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Tuning the size and morphology of zeolitic imidazolate framework-8 in a membrane dispersion reactor

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Zeolitic imidazolate framework-8 (ZIF-8) with different sizes and morphologies were successfully synthesized using a membrane dispersion reactor (MDR). The MDR synthesis applied in this paper was expected to be efficient and economical ways to synthesize ZIF materials.

Zeolitic imidazolate frameworks (ZIFs), a subclass of metal organic frameworks (MOFs), have attracted considerable attention in the past decade owing to their uniform and high porosity, exceptional hydrothermal and chemical stabilities. They are recognized to have promising potential in many applications such as gas separation, chemical sensor and probe, optical and electrical device, porous carbon synthesis, etc.¹⁻⁵

Originally, ZIF-8 was prepared by solvothermal method, in which autogenous high pressure and temperature is desired to produce a high nucleation rate.⁶⁻⁸ So a high boiling solvent such as DMF was used as synthesis agent. Unfortunately, the drawback of this method is that the solvent DMF would be trapped inside the pores of ZIF-8 because the guest organic molecule is larger than the aperture of the SOD cage. In order to obtain a large porosity of ZIF-8 particles, DMF had to be removed by an extra time-consuming solvent exchange process.⁹ So, the preparation process for ZIF-8 with smaller kinetic diameter at room-temperature is desirable because the low-boiling and volatile solvents (such as methanol) can be easily removed from the ZIF-8 pore network. However, the regulation of the ZIF-8 crystal size and crystal size distribution at the nanoscale level is still a challenge. Despite various kinds of additives or large reactant ratio were used in this method to solve the problem,¹⁰ but various kinds of additives would affect purity of ZIF-8. On the other hand, large reactant ratio would cause a serious waste of raw materials in practical application. So the development of facile and effective strategies for preparing uniform ZIFs nanocrystals with controllable size is still challenging.

Membrane-dispersion reactor (MDR) is a useful method for

preparing different types of nano-sized crystalline particles due to efficient enhancement of mixing and the mass transfer process.^{11(a-f)} In the MDR, one reactant solution permeates through the micropores of ultrafiltration membranes into another solution. The permeate drop size is comparable with that of the micropores, resulting in decrease in characteristic diffusion time and improvement of micromixing, leading to high supersaturation.^{11(g)}

On the other hand, the supersaturation distribution is uniform due to the large number of feed introduction points, which is conducive to get uniform particle size distribution. Thus, the MDR is a very effective method to generate nano-particles with narrow size distribution.

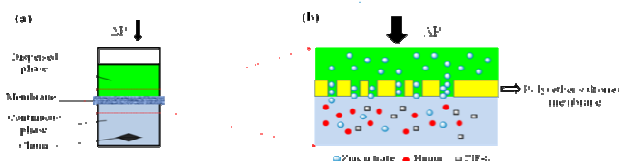


Fig. 1 (a) Schematic diagram of ZIF-8 preparation and the module structure (b) the schematic formation of ZIF-8 via-diffusion of zinc nitrate through the pores of the Poly (ether sulfones) support.

Fig.1 shows a typical membrane reactor experimental setup (a) and the principle of membrane dispersion (b). In this work, we successfully prepared ZIF-8 nano-sized crystalline particles by MDR with poly (ether sulfones) (PES) ultrafiltration membrane with a pore size of 25 nm (Fig. S1) for disperse medium. Zinc nitrate solution and 2-methylimidazole (Hmim) solution were separated by the PES membrane (Fig. 1a). Zinc nitrate solution is dispersed phase, Hmim solution is continuous phase. Before reaction, zinc nitrate solution and Hmim solution were prepared by dissolving 1.000 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 30 mL of methanol, and 1.100 g of Hmim in 30 mL of methanol, respectively. This means that the designed overall molar ratio of $\text{Hmim}/\text{Zn}^{2+}$ is 4. Under a given trans-membrane pressure and certain mixing speed, the zinc nitrate solution pass

through the membrane to react with Hmim at room temperature. The synthesis solution turned milky almost instantly after the zinc nitrate solution disperses into the Hmim solution. After centrifuging, the product was dried at 65 °C overnight in a drying oven. The samples were denoted T 0.02, T 0.04, T 0.06 and T 0.08 (the numbers following the ‘‘T’’ stand for the trans-membrane pressure).

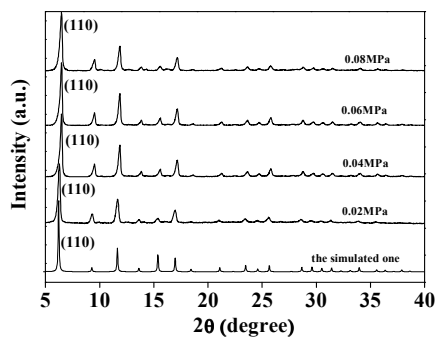


Fig. 2 XRD patterns of the simulated one from ZIF-8 crystal structure data⁶ and as-synthesized ZIF-8 prepared by MDR method under different trans-membrane pressure

The ZIF-8 prepared by MDR under different trans-membrane pressure was examined by XRD (Fig. 2). Compared to the pattern simulated from the published ZIF-8 structure data,⁶ the pattern of the samples in this work are similar to that of the theoretical one. That means all the samples possess typical SOD structure just like the simulated one. Peak broadening can be clearly observed from the sample XRD pattern, indicating the formation of nano-sized crystals.^{11(d)} The grain size of the ZIF-8 nanocrystals under different trans-membrane pressure deduced from Sherrer’s formula for the strongest peak (110) was about 50.5 nm, 47.0 nm, 33.2 nm and 33.6 nm, respectively. As the trans-membrane pressure increased from 0.02 MPa to 0.08 MPa, the grain size of ZIF-8 was decreased initially and then slightly increased. Under 0.06 MPa, the grain size of the ZIF-8 achieves its minimum. The peak positions of samples illustrated that ZIF-8 was successfully synthesized by MDR. Compared with those synthetic methods requiring hours and days, the synthesis process of this work took only several minutes.

The influence of trans-membrane pressure on particle size and uniformity of ZIF-8 was very obvious (Fig. 3). As the trans-membrane pressure increased, the particle size of ZIF-8 was found to decrease initially and then increase. The uniformity of T 0.02 and T 0.04 was low and a little agglomeration was observed (Fig.3a-b). But for T 0.06 and T 0.08 no agglomeration appeared and the morphology of them showed the hexagonal faceted crystals. The particle uniformity of T 0.06 and T 0.08 was better than that of T 0.02 and T 0.04. This result indicates that appropriate trans-membrane pressure is needed to obtain ZIF-8 with small particle size and high particle uniformity. N₂ adsorption-desorption isotherms of T 0.02, T 0.04, T 0.06 and T 0.08 were shown in Fig.4, indicating a type I isotherm. BET results shown in Table S1 were consistent with SEM results. The BET and micropore volume of ZIF-8 were increased initially and then decreased with the increasing of the trans-membrane pressure. Under the trans-membrane pressure of

0.06 MPa, the BET and microporous volume of ZIF-8 reached the maximum values, which are 1365 m²/g (BET), 1790 m²/g (Langmuir surface area) and 0.61 cm³/g, respectively. To our knowledge, this value is close to the highest one reported for ZIF-8 (BET: 1630 m²/g, Langmuir surface area: 1810 m²/g, micropore volume: 0.64 cm³/g).⁶ Generally, ZIF-8 particles prepared at room temperatures have lower BET than those at high temperature.^{10(d)} But through MDR, considerable surface area of ZIF-8 was just performed at room temperatures instead of high temperature.

All the BET results (Table S1) suggested that we had successfully synthesized ZIF-8 with a high porous structure.^{10(a, b, e), 12, 13} This can be attributed the fact that, under a certain trans- membrane pressure, Zn²⁺ diffused slowly through the PES membrane and reacted with Hmim. The local amount of Hmim was excess, in turn the excess Hmim acts as a structure directing agent to form porous structure of ZIF-8.¹⁴

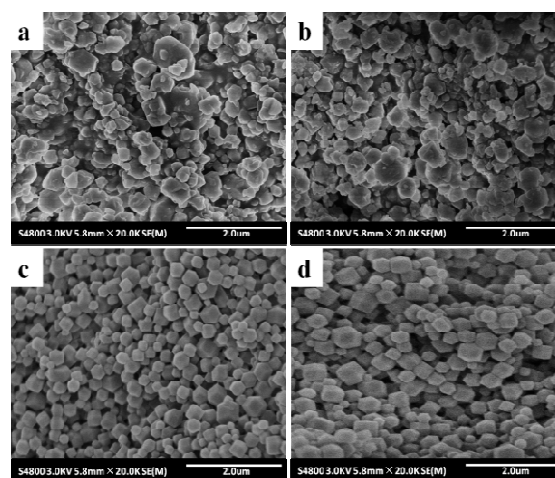


Fig.3 SEM images of as-synthesized ZIF-8 prepared by MDR method under different trans-membrane pressure: (a) 0.02MPa, (b) 0.04MPa, (c) 0.06MPa and (d) 0.08MPa.

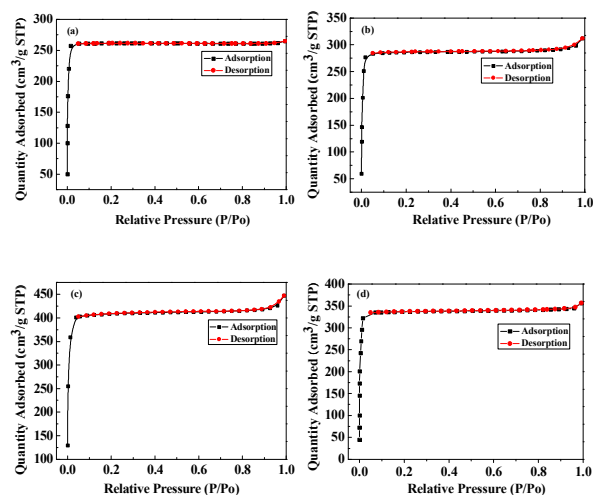
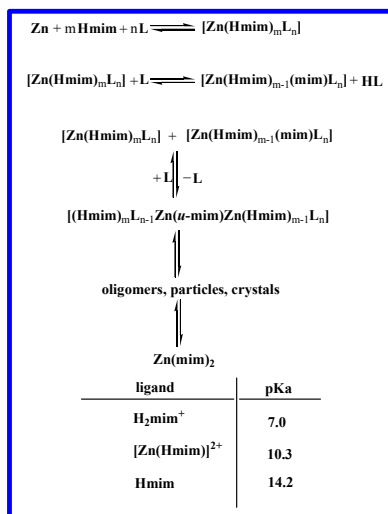


Fig.4. Nitrogen adsorption-desorption isotherm of as-synthesized ZIF-8 prepared by MDR method under different trans-membrane pressure: (a) 0.02MPa, (b) 0.04MPa, (c) 0.06MPa and (d) 0.08MPa.

In order to rationalize the outcome of our present syntheses, we draw lessons from explains of Janosch *et al.*^{10(d)} From Scheme 1, Janosch *et al.*^{10(d)} considered that an excess of Hmim in reaction (i) yielded a high concentration of $[\text{Zn}(\text{Hmim})_m\text{L}_n]$ species ($m > n$). They also stated that only the basic modulating ligands with $\text{pK}_a > 10.3$ could deprotonate the $[\text{Zn}(\text{Hmim})_m\text{L}_n]$ species and thereby accelerated ligand exchange reactions, resulting in an high nucleation rate and consequently in a small crystal size.^{10(d)} For our MDR, due to the uniform aperture of PES ultrafiltration membrane, it provided the micro contact for $\text{Zn}(\text{NO}_3)_2$ and Hmim, which formed high local molar ratio of $\text{Zn}^{2+}/\text{Hmim}$ (far greater than 1:4). So the amount of Hmim was far more excess, which made reaction (i) and (ii) quickly achieved. In addition, the modulating ligand in reaction (iii) was just Hmim itself, and the pK_a (14.2) of Hmim was the largest. Both reasons accelerated deprotonation of the $[\text{Zn}(\text{Hmim})_m\text{L}_n]$, resulting in a very high nucleation rate and a small particle size. When trans-membrane pressure was low (0.02MPa and 0.04MPa), it would decrease diffusion rate of Zn^{2+} . It impacted reaction (i) of Scheme.1 to lead low concentration of $[\text{Zn}(\text{Hmim})_m\text{L}_n]$. Thus nucleation rate of crystals was low, resulting in generating large particle size of ZIF-8. However, it is not true that the greater the trans-membrane pressure the better it is. This may be because excessively high trans-membrane pressures (Fig.3d) would make diffusion rate of Zn^{2+} excessively fast to lead to poor mixing performance, it was bad for preparing ZIF-8 that had good particle uniformity and small particle size.



Scheme 1 Basic reactions of ZIF-8 formation (top) and pK_a values for the conjugate acids of relevant ligands (bottom). Charges of species are omitted in the reaction equations. L denotes all ligands that may be present: Auxiliary modulating ligands as well as NO_3^- , H_2O , and MeOH

We also examined the influence of stirring on ZIF-8. The samples T 0.06 without stirring and gentle stirring showed no changes in the X-ray pattern (Fig. S3). Both of them showed typical SOD structure. The intensity of the diffraction peaks of ZIF-8 with gentle stirring was stronger than that with no stirring. It indicates that ZIF-8 nanocrystal with gentle stirring had higher crystallinity than that with no stirring. So stirring is a necessary factor to prepare ZIF-8 nanocrystal with integrity crystal structure. But an unidentified

XRD pattern is observed in ZIF-8 samples with vigorous stirring. It showed that appropriate stirring is another necessary factor impacting shape of ZIF-8 nanocrystal. From SEM observation (Fig.S4), these samples showed apparent changes. The particle size with vigorous stirring was the biggest, next to that without stirring, last to that with gentle stirring. T 0.06 with vigorous stirring showed plate-like structure, while others showed cubic structure. A type I isotherm was observed in Fig. 5(a,b). The BET and microporous volume of T 0.06 with gentle stirring achieved maximum, the microporous volume was $0.61 \text{ cm}^3/\text{g}$ and the BET was $1365 \text{ m}^2/\text{g}$ (BET), $1790 \text{ m}^2/\text{g}$ (Langmuir surface area), respectively (Table S3). But in Fig.5(c) it shows a type IV isotherm, belong to hysteresis loop of type H3, which indicates aggregates of plate-like particles.¹⁵ The BET and microporous volume of T 0.06 with vigorous stirring achieved minimum, the microporous volume was $0.02 \text{ cm}^3/\text{g}$ and the BET was $58 \text{ m}^2/\text{g}$ (BET), $81 \text{ m}^2/\text{g}$ (Langmuir surface area), respectively. The BET results were consistent with results of Fig. S4 and Fig. S5, which may explain that appropriate stirring could accelerate nucleation rate of crystals to obtain small particle size of ZIF-8.

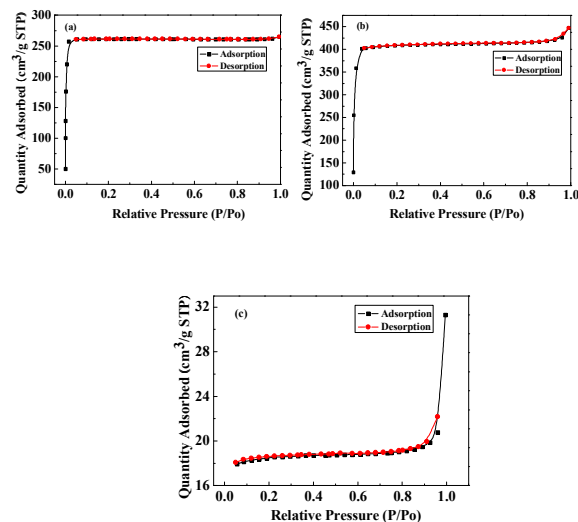


Fig. 5 Nitrogen adsorption-desorption isotherm of T 0.06 (a) without stirring (b) gentle stirring (c) vigorous stirring

In summary, we firstly reported the synthesis of ZIF-8 by the MDR. The synthesis method allowed us to achieve high property of ZIF-8, such as high surface area in a much shorter time. The interesting result from this method was that the morphology of ZIF-8 could be conveniently tuned by MDR. Different morphologies of ZIF-8, such as one-dimensional (rod), two-dimensional (sheet) and three-dimensional (grain), would affect the surface area and particle size of ZIF-8 nanoparticles which had been discussed in this work. Furthermore, the performances of ZIF-8 in energy storage, gas separation and pervaporation¹⁶ would be also influenced significantly. Yao *et al.*¹⁷ firstly reported to prepare ZIF-8 membrane by contra-diffusion method on a macroporous Nylon membrane, which showed considerable H_2/N_2 ideal selectivity and H_2 permeance. Other similar methods, such as, modified the contra-diffusion method¹⁸ and in situ counter-diffusion method¹⁹, were

developed to form ZIF-8 membranes for gas separation. These reports demonstrate potentially general applicability for contra-diffusion method. Recently, Yang *et al.*²⁰ reported a novel preparation method for MOF nanosheets by simple physical grinding in a ball milling jar, which could effectively tune the morphology of MOF. The gas separation membranes prepared by nanosheets of MOF showed very high selectivity of H₂/CO₂. On the other hand, Rodenas *et al.*²¹ prepared MOF nanosheets in a solvent mixtures composed of three different miscible solvents which have different densities. Specific to our work, we also successfully achieved morphology control of ZIF-8 by simple physical method, MDR. Our method is also an efficient and economical way for the preparation of other ZIFs, which is promising for its large-scale industrialization and many other extending applications.

Experimental

zinc nitrate solution and Hmim solution were prepared by dissolving 1.000 g of Zn(NO₃)₂·6H₂O in 30 mL of methanol, and 1.100 g of Hmim in 30 mL of methanol, respectively. Under a given trans-membrane pressure and certain mixing speed, the zinc nitrate solution pass through poly (ether sulfones) (PES) ultrafiltration membrane to react with Hmim at room temperature. The synthesis solution turned milky almost instantly after the zinc nitrate solution disperses into the Hmim solution. After centrifuging, the product was dried at 65 °C overnight in a drying oven.

Notes and references

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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Tuning the size and morphology of zeolitic imidazolate framework-8 in a membrane dispersion reactor

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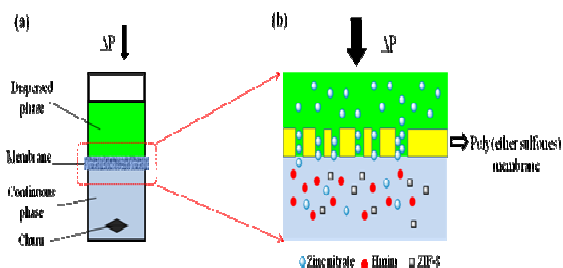
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The MDR can successfully control size and morphology of ZIF-8, which is an efficient and economical way for preparation of ZIFs.

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