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 m$^2$·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 cm$^3$·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

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, zeolite, metal-organic frameworks (MOFs), covalent organic frameworks (COFs), 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). 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. At the same time, ZIF-8 crystals provide Langmuir sites where adsorption of CO$_2$ molecules may take place, 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.

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. For example, Xian et al. synthesized polyethylenimine impregnated ZIF-8 composites with different loading amounts of ZIF-8, but the composite method applied there has greatly reduced the specific surface area. The surface area of the PEI/ZIF-8 composite is 21 m$^2$·g$^{-1}$ when the loading amount is 45%, which is much smaller than 1150 m$^2$·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. 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. 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...
as the matrix of composite materials.\textsuperscript{[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/\textit{Ce}O\textsubscript{2} composite porous material with regular porous structure, and the cerium oxide was evenly dispersed on the PVA skeleton.\textsuperscript{[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 CO\textsubscript{2} 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 (\textit{Zn}(NO\textsubscript{3})\textsubscript{2} \cdot 6\textit{H}2\textit{O}), 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.\textsuperscript{[20]} \textit{Zn}(NO\textsubscript{3})\textsubscript{2} \cdot 6\textit{H}2\textit{O} (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, PVA/ZIF-8-2, and PVA/ZIF-8-3. 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 Barretet-
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.

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 m²·g⁻¹, respectively, which are smaller than 1689.7 m²·g⁻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.
any significant deformation (Figs. 4d–4f), and the maximum strength the materials can hold in direction of alignment is ca. 990 g·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 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\textsubscript{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\textsuperscript{2}g\textsuperscript{-1}, respectively. The PVA/ZIF-8 composite showed the carbon dioxide adsorption quantities of 8.3, 10.7, and 11.3 cm\textsuperscript{3}g\textsuperscript{-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\textsuperscript{3}g\textsuperscript{-1}, respectively. 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\textsubscript{2} adsorption capacity is enhanced with increasing the loading quantity of ZIF-8.

REFERENCES

1. Shen, J.; Liu, G. P.; Huang, K.; Jin, W. Q.; Lee, K. R.; Xu, N. P. Membranes with fast and selective gas-selective channels of laminar graphene oxide for efficient CO\textsubscript{2} capture. Angew. Chem. Int. Ed. 2015, 54, 578–582.
2. Li, X. Q.; Cheng, Y. D.; Zhang, H. Y.; Wang, S. F.; Jiang, Z. Y.; Guo, R. L.; Wu, H. Efficient CO\textsubscript{2} capture by functionalized graphene oxide nanosheets as fillers to fabricate multi-permpervise selective mixed matrix membranes. ACS Appl. Mater. Interfaces 2015, 7, 5528–5537.
3. Hudson, M. R.; Queen, W. L.; Mason, J. A.; Fickel, D. W.; Lobo, R. F.; Brown, C. M. Unconventional, highly selective CO\textsubscript{2} adsorption in zeolite SSZ-13. J. Am. Chem. Soc. 2012, 134, 1970–1973.
4. He, H. M.; Perman, J. A.; Zhu, G. S.; Ma, S. Q. Metal-organic frameworks for CO\textsubscript{2} chemical transformations. Small 2016, 12, 6309–6324.
5. Mozafari, M.; Abedini, R.; Rahimpour, A. Zr-MOFs-incorporated thin film nanocomposite Pebax,1657 membranes dip-coated on polyethylene layer for efficient separation of CO\textsubscript{2}/CH\textsubscript{4}. J. Mater. Chem. A 2018, 6, 12380–12392.
6. Wen, H. M.; Liao, C. J.; Li, L. B.; Alsalme, A.; Aloothman, Z.; Krishna, R.; Wu, H.; Zhou, W.; Hu, J.; Chen, B. L. A metal-organic framework with suitable pore size and dual functionalities for highly efficient post-combustion CO\textsubscript{2} capture. J. Mater. Chem. A 2019, 7, 3128–3134.
7. Zeng, Y. F.; Zou, R. Q.; Zhao, Y. L. Covalent organic frameworks for CO\textsubscript{2} capture. Adv. Mater. 2016, 28, 2855–2873.
8. Zhai, L. P.; Huang, N.; Xu, H.; Chen, Q. H.; Jiang, D. L. A backbone design principle for covalent organic frameworks: the impact of weakly interacting units on CO\textsubscript{2} adsorption. Chem. Commun. 2017, 53, 4242–4245.
9. Park, K. S.; Ni, Z.; Cote, A. P.; Choi, J. Y.; Huang, R. D.; Uribe-Romero, F. J.; Chae, H. K.; O’Keeffe, M.; Yaghi, O. M. Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. Proc. Natl. Acad. Sci. USA 2006, 103, 10186–10191.
10. Gin, D. L.; Noble, R. D. Designing the next generation of chemical separation membranes. Science 2011, 332, 674–676.
11. Diaz, K.; Garrido, L.; Lopez-Gonzalez, M.; del Castillo, L. F.; Riande, E. CO\textsubscript{2} transport in polysulfone membranes containing zeolitic imidazolate frameworks as determined by permeation and PFG NMR techniques. Macromolecules 2010, 43, 316–325.
12. Hu, Y.; Kazemian, H.; Rohani, S.; Huang, Y. N.; Song, Y. In situ high pressure study of ZIF-8 by FTIR spectroscopy. Chem. Commun. 2011, 47, 12694–12696.
13. Gong, X.; Wang, Y. J.; Huang, T. R. ZIF-8-based membranes for carbon dioxide capture and separation. ACS Sustain. Chem. Eng. 2017, 5, 11204–11214.
14. Hess, S. C.; Grass, R. N.; Stark, W. J. MOF channels within porous polymer film: flexible, self-supporting ZIF-8 poly(ether sulfone) composite membrane. Chem. Mater. 2016, 28, 7636–7644.
15. Wu, X. L.; Yang, C.; Ge, J.; Liu, Z. Polydopamine tethered enzyme/metal-organic framework composites with high stability and reusability. Nanoscale 2015, 7, 18883–18886.
16. Xian, S. K.; Xu, F.; Ma, C.; Wu, Y.; Xia, Q. B.; Wang, H. H.; Li, Z. Vapor-enhanced CO\textsubscript{2} adsorption mechanism of composite PEI@ZIF-8 modified by polyethyleneimine for CO\textsubscript{2}/N\textsubscript{2} separation. Chem. Eng. J. 2015, 280, 363–369.
17. Fu, Q. S.; Wen, L.; Zhang, L.; Chen, X. D.; Pun, D.; Ahmed, A.; Yang, Y. H.; Zhang, H. F. Preparation of ice-templated MOF-polymer composite monoliths and their application for wastewater treatment with high capacity and easy recycling. ACS Appl. Mater. Interfaces 2017, 9, 33979–33988.
18. Aslam, M.; Kalyar, M. A.; Raza, Z. A. Polyvinyl alcohol: a review of research status and use of polyvinyl alcohol based nanocomposites. Polym. Eng. Sci. 2018, 58, 2119–2132.
19. Zhang, H. F.; Hussain, I.; Brust, M.; Butler, M. F.; Rannard, S. P.; Cooper, A. I. Aligned two- and three-dimensional structures by directional freezing of polymers and nanocomposites. Nat. Mater. 2005, 4, 787–793.
20. Torad, N. L.; Hu, M.; Kamachi, Y.; Takai, K.; Imura, M.; Naito, M.; Yamauchi, Y. Facile synthesis of nanoporous carbons with controlled particle sizes by direct carbonization of monodispersed ZIF-8 crystals. Chem. Commun. 2013, 49, 2521–2523.
21. Sun, H.; Schiraldi, D. A.; Chen, D. Y.; Wang, D. Q.; Sanchez-Soto, M. Tough polymer aerogels incorporating a conformal inorganic coating for low flammability and durable hydrophobicity. ACS Appl. Mater. Interfaces 2016, 8, 13051–13057.
22. Zhou, Z.; Yang, L.; Wang, Y. F.; He, C.; Liu, T.; Duan, C. Y. Construction of solvent-dependent self-assembled porous Nilll-coordinated frameworks as effective catalysts for chemical transformation of CO\textsubscript{2}. RSC Adv. 2016, 6, 108010–108016.

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