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The controlled regulation of morphology and size of HKUST-1 by "coordination modulation method"

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ABSTRACT

Three types of modulators, including sodium formate, sodium acetate and triethylamine were used to tailor the morphology and size of HKUST-1 crystals by "coordination modulation method". Through exploring the reaction parameters during the synthesis of HKUST-1, fascinating crystals morphologies, including hierarchical octahedral-shape crystals and nanocrystals were obtained by a solvothermal treatment. This paper discloses two essential functions of the modulator for the fabrication of uniform nanocrystals: Adjusting the proper acid–base environment of the reaction medium which governs the nucleation process and capping groups capable of inhibiting crystallites from growing. Moreover, samples were fully characterized by various techniques and the formation mechanism of the hierarchical octahedral-shape crystals was deduced.

1. Introduction

Metal–organic frameworks (MOFs) are a novel class of porous inorganic–organic materials built from metal ions or metal ions clusters and bridging organic linkers [1–5]. Large micropore volumes, high surface areas, varying structure, well-defined pore architecture are the key features of this new porous materials, which have made them extremely attractive for a number of applications such as gas adsorption and storage [6–8], drug release [9–11], sensing [12], as membranes [13,14] and catalysts [15,16]. Previous researches focused more on the design, synthesis, characterization and application of bulk MOFs materials; however, in recent years, nanometer-sized metal organic frameworks (NMOFs) have received great attention due to their interesting characteristics for various nanotechnology and device integration including spin-crossover, templating, biosensing, biomedical imaging and drug delivery [17]. Despite the advantages of nanosized MOFs, difficulties in establishing a general methodology for producing nanoparticle MOFs have limited their universal applications.

To prepare a large-scale uniform NMOFs crystals for practical applications, several synthetic schemes have been developed for the preparation of MOFs nanoparticles, including the microwave-assisted solvothermal method [18], microemulsion method [19–21], ultrasonic wave method [22], and direct mixing method [23]. Ni et al. [18] produced IRMOF-1, IRMOF-2, and IRMOF-3 through a rapid microwave-assisted methodology. The crystal size can be varied from micrometer down to submicrometer scale by manipulating the concentration of the reactant solution. Using water-in-oil microemulsion-based methodology, Lin et al. prepared $Ln(BDC)_{1.5}(H_2O)_2$ NMOFs (Ln = Eu^{3+}, Gd^{3+}, or Tb^{3+} and BDC = 1,4-benzenedicarboxylate) by stirring $LnCl_3$ and bis(methylammonium) BDC in the cationic cetyltrimethylammonium bromide (CTAB)/isooctane/1-hexanol/water microemulsion system. Fairly uniform sized of nanorods were isolated in high yields [19]. Subsequently, they prepared NMOFs of the composition $[Gd_2(bhc)(H_2O)_6]$ by heating a mixture of $[NMeH_3]_6[bhc]$ and $GdCl_3$ in a microemulsion composed of CTAB, 1-hexanol, n-heptane and water at 120 °C [21]. Li et al. synthesized $Cu_3(BTC)_2$ (BTC = benzene-1,3,5-tricarboxylate) nanocrystals by using ultrasonic method for the first time. The reaction of cupric acetate and H_3BTC in a mixed solution of DMF/EtOH/H_2O under ultrasonic irradiation for short reaction times gave $Cu_3(BTC)_2$ in high yields. These nanocrystals have dimensions of a size range of 10–200 nm, which are much smaller than those synthesized using conventional solvothermal method [22]. Huang et al. reported a "direct mixing" synthesis strategy that allows for fast synthesis of bulk quantity of thermally stable and highly porous MOCP nanocrystals (30–150 nm diameter) at room temperature [23]. Although these methods work well in their respective system, it is desirable to present a simple but straightforward methodology for the creation of nanosized MOF crystallites.

In our previous works, we have successfully synthesized single or bimetallic Ln-MOFs nanocrystals using carboxylate salts as capping reagent. Encouraged by the preliminary work, in order to expand the scope of application of coordination modulation

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method and further understand the mechanism of modulator, herein, this method is extendable and applicable to the synthesis of HKUST-1 nanocrystals. Through studying the type and amount of modulator as well as tracking the crystal growth process, the essential functions of modulators for miniaturizing the size of MOF crystals to the nanometer scale were disclosed, which is favor to extend this method to the synthesis of other types of NMOF crystals. Moreover, those structure and property of fascinating crystals morphologies, including bulk crystals, hierarchical octahedral-shape crystals and nanocrystals were investigated by various characterization techniques and their formation mechanism was also discussed.

2. Experimental

2.1. Synthesis of HKUST-1 compounds

Materials andchemicals: copper(II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), sodium acetate (CH_3COONa), sodium formate (HCOONa) were purchased from Sinopharm Chemical Reagent Co., Ltd. 1,3,5-Benzenetricarboxylic acid (H_3BTC, 98%) were purchased from Fluka. Triethylamine was obtained from Aldrich. All chemicals were used without further purification.

2.1.1. Synthesis of HKUST-1 crystals without any addition

A solution of $Cu(NO_3)_2 \cdot 3H_2O$ (1.5 mmol) and BTC (1.0 mmol) was prepared by dissolving them in a water/ethanol solution (12 mL/12 mL). This mixture was defined as the standard solution. Subsequently, the mixed solution was transferred to a 40 mL Teflon-lined autoclave to allow crystal growth at 120 °C for 24 h. After crystallization, the particles were isolated by centrifugation and washed several times with deionized water and ethanol. The resulting solid was dried overnight at ambient temperature before further analysis.

2.1.2. Synthesis of HKUST-1 crystals using sodium formate and sodium acetate

To the standard solution, 0.5–6 mmol sodium formate or 0.5–3 mmol sodium acetate was added in the reaction solution respectively. Subsequently, the mixed solution was transferred to a 40 mL Teflon-lined autoclave to allow crystal growth at 120 °C for 24 h. The washing and drying procedures were the same as before.

2.1.3. Synthesis of HKUST-1 crystals using triethylamine

To the standard solution, 0.5–3 mmol triethylamine was added in the reaction solution. Subsequently, the mixed solution was transferred to a 40 mL Teflon-lined autoclave to allow crystal growth at 120 °C for 24 h. The washing and drying procedures were the same as before.

2.2. Characterization

The crystal size and morphology of samples were characterized using field-emission scanning electron microscopy (Hitachi S4800) at an accelerating voltage of 10 kV. The X-ray power diffraction (PXRD) patterns were collected on a Siemens D5005 diffractometer with Cu Kα radiation (λ = 1.5406 Å) and with a scan speed of 4 s/step and a step size of 0.02°. Thermal gravimetric analysis (TGA) was performed on a Perkin-Elmer TGA thermogravimetric analyzer in the temperature range of 50–1000 °C under nitrogen atmosphere, at a heating rate of 10 °C/min. Infrared spectrum (IR) was collected on a NEXUS FT-IR using KBr technique. Nitrogen physisorption measurements were carried out using a micromeritics ASAP 2020 instrument.

3. Results and discussion

3.1. The structure of HKUST-1

The ($Cu_3(BTC)_2$) MOF ($Cu_3(C_9H_3O_6)_2(H_2O)_3 \cdot xH_2O$, HKUST-1) [24], the polymer framework of HKUST-1 is composed of dimeric cupric tetracarboxylate units (Fig. S1a), with a short Cu–Cu internuclear separation of 2.628(2) Å. This polymer forms face-centered-cubic crystals that contain an intersecting three-dimensional (3D) system of large square-shaped pores (9 Å by 9 Å) (Fig. S1b). We chose to use the HKUST-1 as our target MOF material in this study due to its structural features and thermal stability as well as its potential application prospects.

3.2. Formation of HKUST-1

3.2.1. Influence of sodium formate on HKUST-1

Carboxylate salts such as sodium formate and sodium acetate are effective capping agents in reducing the size of MOFs crystals from micrometer to nanometer. The effect of sodium formate was studied by altering the concentration of sodium formate (given below as equivalents with respect to BTC) in the synthesis solution. The structure of as-prepared samples was studied by X-ray powder diffraction (XRD). As shown in Fig. 1, samples with up to 3 equiv of sodium formate show diffraction patterns identical to those of the simulated one, indicating that the structure of HKUST-1 is well preserved. With addition of 4 equiv of sodium formate, although main peaks are identical to the simulated pattern, a new diffraction peak located at a Bragg angle 2θ of 10.4° appears in the diffractogram implying the sample is not a pure phase. Finally, all peaks of HKUST-1 with addition of 6 equiv of sodium formate disappear and some new peaks appear, implying the information of other phase. The XRD study indicates that the structure of HKUST-1 is not affected by the moderate amount of sodium formate; however, it could be altered by a large amount of sodium formate. Scanning electron micrographic (SEM) images (Fig. 2) show that, bulk crystals with an average size of 20 μm were obtained in the absence of sodium formate. With addition of half equiv of sodium formate, the size of some crystals decreased slightly, pointing out a small amount of sodium formate can affect the crystal size. With addition of 1 equiv of sodium formate, the size of bulk crystals decreased significantly from original 20 μm to 300 nm. Remarkably, spherical monodisperse submicrometer crystals with sizes in the range of 80–250 nm (particle size distribution in Supporting Information

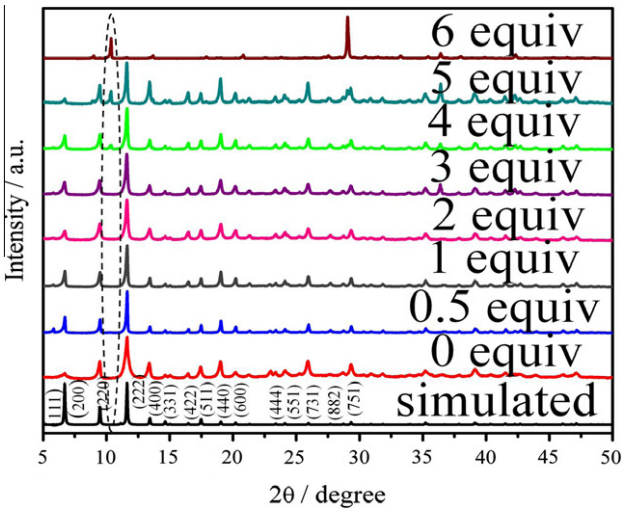

Fig. 1. XRD patterns of HKUST-1 synthesized with different amounts of sodium formate (given as equivalents with respect to BTC).