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Formation of Nanocrystals of a Zinc Pillared-layer Porous Coordination Polymer Using Microwave-assisted Coordination Modulation

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Nanocrystals of three-dimensional pillared-layer type porous coordination polymers, $[Zn_2(ndc)_2(dabco)]_n$, were fabricated by microwave-assisted coordination modulation, and its morphology was controlled by changing the modulator concentration. Adsorption measurement supported that the crystallinity and intrinsic porosity were maintained even for nanosized crystals, comparable to the corresponding micrometer-sized bulk powder crystals.

Porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) assembled from organic ligands and inorganic joints have been widely investigated due to their potential application in gas storage, adsorptive separation, catalysis, and molecular sensing.[1–6] Such properties have been traditionally improved by designing functional organic ligands or inorganic clusters and/or by controlling the overall framework topology. Besides these molecular level functionalizations, methodologies to miniaturize the crystal size of PCPs to mesoscale and nanoscale regimes have been recently developed.[7–9] Thanks to the enhancement of crystal surface contribution or the shortened total diffusion path of resulting nanosized PCP crystals, the crystal downsizing can be recognized as a novel strategy to tune the porous properties.[7–9] In addition, the fabrication of PCP nanocrystals gives a further opportunity for applications in electronics and biomedicine.[10–13]

The key to control crystal sizes of PCPs is to regulate the nucleation kinetics in the crystallization process; rapid nucleation gives small crystals and slow kinetics gives large crystals.[14] The simplest method to produce PCP nanocrystals is to use microwave heating, which induces a rapid nucleation, however, simultaneously results in the production of poor crystalline materials, which significantly decrease the porosity.[15,16] On the other hand, the other approach known as microemulsion requires undesired surfactants that might change the porosity of PCPs.[17,18]

As an alternative method, we recently proposed a novel fabrication protocol, so-called coordination modulation, by changing the coordination equilibrium at the crystal interfaces during the crystallization process, through competitive interactions originating from an additive (modulator) with the same chemical functionality as linker ligands.[19] This rather coordination chemistry approach allows us to control both crystallization kinetics and thermodynamics by simply altering the concentration of modulators, which affords the control of crystal size and morphology in nano and meso scales, and to synthesize highly crystalline materials.[20,21] However, the application of this method is, to date, limited to a framework system that intrinsically has a rather fast nucleation process.[22–25] This is because the coordination modulation tends to decelerate the nucleation kinetics and helps to grow crystals larger. Therefore, the framework system with slow nucleation kinetics, which grows as a large single crystal, is not suitable.

Here we show that the microwave-assisted coordination modulation controls the crystal size and morphology of the zinc framework that intrinsically grows as submillimeter-sized crystals, $[Zn_2(ndc)_2(dabco)]_n$ (**1**: Figures 1a and 1b),[26] wherein the dicarboxylate ndc ligands link the dizinc clusters to form two-dimensional square lattices which are further connected via
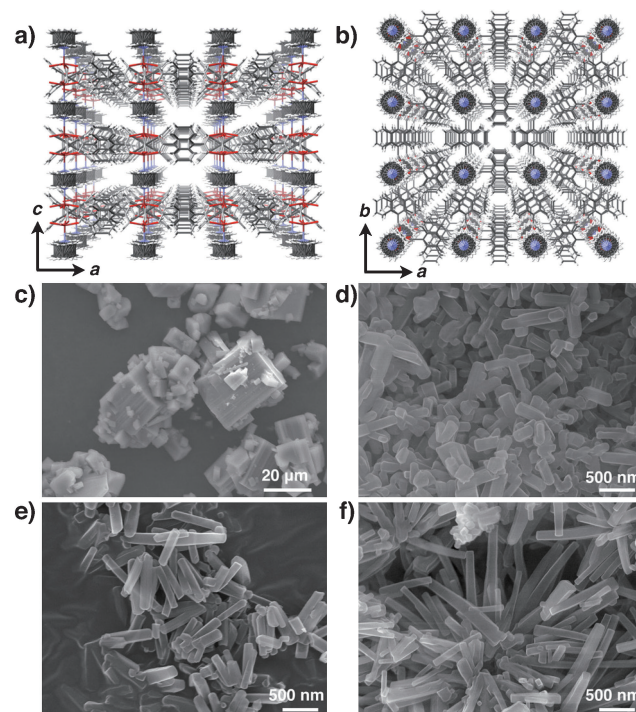

Figure 1. Crystal structure of $[Zn_2(ndc)_2(dabco)]_n$ and its appearance as nanocrystals. a), b) The crystal structure of $[Zn_2(ndc)_2(dabco)]_n$ view a) along the *b* axis and b) along the *c* axis. The naphthalene moieties and dabco molecules are disordered owing to the symmetry. c)–f) FE-SEM images of c) the bulk powder crystals obtained from conventional solvothermal method and the d)–f) nanocrystals obtained from microwave-assisted coordination modulation using d) 0.3 M lauric acid, e) 0.6 M lauric acid, and f) 0.9 M lauric acid.
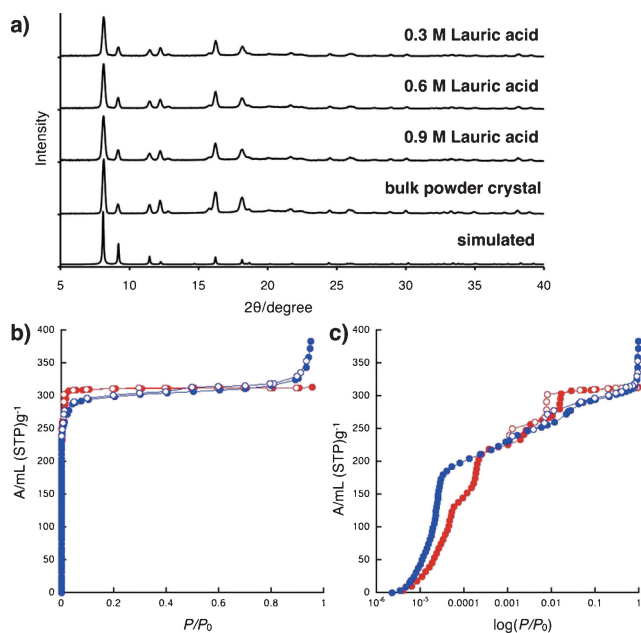
Figure 2. a) PXRD patterns of as-synthesized bulk and nanocrystals of **1**. The simulated patterns are obtained from the single-crystal structure. b) Nitrogen adsorption (solid circle) and desorption (open circle) isotherms of at 77 K of bulk (red) and the smallest nanocrystals obtained with the condition of 0.3 M lauric acid (blue) of **1**. c) Sorption isotherms plotted on a logarithmic scale. STP is standard temperature and pressure.

dabco molecules, (ndc: 1,4-naphthalenedicarboxylate; dabco: 1,4-diazabicyclo[2.2.2]octane).

Nanocrystals of **1** were successfully synthesized when using lauric acid as the modulator; a solution of 1,4-naphthalenedi-carboxylic acid (H$_2$ndc, 0.06 M) and dabco (0.03 M) in dimethylformamide (DMF) was added to a mixture of zinc acetate (0.06 M) and lauric acid (0.3 M) in DMF at room temperature, and the mixture was immediately heated by microwave irradiation at 373 K for 15 min. The field emission scanning electron microscopy (FE-SEM) image of the obtained materials showed the formation of nanosized rod-shape crystals (Figure 1d), which were much smaller than the powder crystals obtained from the conventional solvothermal method (Figure 1c). The lengths of the major and minor axes of nanocrystals are estimated as ca. 350 and 150 nm, respectively. The formation of **1** was confirmed by powder X-ray diffraction (PXRD) measurements (Figure 2a) and thermogravimetric (TG) analysis (Figure S1).[33] The sharpness of diffraction peaks from the nanocrystals corresponded to those from the micrometer-sized bulk powder crystals of **1**. The TG analysis of nanocrystals demonstrated the similar weight loss up to 170 °C, correspond-ing to that of bulk crystals. These results indicate that the nanocrystals of **1** maintain high crystallinity even after minia-turization into nanoscale.

It should be noted that both the microwave irradiation and the choice of lauric acid as the modulator were essential for the production of nanosized crystals of **1**. The conventional heating procedure using an oil bath with modulators did not give nanosized crystals but resulted in the formation of micrometer-sized crystals. This is because the nucleation process was not

accelerated enough to give the nanocrystals. Microwave heating was, therefore, essential to give rapid nucleation of the crystals, and the coordination modulation was important to decelerate the nucleation kinetics. Indeed, the simple microwave irradiation without modulators gave no precipitation. This suggests that the nucleation is too fast to further implement the crystal growth process; all starting materials were consumed to produce a number of very small nuclei. When lauric acid was replaced by acetic acid, the resulting crystals grew much bigger and were obtained as micrometer-sized crystals. This result is most likely attributed to the appropriate acidity of lauric acid and its longer alkyl chain that contribute to the stabilization of the nuclei formed at the early stage of crystallization.

In order to elucidate the effect of the modulator on the morphology of the obtained crystals, the modulator concen-tration was increased (0.6 or 0.9 M) while fixing the concen-trations of other components (while fixing the global concen-tration). As shown in Figures 1e and 1f, the aspect ratio (major axis/minor axis) of nanocrystals became larger with the increase of the modulator concentration, and the rod-shape morphology was more pronounced. This is because this framework system is tetragonal where the four {100} crystal surfaces out of six are terminated by carboxylate ndc linkers and the remaining two {001} surfaces are capped by dabco molecules. Similar tendency was also observed for the formation of nanorods of [Cu$_2$(ndc)$_2$-(dabco)]$_n$.[19] Thus, the major axis in nanocrystals of **1** most likely corresponds to the ⟨001⟩ direction of the framework (the Zn–dabco coordination mode). The higher concentration of modu-lator led to the formation of the nanorods with high aspect ratio because the modulator effectively inhibited the crystal growth in the ⟨100⟩ direction (the Zn–ndc coordination mode). Such morphological control would be useful for the application to the well-defined arrangement of the crystals on the substrate.[27]

The nitrogen sorption isotherm of the smallest nanocrystals obtained with the condition of 0.3 M lauric acid demonstrated a typical Type I profile, which is characteristic sorption behavior of microporous materials[28] (Figure 2b). The observed adsorption capacity was almost the same as that of micrometer-sized bulk crystal of **1**, which suggested that the crystal downsizing of **1** was successfully demonstrated with the maintenance of the intrinsic porous properties. A sudden increase of adsorption at the high relative pressure region (near $P/P_0 = 1$) observed for the nanocrystals can be related to physisorbed liquid nitrogen on the crystal surfaces of the nanocrystals.[20] Such a phenomenon is not observed for the bulk crystals that present a much lower crystal surface area. Meanwhile, although the total adsorption capacity of the nanocrystals at a very low relative pressure region ($P/P_0 = 0.001$) is almost the same as that of the bulk crystals, as shown in Figure 2c we observed a tiny but significant difference of adsorption property between the bulk crystals and the nanocrystals at $P/P_0 < 0.0001$; the nanocrystals started to adsorb nitrogen at the lower pressure. Such a behavior was also observed in another framework system; however, it still remains difficult to fully address this issue.[18] One of the plausible reasons is attributed to the change of the surface structure caused by the possible presence of lauric acid as the modulator on the crystal surface.

In conclusion, we exhibited the synthesis of the nanocrystals of [Zn$_2$(ndc)$_2$(dabco)]$_n$ (**1**), using the combination of microwave irradiation and the coordination modulation method. It was also

revealed that the morphology of the nanorods could be tuned by changing the modulator concentrations. We believe that this study opens a way to construct not only an isoreticular series of nanocrystals of $[Zn_2(dicarboxylate)_2(amine)]_n$[29–32] but also other frameworks that have a slow nucleation process.

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