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Short Communication

Nanopolyhedrons and mesoporous supra-structures of Zeolitic Imidazolate framework with high adsorption performance

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ABSTRACT

Zeolitic Imidazolate framework (ZIF-90) polyhedron (Zn(ICA)-1) was synthesized via diffusion of triethlyamine (TEA) and hexane solution into the *N*,*N*′-dimethylformamide (DMF) solution of imidazole-2-carboxyaldehyde (ICA) and $Zn(NO_3)_2{\cdot}6H_2O$ at room temperature. And suprastructure (Zn(ICA)-2) were synthesized via direct addition of TEA to the *N*,*N*′-dimethylformamide (DMF) solution of imidazole-2-carboxyaldehyde (ICA) and $Zn(NO_3)_2{\cdot}6H_2O$ at room temperature. The scanning electron microscopy (SEM) measurement indicated that the sample of Zn(ICA)-1 showed polyhedron morphology with the diameter of 300–400 nm and the sample of Zn(ICA)-2 showed super-structural morphology. XRD results indicated that Zn(ICA)-1 has the crystalline structure of ZIF-90 and Zn(ICA)-2 is amorphous. The gases adsorption measurement results showed that the sample Zn(ICA)-2 exhibited mesoporous structure.

1. Introduction

Zeolitic Imidazolate frameworks (ZIFs) are porous crystalline materials with tetrahedral networks that resemble those of zeolites: transition metals such as zinc and cobalt replace the sites of tetrahedrally coordinated silicon atoms, and imidazolate links replace oxygen bridges [1,2]. For the prominent thermal stability and chemical stability, ZIFs are ideal platforms for performing useful organic transformations under some strong reaction conditions [3–6] and gases separation performance [5,7].

Coordination polymer nanomaterials have recently been received much attention [8–15] for their excellent enhanced performance compared with their corresponding bulky crystals [16–19]. However, few reports have investigated the morphology-dependent adsorption performance for nanomaterials of porous coordination polymer. We are quite interested in constructing and controlling meso/nano-structures of novel MOFs with intriguing properties [20–30]. Hierarchical supra-nanostructures of Cu–BDC and Cr–BDC [20] (BDC = 1, 4-benzenedicarboxylate) were fabricated, supra-nanostructure of MOF-5 [21] and HKUST-1 [22] (SNHKUST-1) were successfully prepared for the enhanced H_2 adsorption enthalpy in our laboratory. In order to further expand our research, herein, ZIF-90 nanooctahedron (Zn(ICA)-1) and ZIF-90 suprastructure (Zn(ICA)-2) were prepared from the reaction of imidazole-2-carboxyaldehyde (ICA) and $Zn(NO_3)_2{\cdot}6H_2O$.

2. Experimental

2.1. Materials

Imidazole-2-carboxyaldehyde was purchased from Alfa Aesar. $Zn(NO_3)_2{\cdot}6H_2O$, triethlyamine (TEA) and *N*,*N*′-dimethylformamide (DMF) were purchased from Nanjing Chemical Company.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were collected in a Shimadzu XRD-6000 (operating at 40 kV and 30 mA) with a Cu Kα radiation (wavelength $\lambda = 1.5147$ Å). Elemental analyses were carried out with an Elementar Vario micro-analyzer. The infrared (IR) spectra were recorded on a Bruker Equinox 55 FT-IR spectrometer using the KBr pellet technique. Thermal gravity analysis (TGA) were obtained on a STA 449 C DSC–TGA analyzer. And the samples were dried under vacuum at 130 °C for 10 h before all the above measurement. Scanning electron microscopy (SEM) images were obtained on a Hitachi S-4800 field emission scanning electronic microscope. Low pressure nitrogen and hydrogen sorption isotherms were measured at 77 K using a Micromeritics ASAP 2020M+C system after the samples were first degassed at 130 °C for 10 h.

2.3. Preparation

2.3.1. Preparation of ZIF-90 bulky crystal [6]

Zinc nitrate tetrahydrate ($Zn(NO_3)_2{\cdot}4H_2O$) (0.1 g) and imidazole-2-carboxyaldehyde (ICA) (0.06 g) in DMF (10 mL) was placed

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in a desiccator under an atmosphere of triethylamine (1 mL) in hexane (40 mL). The reaction was allowed to stand at room temperature for several days. The obtained crystalline powder was filtered and washed with methanol (3 × 5 mL). The product was washed three times with DMF and chloroform, respectively. The product was activated with chloroform (3 × 10 mL) over a three-day period before being dried under vacuum for 10 h at 130 °C.

2.3.2. Preparation of ZIF-90 octahedron (Zn(ICA)-1)

In a 25 mL beaker, 1 mL TEA was dissolved in 10 mL hexane (**A**); in a 250 mL beaker, 0.1 g $Zn(NO_3)_2{\cdot}6H_2O$ and 0.06 g CIA was dissolved in 40 mL DMF (**B**), after stirred for 30 min, **A** was slowly dropped into **B** slowly. White precipitate can be seen at the interface of hexane and DMF. After 4 h standing, collected the white precipitate and washed three times with DMF and chloroform, respectively. The product was activated with chloroform (3 × 10 mL) over a three-day period before being dried under vacuum for 10 h at 130 °C. Yield (0.08 g, 75%) CHN calculated for $C_8H_6N_4O_2Zn$: C, 37.60; H, 2.37; N, 21.92% Found: C, 36.83; H, 3.17; N, 20.03%.

2.3.3. Preparation of Zn(ICA)-2

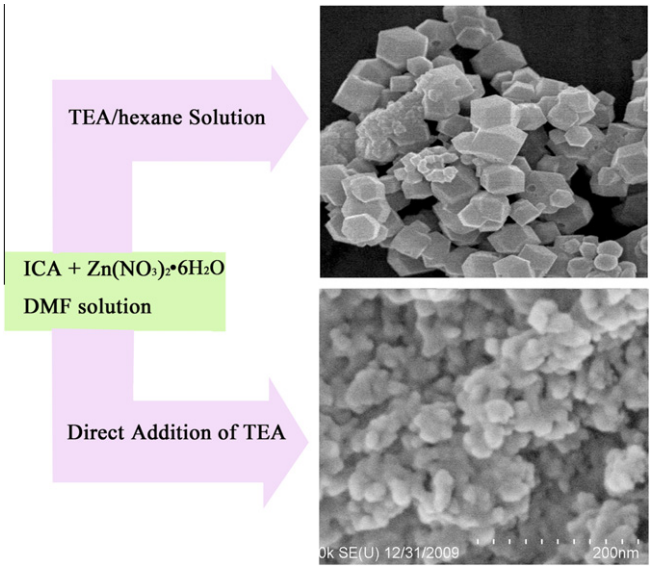
0.55 g $Zn(NO_3)_2{\cdot}6H_2O$ and 0.29 g ICA were dissolved in 100 mL DMF. 1 mL TEA was added into the above solution. After two hours at room temperature, collected the precipitate with centrifugation and washed with DMF and chloroform three times, respectively. The product was activated with chloroform (3 × 10 mL) over a three-day period before being dried under vacuum for 10 h at 130 °C. Yield (0.08 g, 70.3%) CHN calculated for $C_8H_6N_4O_2Zn$: C, 37.60; H, 2.37; N, 21.92% Found: C, 36.49; H, 2.31; N, 19.848%.

3. Results and discussion

Scheme 1 shows the synthetic route of ZIF-90 nanooctahedron and mesoporous suprastructures. It can be seen that the addition method of TEA availably affected the morphology of the samples. Elemental analysis performed on guest free ZIF-90 gave the expected formula, $Zn(C_4H_3N_2O)_2$. IR spectra indicated the presence of aldehyde for a strong band at 1678 cm^{-1}(νCdO) was observed. As shown in Fig. 1, compared with an XRD patterns taken from powder samples and the pattern from simulated data, Zn(ICA)-1 shows ZIF-90 structure. But the powder XRD pattern of Zn(ICA)-2 (Fig. 1c) exhibits broad diffraction peaks 2θ = 10–20° and 30–40°, an indication of the amorphous phase of Zn(ICA)-2. The formation of amorphous phase may be probably caused by the directly addition of TEA. When TEA was directly added into the DMF solution, the ions Zn^{2+} and ICA reacted immediately and formed large numbers of coordination polymer pieces, these pieces did not grow up to nuclei but accumulated into nanoparticles in the present of mass TEA, these nanoparticles reunited to supra-structure, and mesopores was formed between the nanoparticles.

The SEM images (Fig. 2) display the octahedron-like morphologies of Zn(ICA)-1 with the sizes of 300–400 nm. From the SEM images, it can be found that particles were reunited together, and the mono-dispersion cannot be monitored by Dynamic Light Scattering (DLS). Zn(ICA)-2 exhibits supra-structure morphology formed from irregular nanospheres with the average diameter of the spheres being ca. 20 nm (Fig. 3b). Notably, the mesopores were formed from the nanoparticles in a random manner, which can be seen in the TEM images (Fig. 3c and d). Likewise, the calculated average mesopore diameter with BJH method based on N_2 adsorption data is about 6–9 nm (Fig. 3d).

To confirm the permanent porosity, N_2 sorption measurements of bulky crystalline ZIF-90 (prepared by diffusion method according to Ref. [6]), Zn(ICA)-1 and Zn(ICA)-2 were performed in the same condition. The N_2 adsorption/desorption isotherm (Fig. 4) of Zn(ICA)-1 shows a steep rise in the low-pressure region, indicating the permanent porosity. This adsorption process is similar to the argon adsorption process of ZIF-8 nanoparticles [19]. We presume that the small step at higher pressure (with a hysteresis loop) is due to a gate opening phenomenon [31]. The N_2 adsorption/desorption isotherm of Zn(ICA)-2 exhibits a slight rise at low relative pressure, inferring the adsorption of the surface on the nanoparticles. An interesting feature of the isotherms can be observed for exhibiting abrupt secondary uptake at the relative pressure up to 0.6 and a great adsorption–desorption hysteresis loop between P/P_0 from 0.6 to 0.9, which is the adsorption/desorption isotherms of mesopores (Fig. 4c). The N_2 accessible BET surface area of Zn(ICA)-1 is ca. 947 m^2/g that is lower than that of ZIF-90 (1270 m^2/g)(Table 1). This may possibly indicate that the as-synthesized nanoscale ZIF-90 still contains some nonporous species that could not be desorbed from the particles during the activation step before the sorption measurements [20–22]. The BET surface area of Zn(ICA)-2 is only 251 m^2/g, which mainly caused by the amorphous structure of Zn(ICA)-2.



Scheme 1. Synthetic route of Zn(ICA)-1 and Zn(ICA)-2.

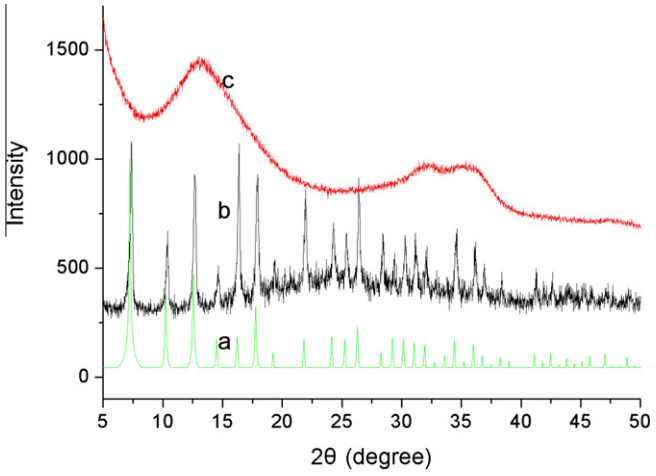


Fig. 1. (a) Simulated XRD pattern of ZIF-90 crystals; (b) Zn(ICA)-1 and (c) Zn(ICA)-2 experimental XRD patterns.