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Fabrication of nanosheets of a fluorescent metal–organic framework $[Zn(BDC)(H_2O)]_n$ (BDC = 1,4-benzenedicarboxylate): Ultrasonic synthesis and sensing of ethylamine

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ABSTRACT

A supramolecular metal–organic framework (MOF) constructed by two-dimensional (2D) infinite coordination polymers, $[Zn(BDC)(H_2O)]_n$ (**1**, BDC = 1,4-benzenedicarboxylate), was synthesized by the reaction of zinc acetate with H_2BDC in dimethylformamide (DMF) under ultrasonic irradiation at ambient temperature and atmospheric pressure. Yield of **1** varied from 43.4% to 53.2% for the reaction time of 10–90 min. Samples with different morphologies, i.e. nanobelts, nanosheets, and microcrystals, were obtained under ultrasound irradiation for different reaction times. Fluorescence emission of nanosheets of $[Zn(BDC)(H_2O)]_n$ was found to be highly sensitive to ethylamine, and solid state fluorescence intensity decreased with increasing contents of ethylamine in acetonitrile solution due to weak fluorescence quenching effect.

Metal–organic frameworks (MOFs) are a new class of crystalline materials built up by metal ions (or metallic clusters) and various polyfunctional organic ligands through strong bonds. MOFs, especially porous MOFs have attracted considerable interest in recent years, owing to not only their intriguing structural motifs but also their potential applications in gas storage, medicine, catalysis, selective guest adsorption, host-guest chemistry, and magnetic materials [1–4]. Some traditional techniques, such as slow vapour or solution diffusion techniques, hydrothermal and solvothermal methods, are commonly applied to prepare these MOFs [5–7]. However, the reaction and crystallization processes using these traditional methods usually take long time (e.g. several days for hydrothermal and solvothermal methods, or several weeks for diffusion method) and have to be performed at high reaction temperature (usually 373–523 K) and pressure (1–10 MPa) in many cases. Recently, a highly efficient route to MOFs has been developed through a microwave assisted hydrothermal method, but the reaction is still carried out at high reaction temperature and pressure [8,9]. Furthermore, compared with the rapid developments and numerous studies on their applications in selective adsorption, molecular exchange and separation, especially the latest howling successes in hydrogen storage [10–12], application of MOFs in sensor technology remains largely unexplored [13,14].

Ultrasonic synthesis method has been widely used to fabricate nanoparticles with special structures in recent years [15–18]. The chemical effect of ultrasound originates from acoustic cavitations within collapsing bubbles, which generates localized hot spots with an exceedingly high transient temperature (5000 K), pressure (1800 atm), and cooling rate (10^{10} K s^{-1}). Hence it offers a very attractive method for the preparation of nanoparticles with different morphologies. Herein, we present ultrasonic synthesis of nanocrystals of a fluorescent MOF, $[Zn(BDC)(H_2O)]_n$ (**1**, BDC = 1,4-benzenedicarboxylate). $[Zn(BDC)(H_2O)]_n$ is a three-dimensional (3D) supramolecular architecture constructed by infinite two-dimensional (2D) coordination polymers through hydrogen bonding [19]. Nanobelts and nanosheets of **1** were obtained under ultrasonic irradiation at ambient temperature. Sensing of ethylamine was tested using nanosheets of **1** based on fluorescence response of nanosheets of **1** to ethylamine.

Ultrasonic syntheses of $[Zn(BDC)(H_2O)]_n$ for the reaction times of 10, 20, 30, 60, and 90 min were carried out under ultrasonic irradiation at ambient temperature and atmospheric pressure [20]. It is found that ultrasonic method is highly efficient for the preparation of MOF **1**. The reaction of zinc acetate with H_2BDC in DMF under ultrasonic irradiation at ambient temperature and atmospheric pressure for 10 min resulted in **1** in an acceptable yield (43.4%, based on H_2BDC). Yield of **1** increase gradually to 53.2% with increasing the reaction time from 10 to 90 min.

Fig. 1 shows XRD patterns of the resulting products obtained by ultrasonic method for different reaction times. For samples prepared for the reaction time of 10, 30, 60, and 90 min, all of the diffraction peaks can be readily indexed to $[Zn(BDC)(H_2O)]_n$ [19], and no obvious peaks of impurities can be detected in these XRD

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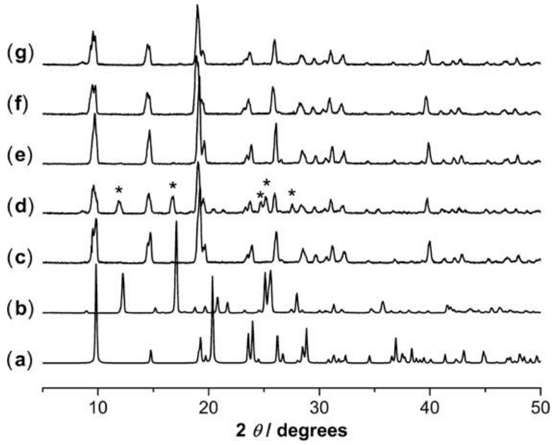

Fig. 1. Powder X-ray diffraction pattern simulated from the crystallographic data of (a) $[Zn(BDC)(H_2O)]_n$, (b) $[Zn(BDC)(H_2O)_2]_n$, and (c)–(g) synthesized by using ultrasonic method for 10, 20, 30, 60, and 90 min, respectively. Diffraction peaks marked with * represent the characterized peaks of $[Zn(BDC)(H_2O)_2]_n$.

patterns. However, for crystals of **1** synthesized at 20 min, some diffraction peaks for impurities were observed (see Fig. 1). These diffraction peaks can be indexed to another zinc 1,4-benzenedicarboxylate coordination polymer, $[Zn(BDC)(H_2O)_2]_n$ [19]. $[Zn(BDC)(H_2O)_2]_n$ is a supramolecular structure constructed by 1D coordination polymeric chains. This result suggests that a crystal-to-crystal transformation from the 2D MOF **1** to 1D coordination polymer $[Zn(BDC)(H_2O)_2]_n$ may take place in this experiod. Furthermore, the XRD patterns of all samples obtained in the present work exhibit weak and broad diffraction peaks, indicating that the samples are composed of small crystals with a crystalline size in nano-scale.

The morphologies and size or nanostructure of the as-prepared samples for different reaction times were characterized by TEM, and the results are shown in Fig. 2. Nanobelts of **1** with a width of 150–300 nm and a length of 2–5 μm were obtained by the reaction of $Zn(OAc)_2$ and H_2BDC in DMF under ultrasound irradiation for 10 min. Nanosheets were formed with an increase in the reaction time to 20 min. These nanosheets have regularly quadrate morphologies with sizes of the range of 500 nm to 2 μm. Further increases of the reaction time led to an increase in dimensions of nanosheets of **1**. When the reaction time increased to 60 min, however, some microcrystals with a size range of several hundreds nanometers up to 10 μm were observed. When the reaction time is increased to 90 min, microcrystals with large dimensions could not be detected, and nanosheets in a wide size range with irregular shapes were observed again. This result suggests that microcrystals of $[Zn(BDC)(H_2O)]_n$ are destroyed under ultrasound irradiation for a long reaction time, and these microcrystals are changed into nanosheets due to weak bonding interactions between 2D coordination polymers.

The sensing of ethylamine in acetonitrile solution using nanosheets of **1** synthesized at 30 min was quantitatively analyzed by a fluorescence spectrometric titration experiment [13]. Samples obtained for 10, 30, 60, and 90 min in the present work exhibited strong blue solid state fluorescence with emission maximum at 446 nm upon excitation at 332 nm, which could be assigned to the fluorescence from intra-ligand emission excited state. Corresponding fluorescence spectra of **1** was recorded upon excitation at 332 nm after injecting various amounts of ethylamine into a 1-cm cuvette containing 2.00 mL of acetonitrile, in which a slice of glass coated with nanosheets of **1** was fixed. Variation of emission intensity with concentration of ethylamine was obtained. As can be seen from Figs. 3 and 4, the emission intensity of $[Zn(BDC)(H_2O)]_n$ nanosheets decreases significantly with the addition of ethylamine to acetonitrile solution when volume of ethylamine is less than 100 μL. With increasing volume of ethylamine from 100 to 350 μL, the emission intensity decreased gradually with a linear trend, and the emission intensity decreased from approximately 6300 to 4200. Further increase of contents of ethylamine just resulted in slight decrease of emission intensity and a fluorescence quenching effect was observed, which is due to partial coordination of the weak ligand ethylamine to the framework $[Zn(BDC)(H_2O)]_n$.

In summary, we have demonstrated that rapid synthesis of MOFs in nanoscale can be realized by using an ultrasonic method. Nanobelts, nanosheets, and microcrystals of a 3D supramolecular MOF constructed by 2D infinite coordination polymers,

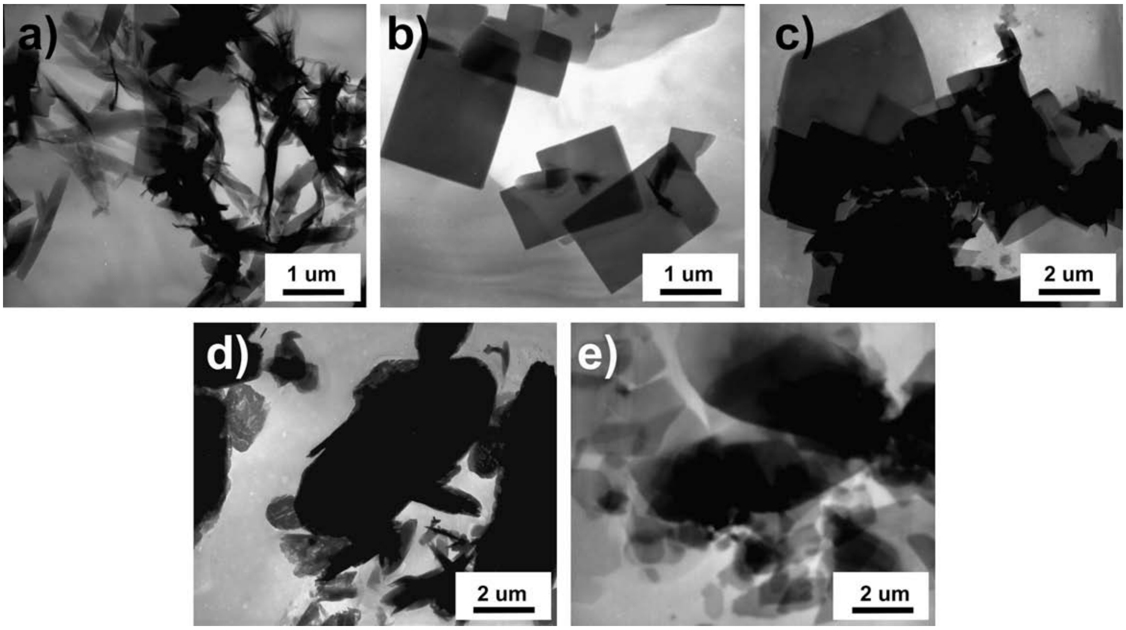

Fig. 2. TEM images of $[Zn(BDC)(H_2O)]_n$ synthesized using ultrasonic method for various reaction times: (a) 10, (b) 20, (c) 30, (d) 60, and (e) 90 min.

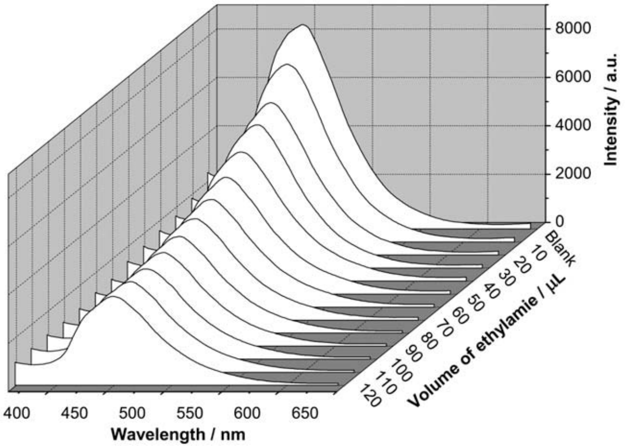

Fig. 3. Variation of emission spectra of $[Zn(BDC)(H_2O)]_n$ nanosheets with volume of ethylamine in 2 mL of acetonitrile. The excitation wavelength is 332 nm.

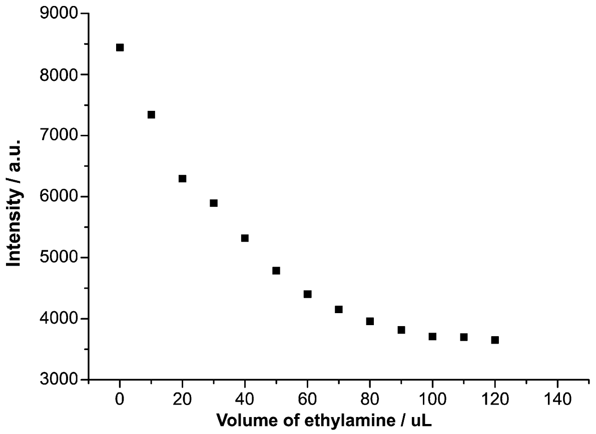

Fig. 4. Plot of intensity at fluorescence emission wavelength of 446 nm of nanosheets of **1** versus volume of ethylamine in 2 mL of acetonitrile. The excitation wavelength is 332 nm.

$[Zn(BDC)(H_2O)]_n$, were prepared for short reaction times (10–90 min) at ambient temperature. The results suggest that ultrasonic synthesis is an excellent candidate for preparing MOFs with high efficiency and low cost. Fluorescence property of $[Zn(BDC)(H_2O)]_n$ nanosheets was found to be highly sensitive to ethylamine. The results presented in this work may be helpful for scientists to develop functionalized MOFs in nanoscale with various physicochemical properties and to design novel fluorescence sensor for the sensing of organic guests.

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[20] *Preparation of* $[Zn(BDC)(H_2O)]_n$ (***1***): nanobelts, nanosheets, and microcrystals of the MOF $[Zn(BDC)(H_2O)]_n$ were synthesized under ultrasonic irradiation at a frequency of 40 KHz for the reaction times of 10, 20, 30, 60, and 90 min, and the ultrasonic output was kept to be 60 W. Typically, H_2BDC (0.324 g, 1.95 mmol) was dissolved in 8 mL of dimethylformamide (DMF), and then mixed with zinc acetate dihydrate (0.439 g, 2.0 mmol) dissolved in 2 mL of DMF in a test tube (20 mL). The test tubes were fixed in the bath of the ultrasonic generator, and the reactions were carried out at ambient temperature. After the ultrasonic irradiation for different reaction times, the products were isolated by centrifugation. The precipitation was washed with water (10 mL × 3) and ethanol (10 mL × 3), respectively, and then dried at room temperature in vacuum (0.095 MPa) for 12 h. Yield of **1** varied from 43.4% to 53.2% based on H_2BDC depending on different reaction times.