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ARTICLE TYPE

Growth of large single MOF crystals and effective separation of organic dyes

Lina Li,^a Fuxing Sun,^a Jiangtao Jia,^a Tsolmon Borjigin,^a and Guangshan Zhu^{*ab}

Through the optimization of synthesis conditions, we obtained large $\text{Cu}_3(\text{BTC})_2$ crystals with the diameter of 2~4 mm. Such large crystals could be utilized as “chromatographic columns” for effective separation of organic dyes such as thionine (TH) and Pyronin B (PB). It was found that the concentration of hydron was the key factor to get the large pure crystals. This strategy could be used to grow other hydrophilic MOFs.

1. Introduction

Metal–organic frameworks (MOFs) representing an interface between organic and inorganic compounds¹ were discovered at the end of 20th century which started a new era and brought new thoughts and ideas to the field of the whole chemistry.² The combination of organic ligands as linkers with metal–oxo clusters³ as nodes to metal–organic frameworks is currently a field of high activity.⁴ MOFs, established as a new class of porous crystalline materials, provide almost the highest porosities⁵ and surface areas on a weight-specific basis so far. Thanks to its low volume fraction, MOFs are widely regarded as promising materials for applications, such as gas adsorption⁶, storage⁷, separation⁸ chemical sensing devices⁹, and catalysis.^{7, 10}

In the hot research field of crystal separation and chromatograph¹¹, a host of applications utilized MOF's physical absorption as the main principle¹², and more importantly its regular and unique pore channels can be taken advantages as stationary phase. Especially, when the size of MOF crystals were promoted to millimeter level, the advantages of large single MOF crystals would appear, such as the direct separation application and exploration of separation mechanism on the visible level. It is revealed that large single MOF crystals in millimeter range can be used in chromatograph and in microscopic response. Researches about large single MOF crystals are of significant value in the mechanism exploration of molecule diffusion in MOFs.^{13, 14} However, it is difficult to grow large single MOF crystals in millimeter level, and generally the crystals obtained are in the micrometer (μm) level. Until now, only MOF-5 large single crystals under millimeter level have been reported, whose average sizes was around $2\times 2\times 1$ (mm).¹⁵ There are still no reports about the growth mechanism of large single MOF crystals. Hence, how to obtain large single MOF crystals has become an important issue to be solved. $\text{Cu}_3(\text{BTC})_2$, as another classic MOF material, is well-known because of its excellent porosity. Moreover, $\text{Cu}_3(\text{BTC})_2$ is more stable than MOF-5, which is of more benefit for research and practical applications. It possesses a three-dimensional system of channels with a pore size of 1 nm

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Figure 1. The digital photographs of $\text{Cu}_3(\text{BTC})_2$ single crystals obtained with the volume ratios of DMF/nitric acid of (a) 4:1, (b) 1:1, (c) 1:2 and (d) 1:4, respectively. All black scale bars = 5 mm. (insert: magnified photographs by optical microscope)

accessible porosity of about 40% in the solid.¹⁶ Another pore feature of $\text{Cu}_3(\text{BTC})_2$ is its exposed metal sites in quantity which make it possess different characters over other MOFs such as its preferential adsorption of quadrupole molecules¹⁷. The exposed metal sites also lead to adsorptive separation for some small molecules.^{18, 19} Besides its high Lewis acidity makes it more suitable for catalytic purposes.²⁰ For example, the membrane of $\text{Cu}_3(\text{BTC})_2$ shows a great potential for hydrogen purification and separation.²¹ Herein, we report the large $\text{Cu}_3(\text{BTC})_2$ crystals with the diameter of 2~4 mm obtained through the optimization of synthesis conditions (Figure 1). The large single $\text{Cu}_3(\text{BTC})_2$ crystals can be used to effectively separate mixtures of organic dyes by acting force instead of dye molecule sizes. Taking the advantages of organic dyes as markers, large single $\text{Cu}_3(\text{BTC})_2$ crystals shows potential application value in the area of amine separation. Moreover, a crystal growth mechanism is proposed to explain the formation of large $\text{Cu}_3(\text{BTC})_2$ crystal.

2. Experimental

2.1 Preparation of large $\text{Cu}_3(\text{BTC})_2$ crystals

In a typical process, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.752 g) was dissolved in DMF (15 ml) in a 50 ml beaker (beaker A). The benzene tricarboxylate (0.422 g) was dissolved in DMF (10 ml) in another beaker (beaker B). After 20 minutes' stirring at 25 °C respectively, mixed 3 ml copper nitrate solution from beaker A with 2 ml BTC solution from beaker B in a 50 ml beaker. Then added 2 mol/L nitric acid (20 ml) into the 25 ml beaker and mixed it with slight shake. Covered the beaker with plastic wrap tightly and made sure of its leakproofness. Transferred it to a freezing environment for about 1 day before transferred to a drying oven of 85 °C, where kept it for the next 7 days.

Before the dye separation, $\text{Cu}_3(\text{BTC})_2$ crystals were soaked in dichloromethane and then get rid of solvent molecules in 403 K vacuum conditions. Then 0.01 mol TH and 0.01 mol PB were added into a 250 ml bottle and 200 ml ethanol was added to dissolve two dyes. Then put several $\text{Cu}_3(\text{BTC})_2$ crystals in the solution and kept the bottle standing with the cover tight. Then the separation result could be observed with Laser Confocal Scanning Fluorescence Microscopy.

2.2 Characterization

Powder X-ray diffractions (XRD) were carried out with $\text{Cu-K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) at 40 kV on Scintag X1 diffractometer, 35 mA. The FCFM photographs were from Laser Confocal Scanning Fluorescence Microscopy FV1000. All digital photographs were taken by Sony w630 and Canon D500, while the magnified photographs were taken by operating camera LED 1000 from Leica Microsystems.

3. Results and discussion

3.1 Preparation of $\text{Cu}_3(\text{BTC})_2$

$\text{Cu}_3(\text{BTC})_2$ was firstly synthesized in a solution of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and trimesic acid under solvothermal conditions.¹⁶ The technique consists of hydrothermal formation of $\text{Cu}_3(\text{BTC})_2$ at 383 K from a premixed ethanolic aqueous solution (1 : 1 vol) that contained trimesic acid and $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ over 18 hours. Other works showed the reaction temperature could be adjusted from 383 to 425 K to synthesize $\text{Cu}_3(\text{BTC})_2$ crystals.²² It was also reported that the effect of synthesis conditions on the morphology and crystal size of $\text{Cu}_3(\text{BTC})_2$ could be determined through optimizing the synthetic conditions.²³ We prepared the $\text{Cu}_3(\text{BTC})_2$ crystals according to these methods. The crystal sizes of $\text{Cu}_3(\text{BTC})_2$ obtained were usually limited between 100 and 300 μm . On those bases, we investigated impact factors on the crystal size and optimize the synthesis conditions.

To obtain large $\text{Cu}_3(\text{BTC})_2$ crystals, firstly, we chose DMF and water as solvent due to preliminary preparation experience. Different reaction ratios and temperatures had been explored, which showed temperature was an important factor in controlling the crystal size and morphology for entropic reasons.¹⁷ A series of experiments were carried out from 333 K to 443 K, which showed that 358 K is the optimized temperature for crystal growth. Subsequently, different amounts of acid were used in the reaction system. Surprisingly, the size of $\text{Cu}_3(\text{BTC})_2$ crystals began to grow beyond expectation. It is apparent that the size increased with the proportion of acid in the system. The diameter of the largest crystals could reach 4 mm (Figure 1d) when the volume percentage of nitric acid is about 80%. At the same time,

the crystallization time extended from 48 hours to one week.

Figure 2. XRD patterns of: (a) calculated from $\text{Cu}_3(\text{BTC})_2$ structure; (b) one single crystal from the hexagon face (c) powder ground from single crystals.

However, when the proportion of nitric acid in the system is over 85%, only the inorganic salt $\text{Cu}(\text{NO}_3)_2$ could be obtained.

During that process, the pH changed greatly. Before the heating part, the pH in this system was below zero, but after that, it increased to 6.5, which proved the neutralization in the reaction system.

3.2 Analysis of crystal purity

As shown in Figure 2, the XRD pattern of the powder ground from large single crystals (Figure 2c) agrees very well with the calculated one (Figure 2a), which indicates a pure phase of $\text{Cu}_3(\text{BTC})_2$. Figure 2b shows the XRD pattern of one cross-section of a single crystal with the peaks at $2\theta = 5.806^\circ$, 11.627° , 17.479° and 23.377° which can be indexed to (111), (222), (333), and (444) respectively. It demonstrated that the direction of the cross-section is the [111] direction corresponding to the hexagon face of the crystal morphology, which coincided with the measuring conditions. These results show that the large crystal was absolutely pure and single with high quality.

3.3 Effective dye separation

Encouraged by the high quality of the large $\text{Cu}_3(\text{BTC})_2$ single crystals and dyes could be absorbed through immersion^{24, 25}, organic dye separation experiments were conducted. Organic dyes, thionine (TH) and Pyronin B (PB), were chosen for their similar molecule sizes and fluorescence property. Both the sizes of two dyes are 0.8-0.9 nm in length and 0.4-0.5 nm in width, which are appropriate for the 1 nm pore channels of $\text{Cu}_3(\text{BTC})_2$.¹⁶ The main difference between these two dyes is that the end groups of TH are two amino groups while those of PB are diethyl-amino groups instead. In the term of fluorescence property, excitation and emission of the two dyes occur at different wavelengths (excitation/emission: 543 nm/570-615 nm for PB; 633 nm/670-770 nm for TH).¹⁵ Therefore, TH and PB can be identified without mutual interference. PB/TH of fluorescent dyes were chosen to be separated in ethanol solution by the large $\text{Cu}_3(\text{BTC})_2$ crystals. (Figure 3a) The separation results were characterized with the help of fluorescence confocal microscopy (FCFM). Because of the point-by-point excitation and detection,

the transport and distribution process can be observed by microscopy, especially the inner part of single crystals. Due to the

Figure 3. (a) Chemical structures of TH and PB; (b, c) photographs from FCFM revealing optical side-on views of the Cu₃(BTC)₂ crystals separating mixture of TH (red) and PB (yellow) after 3 days (b) and 7 days (c) immersion. The “o” stands for the outside of the crystal while “i” stands for the inner part of it.

Figure 4. Experimental concentration profiles measured by FCFM during separation of TH (a) and PB (b) dyes from the outside (o) to the inside (i) in the Figure 3 in a Cu₃(BTC)₂ crystal after 7 days separation.

fact that the dyes and other separable materials get into the crystals by free diffusion, so the crystals can be reused after soaking. The experimental results indicated that more than 99 % of the dyes had been eliminated after 3 days' soaking. In this way, the use of Cu₃(BTC)₂ as effective separation medium is not only feasible but also economical and environmental.

Figure 3 shows diffusion results of TH and PB in a Cu₃(BTC)₂ crystal after 7 days immersing in their ethanol solution. It is demonstrated that the PB had diffused into the inner part of the crystal, while TH still stays at the outer layer. The concentration profiles of the PB and TH dyes at 7 days' separation are presented in Figure 4, showing the different dyes can be separated from each other. The distance between the two bands of dye molecules in one Cu₃(BTC)₂ crystal was about 160 μm. Normally, small molecules should diffuse faster than bigger ones. In this case, the larger one PB, however, diffused further in the crystals, which is opposite to the separation results of PB and TH in MOF-5 crystals.¹⁵ It can be explained with the unique functions of

exposed metal sites,²⁶ such as particular complexation. With the large single crystals of MOF-5, it has been proved that the diffusion progress in MOFs is related with the acting force.¹⁴

Figure 5. The growth curves of Cu₃(BTC)₂ crystals with the composition ratio (DMF : nitric acid) at 1:4 (a), 1:2 (b), 1:1 (c), 2:1 (d) respectively. With different composition of the reaction system, crystals would reach their specific maximum average size at different time.

Unincorporated dyes were rapidly transported through its channels while the dyes with complexing action would be restrained longer in the cages.²⁷ Unlike MOF-5 there are a large amount of unsaturated copper ion sites in Cu₃(BTC)₂ crystals. It is assumed that the unsaturated copper sites in the framework of Cu₃(BTC)₂ had stronger interaction with TH, in which the electron pairs on amino groups were more exposed than those on diethylamino groups of PB.

3.4 Growth mechanism of MOF crystals

In a series of experiments with different acids, except the ones with coordination effect, single Cu₃(BTC)₂ crystals could be obtained. (see supporting information) During the synthesis, the amount of hydron played a key role to obtain large single crystals, just like the suppresser in the growth of large single zeolite crystals.^{28, 29} The large amount of hydron in the system would inhibit the deprotonation of H₃BTC. According to the formula, $K_a = \frac{[H^+]^3[BTC^{3-}]}{[H_3BTC]}$, with the increase of hydron concentration, the quantity of BTC³⁻ anion would decrease. Therefore, it was hard to provide adequate coordinate anions for Cu₃(BTC)₂ crystal growth while crystallization time was extended from 48 hours to 7 days, shown in Figure 5. Low anion content suppressed the opportunity of generating new nucleus. In this way, Cu₃(BTC)₂ crystals were offered with an appropriate chance to grow to a large size. On the other hand, MOF materials were generally metastable in acid condition because the hydron in solvent would break coordinate bond down (see supporting information). When the concentration of hydron reached a certain level, the hydron would attack the coordinate bond due to its great ability to grab electron. Hence the hydron with higher electronegativity might interfere the coordinate stability of atoms with lower electronegativity (e.g. Cu²⁺) from receiving lone pair electrons³⁰. In addition, the acid condition could make DMF, the main solvents in this system, decomposed gradually into dimethylamine when heated to certain temperature.³¹ And in the system the dimethylamine could gradually neutralize the acid in the reaction system. In this way, the two effects of acid above could be weakened little by little during the crystal growing process, thus a delicate synthetic

environment with both the concentration of BTC^{3-} and the number of new nuclei balanced could probably be created, which might offer an appropriate environment for the crystals to grow.

Conclusions

In conclusion, large single MOF crystals are of great significance to study the separation process and growth mechanism of MOFs. Through the optimization of synthesis conditions, large $\text{Cu}_3(\text{BTC})_2$ crystals with the largest diameter of 4 mm have been obtained. Such large crystals could be utilized as “chromatographic columns” for effective separation application. The large single $\text{Cu}_3(\text{BTC})_2$ crystals can be used to effectively separate mixtures of organic dyes, PB and TH. Due to the complexation of amino-group and unsaturated copper sites, the unique pore features of $\text{Cu}_3(\text{BTC})_2$ exhibited a different separation behavior of the PB and TH dyes to MOF-5. It is also found that the concentration of hydronium is the key factor to get the biggest pure crystals. This strategy could be used to grow other hydrophilic MOFs.

Notes and references

^a State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun, China (130012).

Fax: +86 0431 85168331; Tel: +86 0431 85168887. E-mail: zhugs@jlu.edu.cn

^b Queensland Micro- and Nanotechnology Centre, Griffith University, Queensland, 4111, Australia

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