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Preparation and Characterization of Poly(vinyl alcohol)/ZIF-8 Porous Composites by Ice-templating Method with High ZIF-8 Loading Amount

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Abstract A bulk Poly(vinyl alcohol)/ZIF-8 (PVA/ZIF-8) porous composite with aligned porous structure was prepared by ice-templating method. The microstructure of PVA/ZIF-8 porous composites was characterized by scanning electron microscopy (SEM). The results showed that the composites had regular pore structure and ZIF-8 nanoparticles were evenly distributed on the skeleton of PVA. X-ray diffraction (XRD) test results showed that the crystalline structure of ZIF-8 was well preserved in the composites. The specific surface area of the composite was characterized by nitrogen adsorption/desorption test. The specific surface area of the composite was up to $1160 \text{ m}^2\text{-g}^{-1}$. PVA/ZIF-8 porous composites could also support a certain weight with almost no volume shrinkage. The carbon dioxide adsorption quantity of the composite was up to $11.3 \text{ cm}^3\text{-g}^{-1}$, proving that PVA/ZIF-8 porous composite has a good application prospect in the field of carbon dioxide adsorption.

Keywords Poly(vinyl alcohol); ZIF-8; Ice-templating; Porous composite; CO_2 adsorption

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INTRODUCTION

In recent years, the adsorption and conversion of carbon dioxide have become a hot issue of research. A variety of novel materials have been developed for the adsorption of carbon dioxide, such as graphene oxide,^[1,2] zeolite,^[3] metal-organic frameworks (MOFs),^[4–6] covalent organic frameworks (COFs),^[7,8] etc. The efficiency of MOFs to adsorb carbon dioxide is relatively good among them. Zeolitic imidazolate frameworks (ZIFs) is a typical kind of MOFs. In 2006, Yaghi's group reported that they used zinc ions and imidazole-type linkers to prepare zeolitic imidazolate frameworks (ZIFs).^[9] It is very easy to fabricate ZIF-8 and ZIF-8 has many advantages, including high porosity, high surface areas, water stability, and remarkable thermal and chemical stability.^[10] At the same time, ZIF-8 crystals provide Langmuir sites where adsorption of CO_2 molecules may take place,^[11] which make it apply to the adsorption and separation of carbon dioxide. Song's group demonstrated that CO_2 molecules could enter the framework of ZIF-8 under high pressure.^[12]

Notwithstanding the good adsorption capacity of ZIF-8, it is difficult to collect ZIF-8 nanoparticles after the adsorption test. In order to solve this problem, researchers often produce polymer/ZIF-8 composites.^[13–15] For example, Xian *et al.* synthesized polyethylenimine impregnated ZIF-8 compo-

sites with different loading amounts of ZIF-8, but the composite method applied there has greatly reduced the specific surface area.^[16] The surface area of the PEI/ZIF-8 composite is $21 \text{ m}^2\text{-g}^{-1}$ when the loading amount is 45%, which is much smaller than $1150 \text{ m}^2\text{-g}^{-1}$ of ZIF-8. Riande *et al.* prepared a ZIF-8/polysulfone composite membrane for carbon dioxide adsorption and proved that the adsorption amount of carbon dioxide increased as increasing the content of ZIF-8.^[11] However, the biggest percentage of ZIF-8 in the composite is only 30%. It is difficult to disperse ZIF-8 evenly when increasing the content of ZIF-8, which will reduce the mechanical properties of the composite. Zhang *et al.* used ice-templating method to prepare polymer/MOFs monoliths by directional freezing of aqueous chitosan solution containing suspended UiO-66 nanoparticles and subsequent freeze-drying.^[17] The monolith has an aligned layer structure, and UiO-66 is distributed on the surface of chitosan. In the meantime, the loading amount of UiO-66 was up to 66.7%. But chitosan can only be dissolved in acidic solution, under which conditions ZIF-8 cannot exist stably and it has high gas barrier properties, which would weaken the CO_2 adsorption capacity of composite, and the mechanical stability of chitosan/UiO-66 is not good.

Therefore, new methods and polymers are required to prepare the polymer/ZIF-8 composite with high specific surface area, high ZIF-8 loading amount and good mechanical properties. PVA is non-toxic, non-polluting and has good film forming property and biocompatibility, so it is often chosen

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as the matrix of composite materials.^[18] Ice-templating method can be used to prepare PVA porous material. Cooper *et al.* used poly(vinyl alcohol) as matrix, and combined it with cerium oxide to obtain a PVA/CeO₂ composite porous material with regular porous structure, and the cerium oxide was evenly dispersed on the PVA skeleton.^[19]

In this work, we chose PVA as the matrix, dissolved it in the water to obtain an aqueous solution, and then dispersed ZIF-8 uniformly in PVA solution to form the PVA/ZIF-8 dispersion. Afterwards, PVA/ZIF-8 porous composite was prepared by ice-templating method. The pore structure, crystal structure and specific surface area were characterized by scanning electron microscopy, XRD and nitrogen adsorption/desorption experiments. The CO₂ adsorption performance was tested to explore the application value of PVA/ZIF-8 porous composites in the field of carbon dioxide adsorption capacity.

EXPERIMENTAL

Materials

2-Methylimidazole (AR) was purchased from Aladdin. Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O), poly(vinyl alcohol) (PVA), and methanol were obtained from TongGuang Chemical Reagent Corp. (Beijing, China). Deionized water was used routinely as required.

Preparation of ZIF-8

ZIF-8 nanoparticles were synthesized according to the procedure reported by Yamauchi's group.^[20] Zn(NO₃)₂·6H₂O (258 mg) and 2-methylimidazole (263 mg) were separately dissolved into methanol (20 mL) to form solution. Then, both of them were mixed together, and stirred for 5 min. The solution was aged at room temperature for 24 h. After that, white powders were precipitated by centrifugation and washed by methanol at room temperature.

Preparation of PVA/ZIF-8 Porous Composites

PVA (0.2 g) was dissolved in deionized water (3.8 mL) under 95 °C to form 5 wt% PVA solution. Then ZIF-8 powders (0.2, 0.4, or 0.6 g) were dispersed into the PVA solution under ultrasonic respectively. The dispersion was placed into a 5 mL centrifuge tube. The tube containing solution was immersed into liquid nitrogen at a speed of 5 cm/min and kept in the liquid nitrogen for 15 min. And the sample was under lyophilization for 48 h in the freeze-dryer to get dry PVA/ZIF-8 porous composite. The three porous composites with different PVA-to-ZIF-8 ratios were denoted as PVA/ZIF-8-1 (weight ratio of PVA to ZIF-8 was 1:1), PVA/ZIF-8-2 (weight ratio of PVA to ZIF-8 was 1:2), and PVA/ZIF-8-3 (weight ratio of PVA to ZIF-8 was 1:3). For control, 5 wt% PVA solution without ZIF-8 was freeze-dried following the same procedure, and the acquired porous composite was denoted as PVA.

Characterization and Measurement

Characterization of PVA/ZIF-8 porous composites

The scanning electron microscopy (SEM, Hitachi SU8020) was used to determine the morphology of ZIF-8 powders and ZIF-8/PVA porous composite. Before evaluation, all samples were sputter-coated with a thin gold layer (~2 nm) using an automated sputter coater (Emitech K550X). The Brunauer-Emmett-Teller (BET) specific surface areas, pore volumes, and Barrette-

Joyner-Halenda (BJH) pore size distributions were obtained by N₂ sorption at 77 K using a BEL-SORP MAX II volumetric adsorption analyzer. X-ray powder diffraction data was collected by a Bruker D8 Advance powder diffractometer using Cu K α radiation and the pattern was scanned over an angular range of 3°–50° (2 θ) with a scan speed of 2 (°)/min and a step size of 0.02°.

Adsorption procedure

The CO₂ adsorption-desorption measurements were performed on a BEL-SORP MAX II instrument at room temperature (298 K) up to atmosphere pressure (101 kPa). Samples of ZIF-8, PVA/ZIF-8-1, PVA/ZIF-8-2, and PVA/ZIF-8-3 were degassed in vacuum overnight (> 12 h) at the temperatures of 373 K, respectively.

RESULTS AND DISCUSSION

Synthesis of PVA/ZIF-8 Porous Composites

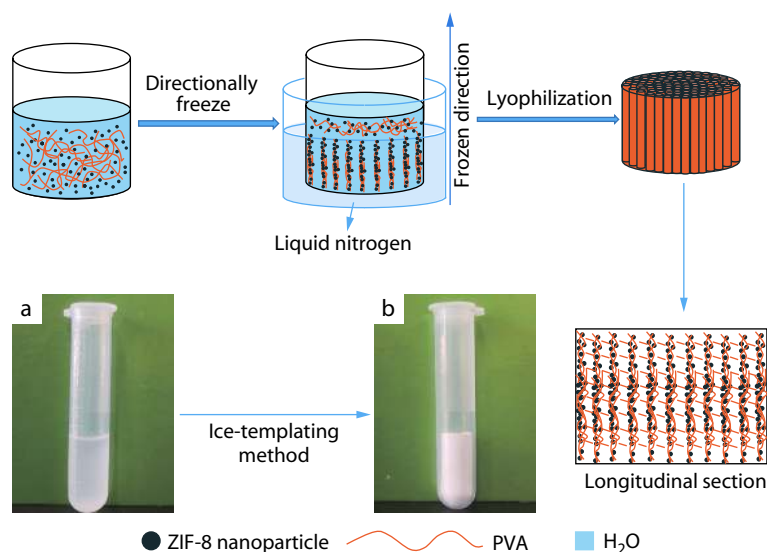
A bulk PVA/ZIF-8 porous composite was prepared by ice-templating and freeze-drying method, and almost no volume shrinkage for the sample was observed after lyophilization (Scheme 1). The concentration of PVA and the mass ratio of ZIF-8 nanoparticles to PVA have a great effect on the synthesis of porous composites. When the mass ratio of ZIF-8 to PVA was 1:1, 3 wt%, 4 wt%, 5 wt%, 6 wt%, and 7 wt% PVA solutions were used to prepare PVA/ZIF-8 porous composites. However, the mechanical properties of the samples prepared with 3 wt% or 4 wt% PVA solution by ice-templating method were very poor. Meanwhile, it was difficult to uniformly disperse ZIF-8 nanoparticles in the 6 wt% or 7 wt% PVA solution. This may be caused by the following reasons. On the one hand, the low concentration will reduce the contact opportunity between PVA molecular chains, resulting in that the skeleton is very loose. On the other hand, when concentration is sufficiently high, the solution viscosity will be too high to disperse ZIF-8, also the ice crystals are difficult to grow in orientation, preventing the formation of oriented porous structures. When the mass ratio of ZIF-8 to PVA is over 3:1, it is difficult to disperse all the nanoparticles in the 5 wt% PVA solution. Thus, 5.0 mg/mL of PVA solution and the mass ratios of 1:1, 2:1, and 3:1 were used to prepare PVA/ZIF-8 porous composites for the following experiments. The ZIF-8 loading amount was up to 75%, when the mass ratio of ZIF-8 to PVA was 3:1.

Scheme 1 illustrates the formation mechanism of PVA/ZIF-8 porous composites with ice-templating and freeze-drying method. PVA and ZIF-8 nanoparticles were dispersed in water first, then the mold containing dispersion was directionally frozen in liquid nitrogen. The solvent first crystallized on the frozen surface and then grew directionally along the frozen direction to form ice crystals of oriented structure. At the same time, the dispersate, including PVA and ZIF-8 nanoparticles, was repelled by the ice crystals, getting close to each other, and then compressed between the ice crystals.^[21] Thereafter, the ice crystals were removed by freeze-drying to obtain the PVA/ZIF-8 porous material that has an oriented structure using ice crystals as template.

Characterization of PVA/ZIF-8 Porous Composites

XRD spectra of PVA/ZIF-8 porous composites

To examine the crystal structure of the ZIF-8 nanoparticles and PVA/ZIF-8 porous composites, wide-angle XRD measurement was performed, and the XRD curves are displayed in Fig. 1. The



Scheme 1 The proposed formation mechanism of PVA/ZIF-8 porous composite. (a) Photograph of PVA/ZIF-8 dispersion; (b) Photograph of PVA/ZIF-8 porous composite.

XRD pattern of experimental ZIF-8 matched with the well-known ZIF-8 crystal structure, manifesting that we got the right ZIF-8 nanoparticles. And all the XRD patterns of PVA/ZIF-8 porous composites with different mass ratios of ZIF-8 to PVA were essentially identical. It suggests that the ZIF-8 crystalline structure was well preserved after the recombination with PVA. Here, the well reserved ZIF-8 structure after recombining with PVA was owing to the excellent water-resistance property of ZIF-8.

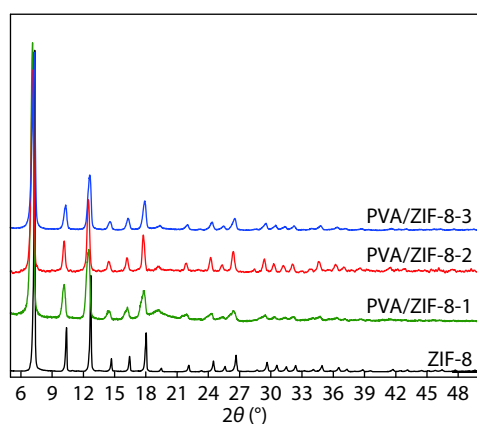


Fig. 1 XRD patterns of ZIF-8, PVA/ZIF-8-1, PVA/ZIF-8-2, and PVA/ZIF-8-3.

Microstructure of PVA/ZIF-8 porous composites

Scanning electron microscopy was used to characterize the microstructure of ZIF-8, PVA samples, and PVA/ZIF-8 porous composites. Fig. 2(a) shows the SEM image of ZIF-8 nanoparticles with an average diameter of ca. 50 nm, which is consistent with the report. The pore structures of PVA samples are shown in Figs. 2(b) and 2(c). We prepared a PVA sample with aligned pore structure, in which the PVA skeleton exhibited a “fish-bone” shape. The diameter of the pores in PVA sample was approximately 10–15 μm . Similar porous structure was also seen in the PVA/ZIF-8 porous composites (Figs. 2d, 2g, and 2j)

produced by slowly lowering an aqueous dispersion of PVA/ZIF-8 into liquid nitrogen, and the images from the longitudinal section (Figs. 2f, 2i, and 2l) proved that the PVA/ZIF-8 composites maintained the “fish-bone” morphology after the compositing process and the additional freeze-drying step. All these prove that the presence of ZIF-8 does not affect the skeleton structure of PVA by ice-templating method. Imaging at higher magnifications from the cross section (Figs. 2e, 2h, and 2k) revealed that the ZIF-8 nanoparticles were evenly distributed over the PVA skeleton, which is consistent with the proposed formation mechanism shown in Scheme 1.

Surface area and porosity of PVA/ZIF-8 porous composites

The surface area and porosity of the freeze-dried samples are characterized by nitrogen adsorption/desorption experiments. The BET surface areas of PVA/ZIF-8-1, PVA/ZIF-8-2, and PVA/ZIF-8-3 are 614.44, 1015.8, 1060.2 m^2g^{-1} , respectively, which are smaller than 1689.7 m^2g^{-1} of ZIF-8. This is expected because ice-templating generates macropores that do not contribute significantly to the surface area. The adsorption/desorption isotherms (Fig. 3a) exhibit a typical type II curve, suggesting that there are a large number of micropores and some mesopores maybe from the interstitial space of ZIF-8 nanoparticles in the structure, which can be proved by the pore size distribution curve. The pore size distribution was determined by the Barrett-Joyner-Halenda (BJH) method. As shown in Fig. 3(b), the BJH mean pore diameter of PVA/ZIF-8 porous composites is 1.7 nm, proving that the PVA/ZIF-8 porous composites are mainly composed of microporous structures, same to the ZIF-8 nanoparticles. The pore size distribution also shows the presence of micropores (Fig. 3b).

Properties of PVA/ZIF-8 Porous Composites

Mechanical properties of PVA/ZIF-8 porous composites

We cut the PVA/ZIF-8 sample into monolith with a diameter of ca. 1.0 cm and a height of ca. 1.0 cm (Figs. 4a–4c). The as-obtained PVA/ZIF-8 porous composite exhibits high mechanical strength and can support a 200 g weight without causing

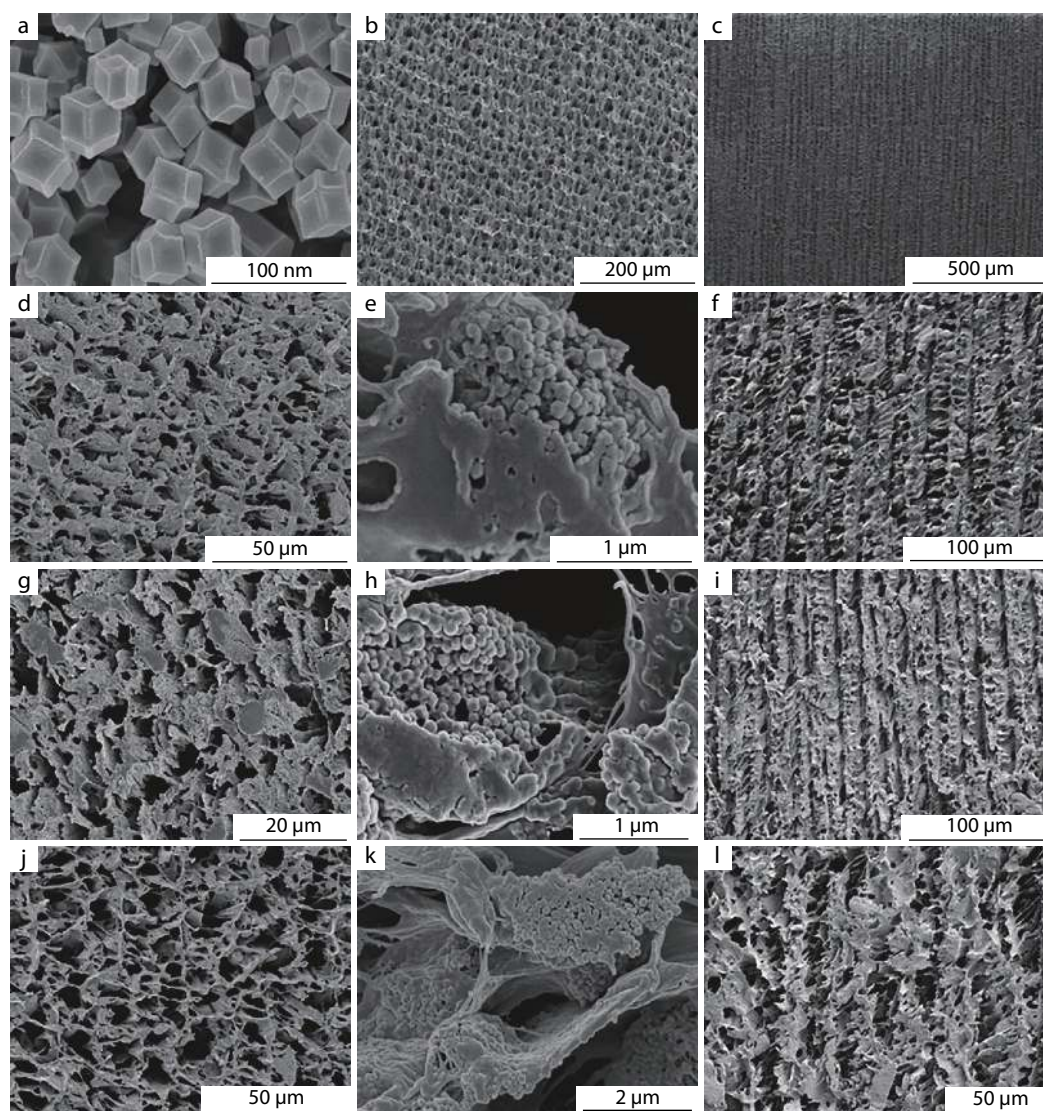


Fig. 2 Pore structures by SEM imaging of (a) ZIF-8 nanoparticles, (b, c) free-dried PVA samples, (d, e, f) freeze-dried PVA/ZIF-8-1, (g, h, i) freeze-dried PVA/ZIF-8-2, and (j, k, l) freeze-dried PVA/ZIF-8-3.

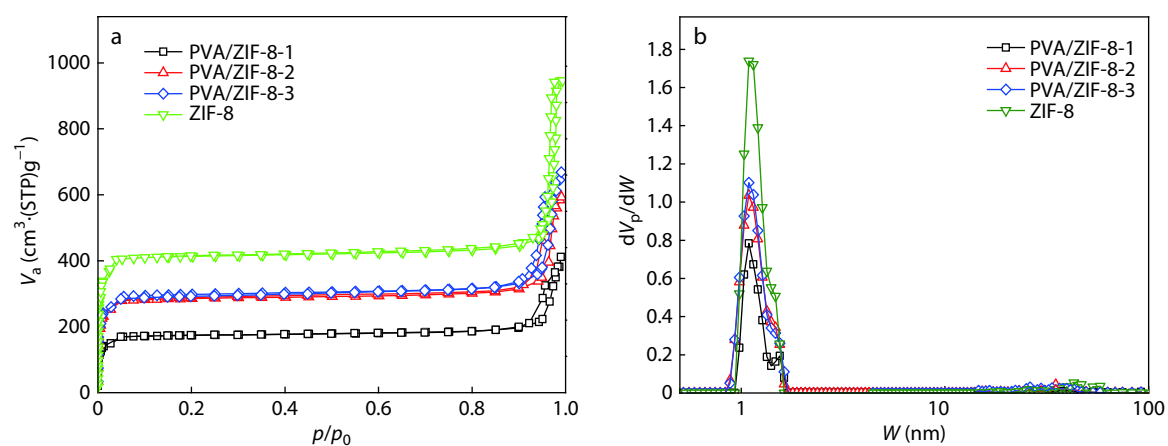


Fig. 3 Surface area and porosity of the freeze-dried samples. (a) N_2 adsorption and desorption isotherms of ZIF-8, PVA/ZIF-8-1, PVA/ZIF-8-2, and PVA/ZIF-8-3; (b) Pore size distribution profiles of ZIF-8, PVA/ZIF-8-1, PVA/ZIF-8-2, and PVA/ZIF-8-3.

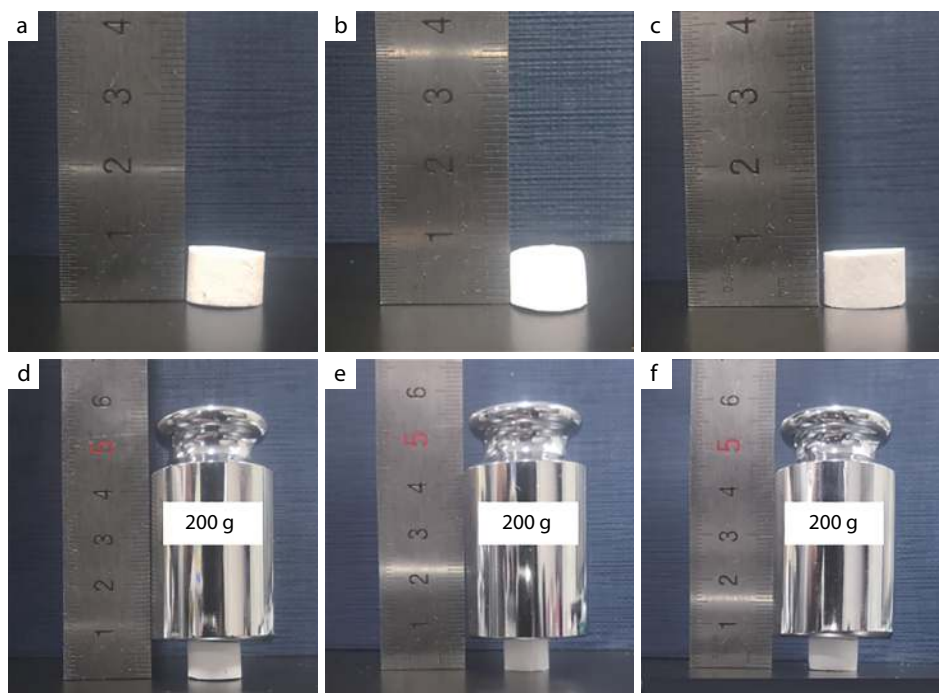


Fig. 4 Photographs of (a) PVA/ZIF-8-1, (b) PVA/ZIF-8-2, and (c) PVA/ZIF-8-3. A loading test by applying a 200 g weight on top of (d) PVA/ZIF-8-1, (e) PVA/ZIF-8-2, and (f) PVA/ZIF-8-3.

any significant deformation (Figs. 4d–4f), and the maximum strength the materials can hold in direction of alignment is ca. $990 \text{ g}\cdot\text{cm}^{-2}$. With a low density, such mechanical strength is impressive and may be ascribed to the well-defined and interconnected 3D porous network formed by the cross-linked PVA, as confirmed by SEM images (Fig. 2). In general, the compressive strength observed perpendicular to this axis may be half of that in the aligned axis.^[19] This is because that the monolith will suffer from a progressive and spatially heterogeneous load-induced collapse in the direction perpendicular to the axis.

CO₂ adsorption capacity of PVA/ZIF-8 porous composites

Owing to their high porosity and nitrogen-containing structure, ZIF-8 nanoparticles are known to have high adsorption capability towards carbon dioxide. We tested the CO₂ adsorption properties of PVA/ZIF-8 porous composites at 298 K, 101 kPa, and the results are shown in Table 1 and Fig. 5. The CO₂ adsorption amounts of PVA/ZIF-8-1, PVA/ZIF-8-2, and PVA/ZIF-8-3 are 8.3, 10.7, and 11.7 cm³·g^{−1}, respectively. We can find that as the ZIF-8 loading amount increases, the amount of carbon dioxide adsorbed by the composite increases, which is consistent with the change in BET specific surface area of the PVA/ZIF-8 porous composites.

To gain further insight into the effect of compounding with PVA on the adsorption performance of ZIF-8 on carbon dioxide, we compared the carbon dioxide adsorption of PVA/ZIF-8 porous composites with that of ZIF-8 reported before. The adsorption amount at room temperature and ambient atmosphere measured by previous groups were 9–16 cm³·g^{−1} for ZIF-8, which is similar to PVA/ZIF-8 porous composites, indicating that the combination with PVA does not affect the carbon dioxide adsorption capacity of ZIF-8. This is because

Table 1 CO₂ adsorption amounts of PVA/ZIF-8 porous composites.

Sample	CO ₂ adsorption quantity (cm ³ ·g ^{−1})
PVA/ZIF-8-1	8.3
PVA/ZIF-8-2	10.7
PVA/ZIF-8-3	11.3

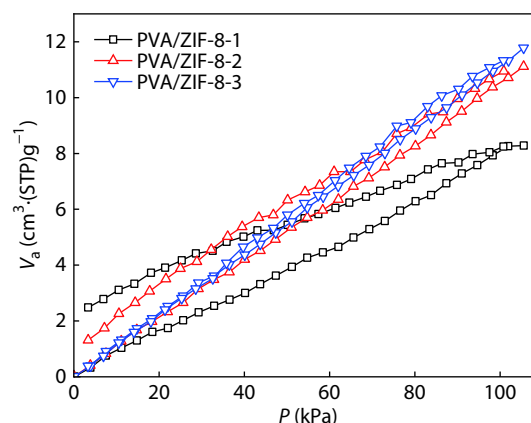


Fig. 5 CO₂ adsorption/desorption isotherms at 298 K, 101 kPa for PVA/ZIF-8-1, PVA/ZIF-8-2, and PVA/ZIF-8-3.

solely physical driving force was detected for ZIF-8 during the CO₂ adsorption measurements.^[22] BET specific surface area plays a decisive role in the CO₂ adsorption process of PVA/ZIF-8 porous composites.

Having high specific surface area, good mechanical and carbon dioxide adsorption properties at the same time, the PVA/ZIF-8 porous composite has a good application prospect in the field of carbon dioxide adsorption.

CONCLUSIONS

In summary, we prepared a PVA/ZIF-8 porous composite with ice-templating method. The ZIF-8 loading amount can be up to 75%. The obtained PVA/ZIF-8 porous composite material has good mechanical properties and can support a weight of 200 g with almost no volume shrinkage. The SEM images confirmed that PVA/ZIF-8 porous composite has an aligned porous structure, and ZIF-8 nanoparticles are uniformly distributed on the PVA skeleton. The XRD patterns proved that the crystalline structure of ZIF-8 is well preserved in the composites. The N_2 adsorption/desorption experiment showed that the porous composites have high specific surface area and the BET surface areas of PVA/ZIF-8-1, PVA/ZIF-8-2, and PVA/ZIF-8-3 are 614.44, 1015.8, and 1060.2 $m^2 \cdot g^{-1}$, respectively. The PVA/ZIF-8-1, PVA/ZIF-8-2, and PVA/ZIF-8-3 porous composites showed carbon dioxide adsorption quantities of 8.3, 10.7, and 11.3 $cm^3 \cdot g^{-1}$. This is similar to that of ZIF-8, indicating that the combination with PVA does not affect the carbon dioxide adsorption capacity of ZIF-8. The CO_2 adsorption capacity is enhanced with increasing the loading quantity of ZIF-8.

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