 22, 853–857.

(12) Fan, X.; Zhang, L.; Zhang, G.; Shu, Z.; Shi, J. Chitosan derived nitrogen-doped microporous carbons for high performance CO2 capture. *Carbon* 2013, 61, 423–430.

(13) Wang, Y.; Ou, H.; Zeng, S.; Pan, Y.; Wang, R.; Wang, X.; Sun, Q.; Zhang, Z.; Qiu, S. A one-step carbonization route towards...
natto and uniform Size. Biocompatible ordered mesoporous carbon nanospheres with tunable supercapacitance and CO2 capture performance. ACS Appl. Mater. Interfaces 2014, 6, 18849–18859.

(16) Sevilla, M.; Fuertes, A. B. Sustainable porous carbons with a superior performance for CO2 capture. Energy Environ. Sci. 2011, 4, 1765–1771.

(17) Wahby, A.; Ramos-Fernández, J. M.; Martínez-Escandell, M.; Sepúlveda-Escribano, A.; Silvestre-Albero, J.; Rodríguez-Reinoso, F. High-surface-area carbon molecular sieves for selective CO2 adsorption. ChemSusChem 2010, 3, 974–981.

(18) Sevilla, M.; Falco, C.; Titirici, M.-M.; Fuertes, A. B. High-performance CO2 sorbents from algae. RSC Adv. 2012, 2, 12792–12797.

(19) Wang, X.; Yuan, B.; Zhou, X.; Xia, Q.; Li, Y.; An, D.; Li, Z. Novel glucose-based adsorbents (Glc-Cs) with high CO2 capacity and excellent CO2/CH4/N2 adsorption selectivity. Chem. Eng. J. 2017, 27, 51–59.

(20) Chang, B.; Zhang, S.; Yin, H.; Yang, B. Convenient and large-scale synthesis of nitrogen-rich hierarchical porous carbon spheres for supercapacitors and CO2 capture. Appl. Surf. Sci. 2017, 412, 606–615.

(21) Ma, X.; Li, Y.; Cao, M.; Hu, C. A novel activating strategy to achieve highly porous carbon monoliths for CO2 capture. J. Mater. Chem. A 2014, 2, 4819–4826.

(22) Kim, Y. K.; Kim, G. M.; Lee, J. W. Highly porous N-doped carbon impregnated with sodium for efficient CO2 capture. J. Mater. Chem. A 2015, 3, 10919–10927.

(23) Chang, B.; Guan, D.; Tian, Y.; Yang, Z.; Dong, X. Convenient synthesis of porous carbon nanospheres with tunable pore structure and excellent adsorption capacity. J. Hazard. Mater. 2013, 262, 256–264.

(24) Pol, V.; Shrestha, L. K.; Ariga, K. Tunable, functional carbon spheres derived from rapid synthesis of resorcinol-formaldehyde resins. ACS Appl. Mater. Interfaces 2014, 6, 10649–10655.

(25) Fang, Y.; Gu, D.; Zou, Y.; Wu, Z.; Li, F.; Che, R.; Deng, Y.; Tu, B.; Zhao, D. A low-concentration hydrothermal synthesis of biocompatible ordered mesoporous carbon nanospheres with tunable and uniform Size. Angew. Chem., Int. Ed. 2010, 49, 7987–7991.

(26) Wang, B.; Wang, P.; Yan, X.; Lang, J.; Peng, C.; Xue, Q. Promising porous carbon derived from celte leaves with outstanding supercapacitance and CO2 capture performance. ACS Appl. Mater. Interfaces 2012, 4, 5800–5806.

(27) Wang, Y.; Chang, B.; Guan, D.; Dong, X. Mesoporous activated carbon spheres derived from resorcinol-formaldehyde resin with high performance for supercapacitors. J. Solid State Electrochem. 2015, 19, 1783–1791.

(28) Li, Y.; Zou, B.; Hu, C.; Cao, M. Nitrogen-doped porous carbon nanofiber webs for efficient CO2 capture and conversion. Carbon 2016, 99, 79–89.

(29) Wei, L.; Sevilla, M.; Fuertes, A. B.; Mokaya, R.; Yushin, G. Hydrothermal carbonization of abundant renewable natural organic chemicals for high-performance supercapacitor electrodes. Adv. Energy Mater. 2011, 1, 356–361.

(30) Hao, E.; Liu, W.; Liu, S.; Zhang, Y.; Wang, H.; Chen, S.; Cheng, F.; Zhao, S.; Yang, H. Rich sulfur doped porous carbon materials derived from ginkgo leaves for multiple electrochemical energy storage devices. J. Mater. Chem. A 2017, 5, 2204–2214.

(31) Xuan, H.; Wang, Y.; Lin, G.; Wang, F.; Zhou, L.; Dong, X.; Chen, Z. Air-assisted activation strategy for porous carbon spheres to give enhanced electrochemical performance. RSC Adv. 2016, 6, 15313–15319.

(32) Torad, N. L.; Hu, M.; Ishihara, S.; Sukegawa, H.; Belik, A. A.; Imura, M.; Ariga, K.; Sakka, Y.; Yamamura, Y. Direct synthesis of MOF-derived nanoporous carbon with magnetic Co nanoparticles toward efficient water treatment. Small 2014, 10, 2069–2107.

(33) Salunkhe, R. R.; Young, C.; Tang, J.; Takei, T.; Ide, Y.; Kobayashi, N.; Yamauchi, Y. A high-performance supercapacitor cell based on ZIF-8-derived nanoporous carbon using an organic electrolyte. Chem. Commun. 2016, 52, 4764–4767.

(34) Sun, X.; Li, Y. Colloidal carbon spheres and their core/shell structures with noble-metal nanoparticles. Angew. Chem., Int. Ed. 2004, 43, 597–601.

(35) Demir-Cakan, R.; Baccile, N.; Antonietti, M.; Titirici, M.-M. Carboxylate-rich carbonaceous materials via one-step hydrothermal carbonization of glucose in the presence of acrylic acid. Chem. Mater. 2009, 21, 484–490.

(36) Ikeda, S.; Tachi, K.; Ng, Y. H.; Icoma, Y.; Sakata, T.; Mori, H.; Harada, T.; Matsumura, M. Selective adsorption of glucose-derived carbon precursor on amino-functionalized porous silica for fabrication of hollow carbon spheres with hollow walls. Chem. Mater. 2007, 19, 4335–4340.

(37) Wang, L.; Yang, R. T. Significantly increased CO2 adsorption performance of nanostructured templated carbon by tuning surface area and nitrogen doping. J. Phys. Chem. C 2012, 116, 1099–1106.

(38) Sangchoom, W.; Mokaya, R. Valorization of lignin waste: Carbons from hydrothermal carbonization of renewable lignin as superior sorbents for CO2 and hydrogen storage. ACS Sustainable Chem. Eng. 2015, 3, 1658–1667.

(39) Adeniran, B.; Mokaya, R. Low temperature synthesized carbon nanotube superstructures with superior CO2 and hydrogen storage capacity. J. Mater. Chem. A 2015, 3, 5148–5161.

(40) Hu, X.; Radosz, M.; Cychosz, K. A.; Thomsmes, M. CO2-filling capacity and selectivity of carbon nanopores: synthesis, texture, and pore-size distribution from quenched-solid density functional theory (QSDFT). Environ. Sci. Technol. 2011, 45, 7068–7074.

(41) Cai, J.; Qi, J.; Yang, C.; Zhao, X. Poly(vinylidene chloride)-based carbon with ultrahigh microporosity and outstanding performance for CH4 and H2 Storage and CO2 Capture. ACS Appl. Mater. Interfaces 2014, 6, 3703–3711.

(42) Balahmar, N.; Al-Jumialy, A. S.; Mokaya, R. Biomass to porous carbon in one step: directly activated biomass for high performance CO2 storage. J. Mater. Chem. A 2017, 5, 12330–12339.

(43) Chen, C.; Kim, J.; Ahn, W.-S. Efficient carbon dioxide capture over a nitrogen-rich carbon having a hierarchical micro-mesopore structure. Fuel 2012, 95, 360–364.

(44) Adeniran, B.; Masika, E.; Mokaya, R. A family of microporous carbons prepared via a simple metal salt carbonization route with high selectivity for exceptional gravimetric and volumetric post combustion CO2 capture. J. Mater. Chem. A 2014, 2, 14696–14710.

(45) Wei, H.; Deng, S.; Hu, B.; Chen, Z.; Wang, B.; Huang, J.; Yu, G. Granular bamboo-derived activated carbon for high CO2 adsorption: The dominant role of narrow micropores. ChemSusChem 2012, 5, 2346–2350.

(46) Kumar, V. K.; Gadipelli, S.; Preuss, K.; Porwal, H.; Zhao, T.; Guo, Z. X.; Titirici, M.-M. Salt templating with pore padding: hierarchical pore tailoring towards functionalised porous carbons. ChemSusChem 2017, 10, 199–209.

(47) Sevilla, M.; Valle-Vigón, P.; Fuertes, A. B. N-doped polypropylene-based porous carbons for CO2 capture. Adv. Funct. Mater. 2011, 21, 2781–2787.

(48) Zhu, X.; Do-Thanh, C.-L.; Murdock, C. R.; Nelson, K. M.; Tian, C.; Brown, S.; Mahurin, S. M.; et al. Efficient CO2 capture by a 3D porous polymer derived from troger’s base. ACS Macro Lett. 2013, 2, 660–663.

(49) Modak, A.; Bhaumik, A. Porous carbon derived via KOH activation of a hypercrosslinked porous organic polymeroficient CO2, CH4, H2 adsorptions and high CO2/N2 selectivity. J. Solid State Chem. 2015, 232, 157–162.

(50) Hutson, N. D.; Speakman, S. A.; Payzant, E. A. Structural effects on the high temperature adsorption of CO2 on a synthetic hydrotalcite. Chem. Mater. 2004, 16, 4135–4143.
Zhang, Z.; Wang, B.; Zhu, C.; Gao, P.; Tang, Z.; Sun, N.; Wei, W.; Sun, Y. Facile one-pot synthesis of mesoporous carbon and N-doped carbon for CO2 capture by a novel melting-assisted solvent-free method. *J. Mater. Chem. A* 2015, 3, 23990−23999.

Zhang, C.; Song, W.; Ma, Q.; Xie, L.; Zhang, X.; Guo, H. Enhancement of CO2 capture on biomass-based carbon from black locust by KOH activation and ammonia modification. *Energy Fuels* 2016, 30, 4181−4190.

Lee, J. H.; Lee, H. J.; Lim, S. Y.; Kim, B. G.; Choi, J. W. Combined CO2-philicity and ordered meso-porosity for highly selective CO2 capture at high temperatures. *J. Am. Chem. Soc.* 2015, 137, 7210−7216.

Du, R.; Zhang, N.; Xu, H.; Mao, N.; Duan, W.; Wang, J.; Zhao, Q.; Liu, Z.; Zhang, J. CMP aerogels: ultrahigh-surface-area carbon-based monolithic materials with superb sorption performance. *Adv. Mater.* 2014, 26, 8053−8058.

Tian, W.; Zhang, H.; Sun, H.; Suvorova, A.; Saunders, M.; Tade, M.; Wang, S. Heteroatom (N or N-S)-doping induced layered and honeycomb microstructures of porous carbons for CO2 capture and energy applications. *Adv. Funct. Mater.* 2016, 26, 8651−8661.