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## ARTICLE

# Formation of Hollow and Mesoporous Structure in Single-Crystalline Microcrystals of Metal-Organic Frameworks via a Double-Solvent Mediated Overgrowth

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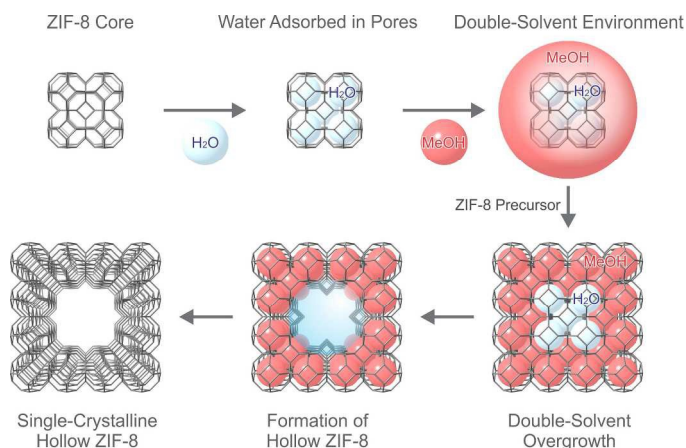
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The formation of hierarchical porosity in metal-organic frameworks (MOFs) could benefit various applications of MOFs such as gas storage and separation. Having single-crystalline microcrystals instead of poly-crystalline composites is critical for these potential applications of MOFs with hierarchical porosity. We developed a room temperature synthetic method to generate uniform hollow and mesoporous zeolitic imidazolate framework-8 (ZIF-8) microcrystals with a single-crystalline structure via overgrowing ZIF-8 shell in methanol solution on ZIF-8 core with water adsorbed in the pores. The cavities formed as a result of the different solvent micro-environment. This double solvent mediated overgrowth method could be applied to form other MOFs with hierarchical porosity.

Metal-organic frameworks (MOFs)<sup>1,2</sup> are crystalline microporous materials with great potential in gas storage,<sup>3-5</sup> catalysis,<sup>6-8</sup> and biomedicine.<sup>9-11</sup> Creating MOF crystals with hierarchical porosity, such as hollow cavities or mesopores, has gained attention recently due to the addition of storage capacity and the promotion of diffusion.<sup>12-19</sup> The use of surfactant ligands to create mesopores and macropores in MOF crystals has been reported.<sup>20</sup> The advantage of this method lies in the simplicity of the one-step synthesis and the high degree of crystallinity; however, the selection of surfactant ligands could be quite MOF-specific. Overgrowth of MOFs on sacrificial templates and then subsequently removal of the templates is a more straightforward and non-specific method to generate hierarchical porosity in MOF crystals.<sup>21-23</sup> The template selection and removal conditions need to be carefully designed to avoid the formation of large amount of defects or poly-crystalline MOF crystals, which is critical to the applications that require molecular selectivity.<sup>24</sup> Regardless, these works demonstrate the advantages of hierarchical porosity; therefore, it is desired to develop more general methods to create hierarchical porosity in single-crystalline MOF microcrystals.

Solvent effects observed generally in coordination chemistry suggest that the solvent could have a strong directing effect on the pathways of formation or decomposition of MOFs. Varying the solvent could alter the formation energy of MOFs, stabilize intermediates and transition states, and even provide new pathways from its direct participation in elementary reactions. The solvent has been observed to affect many properties of MOFs, such as their stability, crystal sizes and shapes, as well as the rates of crystal growth and post-synthetic

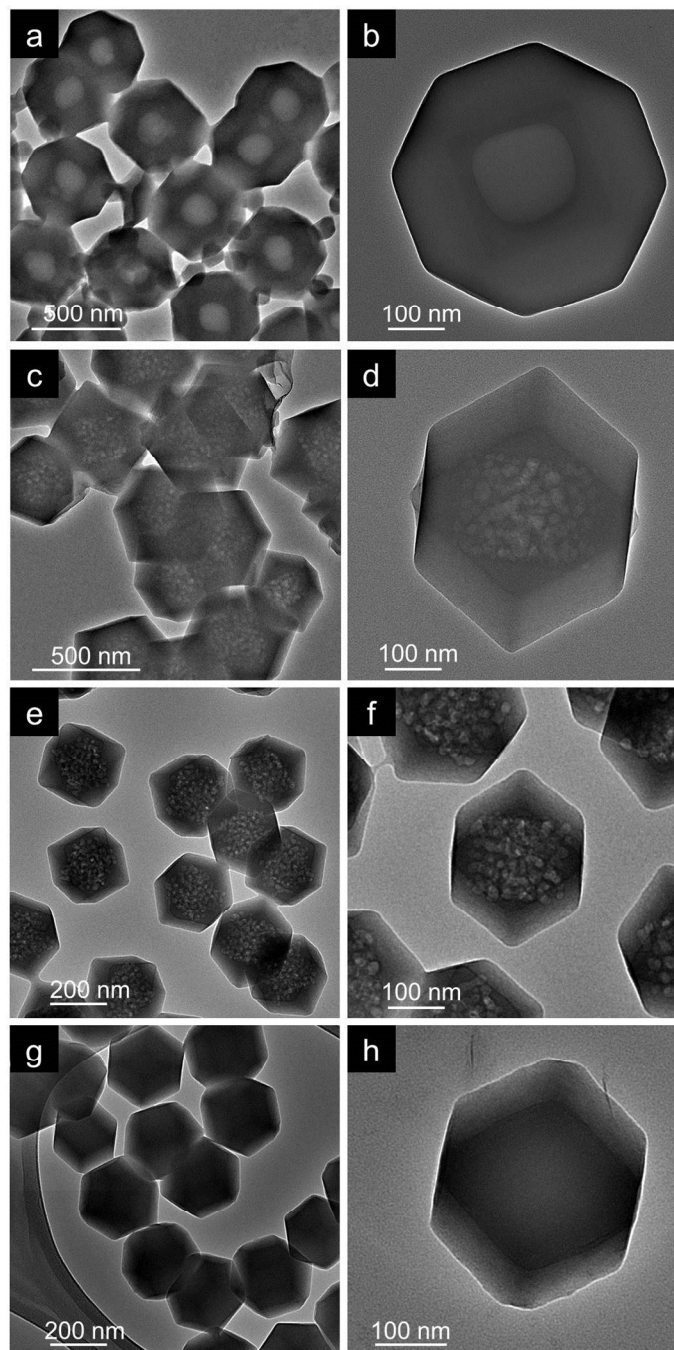
ligand and ion exchange.<sup>25-29</sup> We believe that the solvent effect could be utilized as a part of the synthetic toolbox.



**Scheme 1.** Double-solvent mediated overgrowth of ZIF-8.

Toward this design principle, we developed a double-solvent mediated overgrowth strategy. In this method, uniform MOF microcrystals with the first solvent trapped in the pores are used as cores to seed the overgrowth of MOF shell in the second solvent (Scheme 1). The solvent molecules trapped in the MOF crystal cores do not rapidly exchange with the solvent molecules in the overgrowth solution during the overgrowth process due to the slow diffusion rate in the microporous materials,<sup>30,31</sup> so it creates a local double solvent environment

of internal core solvent and external overgrowth solvent. We found that, with the appropriate combination of solvents, the core MOF could serve as a sacrificial template to form uniform MOF microcrystals with hollow or mesoporous structures (**Figure 1**). Because the template core and overgrowth shell are exactly the same MOF and the core is single-crystalline, it promotes the formation of single-crystalline overgrowth MOF.<sup>21</sup>



**Figure 1.** TEM images of (a-b) hollow ZIF-8, (c-f) mesoporous ZIF-8, and (g-h) solid ZIF-8.

Our first indication that solvent effects could be useful for generating MOF crystals with hierarchical porosity came

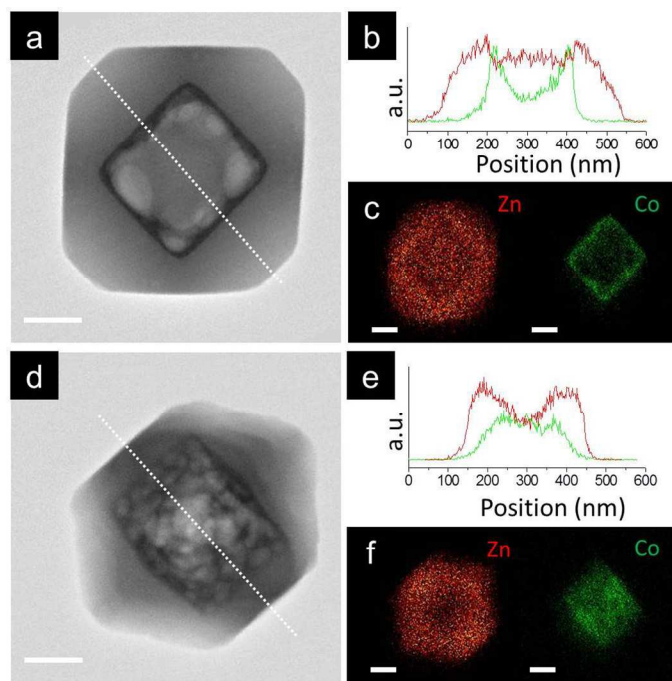
during attempts to carry out overgrowth on ZIF-8 microcrystals under a water-methanol double-solvent condition. ZIF-8 forms in both water and methanol but the formation conditions are very different. Stable ZIF-8 microcrystals form in water only with large excesses of linker molecules as compared to the methanol condition.<sup>32,33</sup> For the aqueous synthesis and overgrowth condition, we use a growth solution with the precursors 2-methylimidazole (2-mim) and  $Zn(NO_3)_2$  in a ratio of 55:1 (2-mim/Zn), whereas for the methanol condition the ratio is 1:1. Cetyltrimethylammonium bromide (CTAB) is used in the aqueous condition in order to control the size and shape of ZIF-8.<sup>34</sup> The crystal shape of ZIF-8 synthesized or overgrown is cubic in water and truncated rhombic dodecahedral or rhombic dodecahedral in methanol. This CTAB-induced shape difference has been reported before and provides a great tool to track the overgrowth in different solvents.<sup>35</sup>

We synthesized uniform cubic size-tunable ZIF-8 microcrystal cores (**Figure S1a**) under aqueous condition and then collected the solid products via centrifugation without removal of the water molecules adsorbed in the ZIF-8 pores. These ZIF-8 microcrystal cores (200 nm) with water molecules trapped in the pores were then transferred to the methanol solution of  $Zn(NO_3)_2$  and 2-mim to carry out the overgrowth. After one hour, instead of the anticipated larger solid ZIF-8 microcrystals, we observed larger microcrystals (450 nm) with hollow central cavities (**Figures 1a,b**). The imprint left by the cubic ZIF-8 cores could be clearly seen. The sharp truncated rhombic dodecahedral shape was observed in all the samples, indicating that the hollow ZIF-8 microcrystals are single-crystalline. Powder X-ray diffraction (PXRD) patterns demonstrate that ZIF-8 is the only crystalline phase (**Figure S2**) and  $N_2$  adsorption-desorption isotherms collected at 77 K are type I, indicating the microporosity of the hollow ZIF-8 (**Figure S3**). The BET surface area of the hollow ZIF-8 was calculated to be  $1276 \text{ m}^2/\text{g}$ .

To verify whether the hollow structure was generated due to the water-methanol double-solvent environment, three control experiments were carried out. First, we carried out the overgrowth under aqueous condition instead of methanol on the same ZIF-8 cores with water trapped in the pores. In this case, both internal and external solvent environments were water. Solid larger ZIF-8 crystals with cubic shape formed under this water-water overgrowth condition and no hollow structure was observed under TEM (**Figure S4a-b**). Second, we removed water from the ZIF-8 cores (150 nm) by heating at  $150 \text{ }^\circ\text{C}$  under vacuum and then filled the pores with methanol before the overgrowth under methanol condition. This methanol-methanol overgrowth also led to solid rhombic dodecahedral ZIF-8 crystals (**Figures 1g-h**). Finally, we carried out the overgrowth under aqueous conditions on the ZIF-8 cores with methanol trapped in the pores. Again, solid larger ZIF-8 crystals formed under this methanol-water condition (**Figure S4c-d**). These three control experiments clearly indicate that only the double-solvent conditions of internal water and external methanol environment lead to the formation of the hollow structure. Notably, CTAB surfactant could also contribute to the creation of cavities;<sup>36</sup> however, these control experiments confirm that the cavities do not come from the surfactant micelles. We propose that, during the formation of shell ZIF-8 under the water-methanol double-solvent overgrowth, the pH of the internal water environment drops due to the deprotonation of the 2-mim in the external methanol environment,<sup>8</sup> and ZIF-8 is not stable at this condition in water

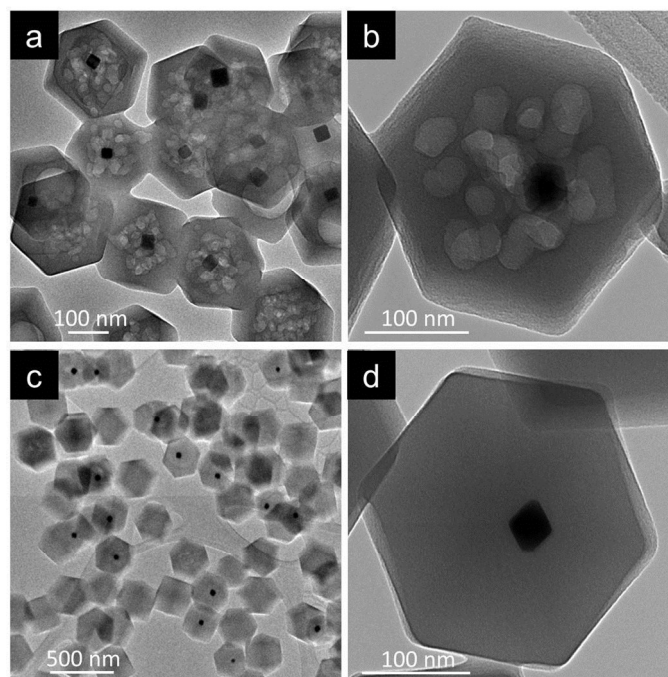
so it dissociates and forms a hollow cavity.<sup>11</sup> It is worth mentioning that the water-water or methanol-water condition generates the solid product because of the large excesses of linker molecules during the aqueous overgrowth. Without the excesses of the linkers, the ZIF-8 cores are etched away in water. In contrast, when excesses of linkers (2-mim/Zn = 55) was used under water-methanol condition, although we observed the formation of free ZIF-8 nanocrystals rather than overgrowth, it is clear that no hollow structure formed (**Figure S5**). These results support that the excess of linkers is needed to stabilize ZIF-8 cores during the overgrowth with the presence of water. The detailed mechanism is under investigation.

To monitor the cavity formation, we used ZIF-67 microcrystals as the cores to carry out the same overgrowth and used energy-dispersive X-ray (EDX) spectroscopy associated with TEM to trace the metal ions. ZIF-8 and ZIF-67 can be synthesized under similar aqueous and methanol conditions. They are of the same crystal topology but have different metal ion nodes. ZIF-8 contains Zn ions as the metal nodes, and ZIF-67 contains Co ions.<sup>37,38</sup> Uniform ZIF-67 microcrystals were synthesized under aqueous conditions (**Figure S1b**), and then the same overgrowth of ZIF-8 was carried out under methanol condition. Under this water-methanol double-solvent condition, similar hollow microcrystals were obtained after one hour overgrowth (**Figure 2a**). EDX mapping and line-scan showed that the hollow microcrystals were mainly composed by Zn ions (ZIF-8). ZIF-67 cores were dissociated and the Co ions were located at the inner surface of the central cavity (**Figure 2b-c**). We also observed higher contrast at the interface of the hollow central cavity under TEM. This could indicate that dissociated species of ZIF-67 were trapped and deposited on the inner surface of the hollow core when the sample was dried. The observation suggested that the linker molecules decomposed from ZIF-67 were also trapped in the hollow cavities. A control experiment of overgrowth of ZIF-8 on ZIF-67 cores under water-water condition was performed. As expected, a solid ZIF-67@ZIF-8 core-shell microcrystal structure was obtained. (**Figure S6**).



**Figure 2.** STEM/EDX line scan and elemental mapping of Co-ZIF-8 overgrowth in methanol. (a-c) 1 hour overgrowth, and (d-f) 6 hour overgrowth. Green color represents Co and red color represents Zn. Scale bar is 100 nm in each image.

After one hour reaction in the water-methanol condition, the Co ions and linkers trapped in the hollow central cavities could be removed by thorough washing to yield hollow ZIF-8. If instead we kept the product under the methanol condition for 6 hours, a mesoporous ZIF-67 core formed (**Figure 2d**). Elemental mapping and line-scan showed a Co-rich core, which indicates that ZIF-67 reforms (**Figure 2e-f**). Compared to water, methanol promotes the reforming of ZIF-67 under low linker concentrations,<sup>32</sup> which may help explain why the core reforms after solvent equilibration. We observed the evolution of the products through a time-dependent TEM study (**Figure S7**). Completely hollow ZIF-8 formed after 1 hour overgrowth. ZIF-67 started to reform after 3 hours and a clear mesoporous core-shell structure was observed after 6 hours. Solid cores are never observed in these prolonged reactions, which could be due to some of the trapped linkers and metal ions diffusing out to solution during the overgrowth or serving as nutrients for the growing ZIF-8 shell. The same process occurred on pure ZIF-8. Hollow (**Figure 1a-b**) and mesoporous (**Figure 1c-d**) ZIF-8 were formed. The observation of core metal ions deposition on inner surface of hollow ZIF-8 may also explain the lower surface area (1276 m<sup>2</sup>/g) of hollow ZIF-8 as compared to pure ZIF-8. After the reformation of mesoporous core ZIF-8, the BET surface area of the mesoporous ZIF-8 increased to 1441 m<sup>2</sup>/g (**Figure S3**).



**Figure 3.** TEM images of (a-b) mesoporous Au@ZIF-8, and (c-d) solid Au@ZIF-8.

The detailed mechanism of this double-solvent mediated method is under investigation; however, it is already clear that it is an efficient way to generate ZIF-8 with hierarchical porosity. To demonstrate the versatility of this method, we have

tuned the size of mesoporous ZIF-8 as well as formed structures with metal nanoparticles embedded in mesoporous ZIF-8. Mesoporous ZIF-8 microcrystals with sizes of 250 nm (**Figure 1e-f**) and 450 nm (**Figure 1c-d**) were synthesized by using different cores with sizes of 150 nm and 200 nm, respectively. Microcrystals of ZIF-8 with a single Au nanoparticle embedded per crystal were synthesized by the method previously reported by our group,<sup>34</sup> and then water-methanol or methanol-methanol overgrowth of ZIF-8 was carried out. The formation of mesoporous Au@ZIF-8 (**Figure 3a-b**) or solid Au@ZIF-8 (**Figure 3c-d**) was directed by using either double solvent or single solvent conditions. We believe that by varying the guests (e.g. metal oxide, quantum dot, small molecule), the structures will have great applications in electrochemistry,<sup>39</sup> luminescence,<sup>40</sup> delivery,<sup>41</sup> and catalysis.<sup>42</sup>

In summary, we have developed a double-solvent mediated overgrowth method to form cavities in single-crystalline MOF microcrystals. ZIF-8 cores with water adsorbed in the pores are used as templates to carry out overgrowth of ZIF-8 shells in methanol. Due to the different solvent effects, hollow and mesoporous structures are created. We believe that this solvent-mediated overgrowth method will have great applications in forming other MOFs with hierarchical porosity.

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