



Synthesis of ZIF-8 and ZIF-67 nanocrystals with well-controllable size distribution through reverse microemulsions

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HIGHLIGHTS

- Synthesized ZIF nanocrystals own extremely small size and narrow size distribution.
- Reverse microemulsion is superior to the conventional water synthesis of ZIFs.
- DLS characterization revealed the controlling mechanism of particle size distribution.

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ABSTRACT

With the particles size down to nanoscale, porous materials with well-controllable dimension will have more promising applications in biologically relevant fields and even in the areas of traditional selective separation and catalysis. By using reverse microemulsions the nanoscale zeolitic imidazolate frameworks (ZIFs) such as ZIF-8 and ZIF-67 were synthesized at room temperature with uniform grain size distribution and extremely small crystal dimension (mean particle size less than 5 nm). The ZIF-8 and ZIF-67 synthesized by reverse microemulsion have much larger surface areas and micropores volume than samples obtained from water, but are comparative to those obtained from methanol. The thermal stability of the synthesized ZIF-8 and ZIF-67 by microemulsion is also excellent. The DLS characterization revealed that it is the size of micelles in microemulsion that controls the dimension of ZIF crystals. This is different comparing to the controlling mechanisms of other common synthesis methods of MOFs. We believe that the microemulsion method developed in this work can enrich the synthesis strategies of other nanoscale ZIF or MOF particles.

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1. Introduction

As a new emerging class of porous materials, metal–organic frameworks (MOFs) have attracted extensive research interests for their potential applications in gas storage and selective separation, catalysis, nonlinear optics, light harvesting, and drug delivery [1–6]. MOFs are composed of inorganic metal-containing nodes or clusters linked by polydentate organic linker ligands. The extraordinary high surface area, tunable pore size, and adjustable internal surface properties are the key features that made them known [7–11]. Although the size of MOF crystals may not be very important in the fields of gas storage and selective separation, the specialized MOFs with small grain size and well-controllable

dimension are necessary in medical applications, such as biosensing [12], drug delivery [13], and biomedical imaging [14]. It was emphasized that MOFs with less controlled bulk size would be unsuitable for many biologically relevant applications compared with materials with dimensions of nanometer and micrometer [15]. With the size reduction of porous particles down to nano-dimensions, there will be an additional potential to optimize the performance of porous materials such as MOFs even in traditional separation and catalytic applications [16–18].

However, most of MOFs were long thought to be too frail for use in practice in that they are easy to collapse once the guest molecules are removed. This puts MOFs at a disadvantage in the competition against the tough inorganic materials such as zeolites, whose pores are exploited in a wide variety of industrial processes, including separation and catalysis [19]. But with the emergence of zeolitic imidazolate frameworks (ZIFs), MOFs may have an opportunity to make their debut in commercial applications. As a subclass of MOFs, the ZIF crystal structures are constructed on

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the basis of the nets of aluminosilicate zeolites, in which the bridging and tetrahedral Si(Al) units are replaced with imidazolate linker and transition metal ion, respectively. This unique framework endows ZIFs with outstanding thermal and chemical stability. For example, the ZIF-8 could maintain its structure for 7 days in boiling water, and it even kept unchanged for up to 24 h in 0.1 and 8 M aqueous sodium hydroxide at 100 °C [20]. Compared to most of other MOFs, this exceptional resistance of ZIF-8 to hydrolysis is outstanding.

According to the recent review articles [16,21], strategies concerning the synthesis of MOFs have been developed for the miniaturization of their crystals: (i) adjustment of reactants/solvents and their concentrations, (ii) alteration of the synthesis conditions such as temperature and time, (iii) different heating types such as solvothermal or microwave-assisted method, and (iv) use of specific additives to restrain crystal growth. Till now, the methods used to fabricate ZIFs with small grain size belong to these strategies [22–26]. In this work, we employed a novel method, i.e. reverse microemulsion (water in non-polar medium) to synthesize ZIFs with nano and well-controlled dimension. Microemulsions provide an efficient means of synthesizing monodispersed nanoparticles [27,28]. In microemulsions, the dispersed phase acts as lots of nano reactors, by which the crystal size and morphology can be well controlled. The pioneering work in the application of microemulsions into MOFs is the synthesis of one uncommon Gadolinium MOF by Lin et al. [14]. But such a synthetic method has not yet proved its feasibility in the controllable preparation of other known MOFs, especially ZIF materials with outstanding thermal and chemical stability. In the present work, we use reverse microemulsions, i.e. water dispersed in water in non-polar medium to fabricate the nanoscale ZIF-8 and ZIF-67 at room temperature. We show here that the nano-sized ZIF crystals fabricated by reverse microemulsion method own well-defined morphologies, narrow size distributions, and the minimal ZIFs size ever known, as well as excellent adsorption properties and thermal stability.

2. Experimental section

The synthesis details using reverse microemulsion method are presented in Scheme 1. Firstly, 1.02 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 50 mL deionized water, which was labeled as solution I. 1.13 g 2-methylimidazole (2-MeIm) and 1.39 g triethylamine (TEA) were dissolved in 50 mL deionized water, which was labeled as solution II. Secondly, added 0.9 mL solution I and 0.9 mL solution II separately into two 0.05 M CTAB/0.5 M 1-hexanol/heptane mixtures (50 mL), which were labeled as microemulsion A and B, respectively. And then stirred these two microemulsions vigorously for 30 min at room temperature. Thirdly, mixed these two microemulsions in a 150 mL volumetric flask with vigorous stirring for 1 h at room temperature. The sample collected through series of centrifugation and filtration was labeled as ZIF-8a. The synthesis procedure of ZIF-67a using microemulsion was same to ZIF-8a and was in detail introduced in the Supporting Material. All the samples were dried under vacuum at 60 °C for 24 h for further use.

For comparison, the common ZIF-8 and ZIF-67 synthesized in water, as well as methanol, were also prepared (see Supporting Material). To distinguish the synthesized ZIFs using microemulsion, the ZIFs synthesized in methanol and water were labeled as ZIF-8b (or ZIF-67b) and ZIF-8c (or ZIF-67c), respectively. The numbering of various ZIFs corresponding to the synthesis conditions is listed in Table 1.

The DLS (Dynamic light scattering) method was used to measure the size of dispersed water droplets, which were stabilized by a surfactant in the predominantly organic phase. Other characterizations including powder X-ray diffraction (XRD), thermal

gravimetric analysis (TGA) measurements, nitrogen adsorption-desorption, and microstructure image measurement (SEM and TEM) can be referred to the Supporting Material.

3. Results and discussion

3.1. Powder X-ray diffraction (PXRD) of synthesized ZIFs

For comparison, the ZIF-8 and ZIF-67 were synthesized by different methods, i.e. the microemulsion synthesis developed in this work and the conventional ways using methanol or water as solvent according to the procedures described in Section 2. Fig. 1 shows the powder X-ray diffraction (PXRD) patterns of the synthesized ZIFs. It can be seen that all fabricated materials here match the corresponding simulated patterns, demonstrating that the products are pure-phase ZIF crystals. Since ZIF-67 is isostructural to ZIF-8, they share the same standard simulation XRD pattern.

3.2. SEM and TEM image of nanocrystals

The microstructures of the synthesized ZIF-8 and ZIF-67 were shown in Fig. 2. The mean particle size of the ZIF-8b synthesized in methanol is 55.4 nm (standard deviation $\sigma = 7.3$), while that of ZIF-67b is much larger with the size of 413.0 nm ($\sigma = 77.2$). Both of them have regular particle morphologies and uniform particle size. For the ZIF-8c and ZIF-67c synthesized in water, the size distribution is obviously not uniform. The mean particle size of ZIF-8c is 120.0 nm ($\sigma = 61.1$). For the ZIF-67c the mean particle size is 177.4 nm ($\sigma = 89.6$). This indicates that the particle size of ZIFs cannot be well controlled when they are synthesized using water as solvent. This phenomenon was ascribed to the overall faster growth kinetics in water phase than in methanol [25].

However, when using reverse microemulsion developed in this work to synthesize ZIFs, the mean particle size is remarkably small, and also the particle size distribution is very narrow, shown in Fig. 2c and f. For example, the mean particle size of ZIF-8a is 2.3 nm ($\sigma = 0.4$). Similarly, the ZIF-67a has the mean particle size of 2.7 nm ($\sigma = 0.5$). Thus it can be seen that when using reverse microemulsion as a media, the ZIFs will have smaller particle size, and the particle morphologies and size distribution can be well controlled. Essentially, the micelles in the microemulsions act as “nano-reactors” that can well control the size of nanoparticles produced inside them. It will be interesting to obtain some information concerning the “nano-reactor”, which may shed some lights on the controlling mechanism of the synthesis of ZIFs in microemulsion.

3.3. Characterization of microemulsion by DLS

Fig. 3a–b show the size distributions of water droplets in microemulsion A and B measured by DLS. The mean size of water droplets in microemulsion A is 10.3 nm, almost as same as those in microemulsion B (11.6 nm). It can be seen that the maximum size of ZIF particles match the size of water drops in microemulsion. Clearly it is the “nano reactors” (water drops) that confine the unlimited growth of ZIF crystals. This is much different from the situation of the synthesis of ZIFs using water or methanol as solvent. Generally speaking, to control the size of MOF crystals several common means were employed, including suitable reactants/solvent types and concentrations, synthesis conditions such as temperatures and heating types, and usage of additives to suppress crystal growth [16]. For example, by accelerating nucleation rate the microwave heating generally generate smaller crystals than the conventional heating [29,30]. This work showed here that the reverse microemulsion synthesis is also an efficient way to well

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