Metal–Organic Frameworks

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Metal–Organic Framework Nanospheres with Well-Ordered Mesopores Synthesized in an Ionic Liquid/CO_2/Surfactant System**

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Porous metal–organic frameworks (MOFs) are crystalline materials composed of metal ions or clusters bridged by organic ligands.[1] These materials have shown great potential in gas storage,[2] separation,[3] and catalysis[4] applications owing to their permanent porosity and stability after desolvation. Several different methods have been developed to synthesize range of MOFs. These include solvothermal,[5] sonochemical,[6] microwave,[7] and mechanosynthesis.[8] Within these traditional methods, solvents such as *N*,*N*-dimethylformamide (DMF), *N*,*N*-diethylformamide (DEF), 1-methyl-2-pyrrolidone (NMP), or water/ethanol are widely used for dissolving both the inorganic and organic precursors.[5–7] Most of the porous MOFs reported to date adopt the microporous regime (pore size < 2 nm), despite the negative effect on the diffusion and mass transfer. The construction of meso-MOFs by using elongated ligands[9] or bulky secondary building blocks is of great interest.[10] Increasing the pore size and framework stability remains a major challenge. More recently, great effort has focused on the design of nanoscale MOFs with different morphologies, such as spheres,[11] cubes,[12] rods,[13] and wheels.[14]

In recent years, supercritical CO_2 ($SCCO_2$) and ionic liquids (ILs), considered as unconventional and green solvents, have received much attention in the synthesis of new materials. The advantages of using $SCCO_2$ as solvent are that it is readily available, inexpensive, nontoxic, and nonflammable. More importantly, the physical and chemical properties of $SCCO_2$ can be easily adjusted and thus are tunable by varying operating pressure and temperature.[15] ILs are also an interesting class of tunable solvents with essentially zero vapor pressure, wide electrochemical window, nonflammability, high thermal stability, and wide liquid range.[16] Thus, such unique properties offer $SCCO_2$ and ILs opportunities to replace conventional solvents in a variety of applications in chemistry and material science.[17]

Herein, we report the synthesis of MOF nanospheres in an IL/$SCCO_2$/surfactant emulsion system. Interestingly and significantly, the MOF nanospheres incorporate well-ordered mesopores, and the walls of the mesopores are constructed by a microporous framework. We believe that these MOF spheres will combine advantages of both microporous and mesoporous materials with the presence of both mesopores and microporous pore walls. For example, the mesopores can enhance the mass transfer, while the microporous pore walls have potential applications in gas separation and catalysis. In addition, this work provides an effective method to prepare MOFs with novel structures by combination of surfactants and suitable solvents.

In a typical experiment, suitable amounts of $Zn(NO_3)_2{\cdot}6H_2O$, 1,4-benzenedicarboxylic acid (H_2BDC), IL 1,1,3,3-tetramethylguanidinium acetate (TMGA), and surfactant *N*-ethyl perfluorooctylsulfonamide (N-EtFOSA) were added into a high-pressure cell, which was controlled at 80 °C. Then, CO_2 was charged into the cell to 16.8 MPa under stirring. The reaction was allowed to proceed for 48 h, and then the precipitates were collected and washed with ethanol several times. Representative low-magnification SEM and TEM images are shown in Figure 1 a,b. Uniform nanospheres with diameter of about 80 nm were formed. From the TEM image at high magnification shown in Figure 1 c, the pore channels along different directions can be observed. Figure 1 d–f clearly shows the formation of highly ordered hexagonal pores in the MOF. The pore size and wall thickness were about 3.0 and 2.5 nm, respectively. The sample was further characterized by dynamic light scattering (DLS) experiments, which show that the particle size is mainly in

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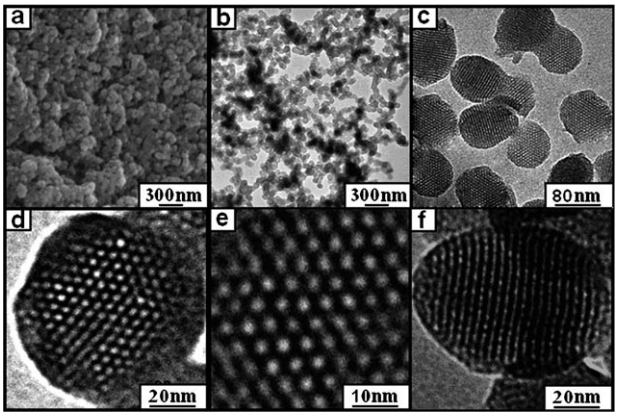

Figure 1. a) SEM and b–f) TEM images of the MOF.

the range 70–110 nm (Figure S1 in the Supporting Information), which coincides well with that obtained from the SEM and TEM images.

The long-range ordered mesopores in the MOF were further characterized by the small-angle X-ray scattering (SAXS) technique. The inset of Figure 2 presents a two-dimensional SAXS image, from which the scattering ring is observed. This result indicates that ordered structure exists in the MOF. By using the two-dimensional data reduction program FIT2D, the one-dimensional SAXS pattern of intensity I versus wave vector q was obtained (Figure 2). The scattering peak at $q = 1.61\ \mathrm{nm}^{-1}$ corresponds to the scattering ring shown in the two-dimensional SAXS image. The d spacing for the sample calculated by $\lambda = 2d\sin\theta$ was 3.9 nm, and the distance between two adjacent pore centers was 4.5 nm ($2/\sqrt{3}d(100)$).[18] The wide-angle powder X-ray diffraction pattern of the MOF was investigated (Figure S2 in the Supporting Information). The crystal structure cannot be identified, mainly because of the small size of the nanoparticles.

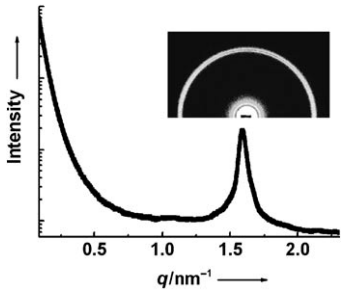

Figure 2. Small-angle X-ray scattering pattern of the MOF. The inset shows the X-ray scattering ring.

The properties of the MOF were further characterized by other techniques. The MOF is stable up to 365 °C, as determined by thermogravimetric analysis (Figure S3 in the Supporting Information). The FTIR spectra of the H_2BDC and MOF are shown in Figure S4. H_2BDC shows two absorption bands of protonated BDC at about 1682 cm^{-1} and 1285 cm^{-1}. In sharp contrast, the MOF shows the strong characteristic absorption for the symmetric and asymmetric vibration of BDC at about 1614 cm^{-1} and 1380 cm^{-1}. The wavenumber difference of the two bands for the MOF is narrowed, indicating that both carboxylate groups of BDC are coordinated to Zn^{II} ions.[9a] Energy-dispersive X-ray (EDX) spectroscopy indicates the presence of zinc, oxygen, and carbon in the MOF prepared (Figure S5).

The porosity of the MOFs was studied by the N_2 adsorption–desorption method after the sample was dried[19] and degassed at 180 °C overnight. The structure of the MOF was not changed after drying and degassing, which was confirmed by XRD analysis (Figure S6). Figure 3a shows the N_2 adsorption–desorption isotherm of the MOF, which exhibits a typical type IV isotherm and shows pore condensation with pronounced adsorption–desorption hysteresis. This result indicates the existence of mesopores in the MOF. The BET (Brunauer, Emmett, and Teller) surface area and total specific pore volume are 756 m^2g^{-1} and 0.53 cm^3g^{-1}, respectively. The mesopore size distribution curve, calculated from Barrett–Joyner–Halenda analysis, shows a pore size distribution centered at around 3.6 nm (Figure 3b).

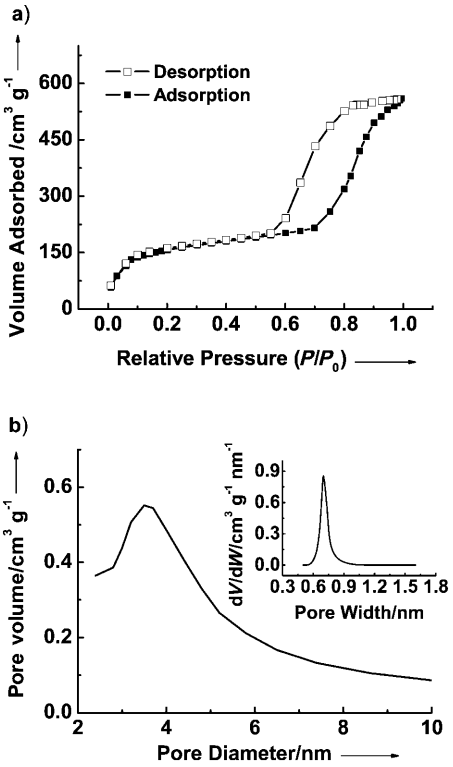

Figure 3. N_2 adsorption–desorption isotherm (a) and mesopore size distribution curve (b) of the MOF. The inset in (b) shows the micropore size distribution curve of the MOF.

Furthermore, the MOF has a high N_2 adsorption capacity when the relative pressure (P/P_0) is as low as 0.01, indicating that the MOF synthesized has micropores. By using the Horvath–Kawazoe method, the micropore size was obtained as 0.7 nm (inset in Figure 3b). The micropore surface area is 482 m^2g^{-1} ($S_{meso}/S_{micro} = 0.57$). The analysis above confirms the formation of hierarchically meso–micro porous MOF, in which the walls of the mesopores are constructed from a microporous framework.

Surfactants have been widely used as templates to prepare mesoporous molecular sieves because they can form cylindrical assemblies.[20] Our previous work showed that TMGA/EtFOSA/CO_2 microemulsions can be formed[21] because the interaction between CO_2 and fluorocarbon tails of the surfactant is strong.[21,22] In this work, we also prepared MOFs at CO_2 pressure of 20.1 MPa, keeping other conditions the same with those described above. MOF nanoparticles with well-ordered mesopores were also obtained (Figure S7). However, MOFs prepared in pure IL without CO_2 and surfactant have no mesoporous structure (Figure S8).

On the basis of the above results and discussion, we propose a possible mechanism for the formation of the novel MOF structure (Figure 4). The surfactant molecules self-assemble into cylindrical micelles with the fluorocarbon chain

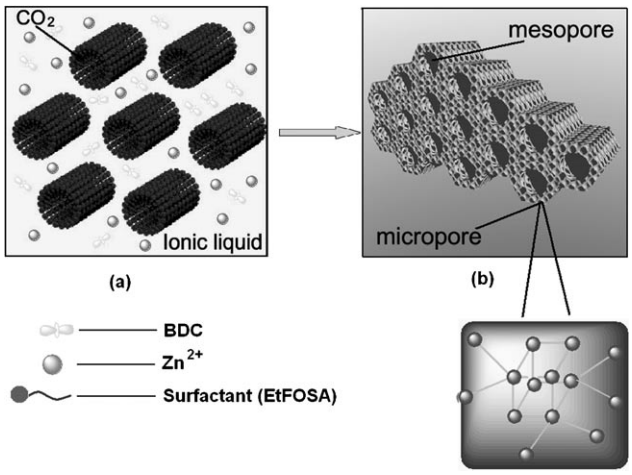

Figure 4. Formation of the MOF in the surfactant/IL/CO_2 system. a) Formation of N-EtFOSA cylindrical micelles; b) MOF with ordered mesopores and microporous structured walls.

directed towards the inside of the micelles, and CO_2 exists as a core of the micelles. The IL, $Zn(NO_3)_2$, and H_2BDC form a continuous phase (Figure 4a). The Zn^{II} metal ions and BDC in the IL form a crystalline microporous framework because of the facile linkage property of Zn^{2+} and BDC, which leaves cavities in the micelles. Therefore, MOFs with well-ordered mesopores and microporous structured walls were formed after removal of the IL, CO_2, and surfactant (Figure 4b).

In summary, MOF nanospheres with long-range ordered mesopores were synthesized in N-EtFOSA/IL/$SCCO_2$ system. This kind of MOF nanostructure has promising applications in gas separation, protein encapsulation, and catalysis with obvious advantages such as enhanced mass transfer. We believe that more MOFs with similar structures can be prepared by this method using other metal ions and ligands.

Experimental Section

Synthesis: $Zn(NO_3)_2{\cdot}6H_2O$ (0.065 g, 0.2 mmol), H_2BDC (0.025 g, 0.15 mmol), N-EtFOSA (0.3 g), and TMGA (0.2 g) were added into a 5 mL high-pressure cell equipped with a magnetic stirrer. The temperature of the cell was controlled at 80 °C. Then, CO_2 was charged into the cell until suitable pressure was reached. After reaction for 48 h, CO_2 was released. The precipitate was collected and washed with ethanol several times.

Characterization: The morphology of the sample obtained was characterized by a HITACHI S-4800 scanning electron microscope equipped with EDX, and JeoL-1010 transmission electron microscope operated at 100 kV. The porosity of the obtained MOF was determined from nitrogen adsorption–desorption isotherms using a Micromeritics ASAP 2020M system. The mesopore size of the MOF was calculated from the adsorption branch by using the BJH model. Small-angle X-ray scattering experiments were carried out at Beamline 4B9A at the Beijing Synchrotron Radiation Facility (BSRF). The data were collected using a CCD detector (MAR) with maximum resolution of 2048 × 2048 pixels. The wavelength used was 1.53 Å, and the distance of sample to detector was 1.660 m.

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