

## Supporting Information

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

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## TABLE OF CONTENTS

<b>Experimental Section</b> .....	S-2
<b>Figure S1.</b> SEM images of water synthesized ZIFs.....	S-4
<b>Figure S2.</b> Powder XRD patterns of hollow and mesoporous ZIF-8 .....	S-4
<b>Figure S3.</b> Nitrogen sorption isotherm of hollow and mesoporous ZIF-8 .....	S-5
<b>Figure S4.</b> SEM and TEM images of ZIF-8@ZIF-8 overgrowth in water.....	S-5
<b>Figure S5.</b> TEM images of ZIF-8@ZIF-8 overgrowth in methanol with excess 2-mim .....	S-6
<b>Figure S6.</b> STEM/EDS line scan and elemental mapping of ZIF-67@ZIF-8 overgrowth in water.....	S-6
<b>Figure S7.</b> Time study of hollow MOF overgrowth in methanol.....	S-7

## Experimental section

**General considerations:** Unless otherwise stated, all the reactions were carried out in the air without taking any precaution to protect reactions from oxygen or moisture. Cetyltrimethylammonium bromide (CTAB, Calbiochem, 98%), hydrogen tetrachloroaurate trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , Sigma-Aldrich, ~50% Au basis), Sodium citrate tribasic dehydrate (Sigma-Aldrich, >99%), zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Sigma-Aldrich, 99%), cobalt(II) nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Sigma-Aldrich, 99.999%), 2-methylimidazole (Sigma-Aldrich, 99%). Ultrapure deionized water (d. i.  $\text{H}_2\text{O}$ , 18.2 M $\Omega$ ) was used for aqueous solution preparations.

**Characterization:** Transmission electron microscope (TEM) images were obtained on JEOL JEM2010F operated at 200 kV. Scanning transmission electron microscope (STEM) and Energy-dispersive X-ray spectroscopy (EDS) mapping experiments were performed on a FEI Probe Cs corrected Titan operating at 200 kV. Scanning electron microscope (SEM) images were obtained on a JEOL JSM6340F. The powder x-ray diffraction patterns (PXRD) were collected on a Bruker AXS diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The nitrogen gas adsorption-desorption was carried out on Micromeritics ASAP 2020.

**Synthesis of 200 nm ZIF-8 and ZIF-67 nanocubes:** The synthesis was carried out following the previous procedure in our lab with some modifications.<sup>1</sup> 1.75 mL aqueous solution of 0.55 mM CTAB and 790 mM 2-methylimidazole mixture was stirred at 500 rpm for 5 minutes. Then 0.250 mL 97.5 mM  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  aqueous solution was injected. The whole solution was stirred for another 5 minutes at 500 rpm. The reaction solution was then left undisturbed at room temperature for 3 hours. The formed ZIF-8 nanocubes were spun down at 5000 rpm for 10 minutes. To form the ZIF-67, the same reaction parameters were followed, just with the use of 97.5 mM  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  aqueous solution instead of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . For synthesis of 150 nm ZIF-8 nanocubes, the same reaction parameters were followed, just with the use of 0.83 mM CTAB instead of 0.55 mM CTAB.

**Synthesis of 150 nm ZIF-8 nano-crystals in methanol:** The synthesis was carried out following the previous procedure in our lab with some modifications<sup>2</sup>. 7.15 mL methanol solution of 562 mM of 2-methylimidazole was stirred at 500 rpm. 7.15 mL methanol solution of 70.5 mM  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was injected. The whole solution was stirred for another 12 hours at 500 rpm. The formed ZIF-8 nano-crystals were spun down at 5000 rpm for 10 minutes.

**Synthesis of solid, hollow and mesoporous ZIF-8:** As-synthesized ZIF-8 cubes were collected by centrifugation and re-suspended in 1 mL methanol. 0.20 mL ZIF-8 cubes were mixed with 2.5 mL 30 mM 2-methylimidazole methanol solution. Then 2.5 mL 30 mM  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  methanol solution was injected. The reaction solution was then left undisturbed at room temperature for 1 hour (hollow ZIF-8) or 6 hours (mesoporous ZIF-8). The formed ZIF-8 nanoparticles were spun down at 5000 rpm for 10 minutes. To form solid ZIF-8, the same reaction parameters were followed, just with vacuum oven dried ZIF-8 cubes in preparing seeds solution.

**Synthesis of ZIF-67@ZIF-8:** Following a similar procedure as the synthesis of hollow ZIF-8, as-synthesized ZIF-67 cubes were suspended in 1 mL methanol prior to the overgrowth step. The reaction solution was then left undisturbed at room temperature for 1 hour (hollow ZIF-67@ZIF-8) or 6 hours

(mesoporous ZIF-67@ZIF-8). The formed ZIF-67@ZIF-8 nanoparticles were spun down at 5000 rpm for 10 minutes.

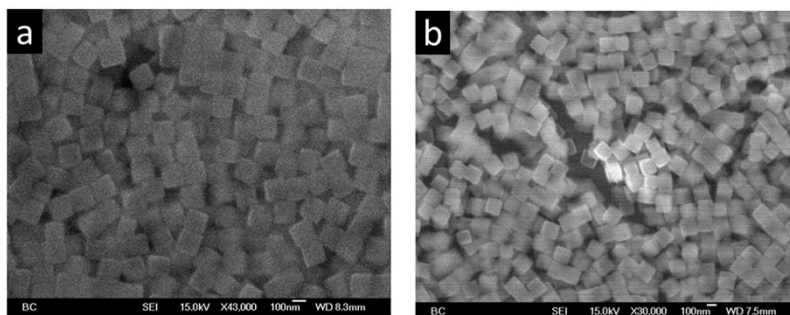
**Synthesis of Au octahedron:** The synthesis was carried out following the previous procedure in our lab with some modifications<sup>1</sup>. 550 mg CTAB was dissolved in 97 mL d. i. H<sub>2</sub>O, following by adding 2.50 mL 0.01 M HAuCl<sub>4</sub> and 0.50 mL 0.1 M trisodium citrate. The mixture solution was transferred into a 200 mL pressure vessel and heated at 110 °C for 24 hours. The formed Au octahedrons were spun down at 6000 rpm for 20 minutes and redispersed in d. i. H<sub>2</sub>O.

**Synthesis of Au@ZIF-8 nanocubes:** The synthesis was carried out following the previous procedure in our lab with some modifications<sup>1</sup>. Following a similar procedure as the synthesis of ZIF-8 nanocubes, ten second after the addition of Zn(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O, 500 μL Au octahedrons solution was injected into the mixture, while the Au octahedrons solution concentrations had already been adjusted to 9.6 μmol metal in 1 mL solution. The whole solution was stirred for another 5 minutes at 500 rpm. The reaction solution was then left undisturbed at room temperature for 3 hours. The formed Au@ZIF-8 nanocubes were spun down at 5000 rpm for 10 minutes.

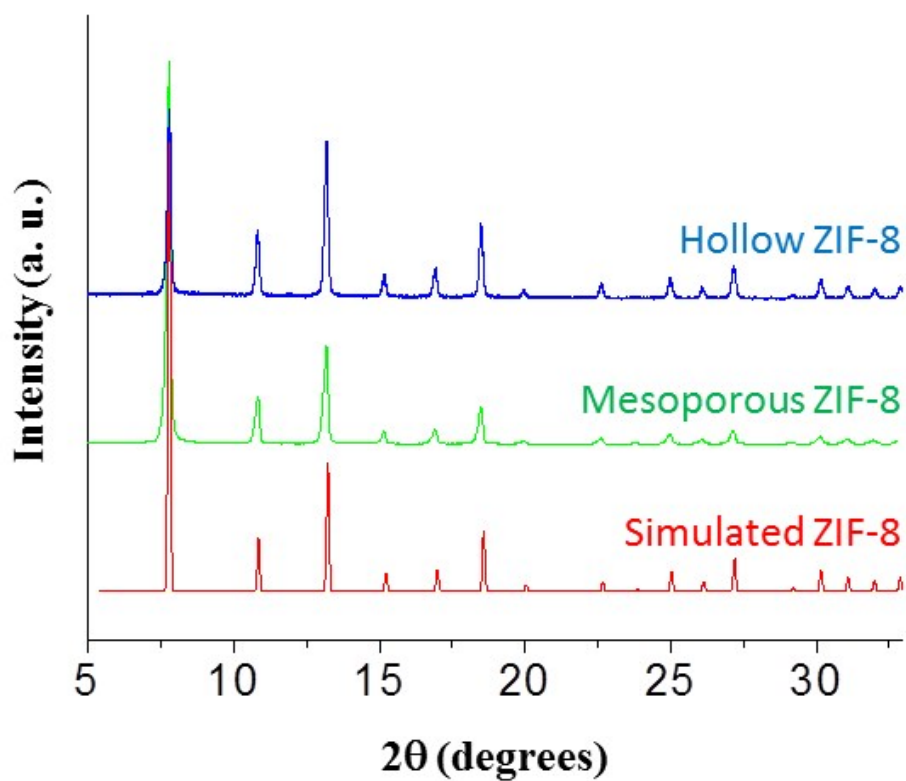
**Synthesis of mesoporous and solid Au@ZIF-8:** Synthesis of mesoporous Au@ZIF-8 following a similar procedure as the synthesis of mesoporous ZIF-8, as-synthesized Au@ZIF-8 cubes were suspended in 1 mL methanol prior to the overgrowth step. The reaction solution was then left undisturbed at room temperature for 6 hours. The formed mesoporous Au@ZIF-8 nanoparticles were spun down at 5000 rpm for 10 minutes. To form solid Au@ZIF-8, the same reaction parameters were followed, just with vacuum oven dried Au@ZIF-8 cubes in preparing seeds solution.

#### References

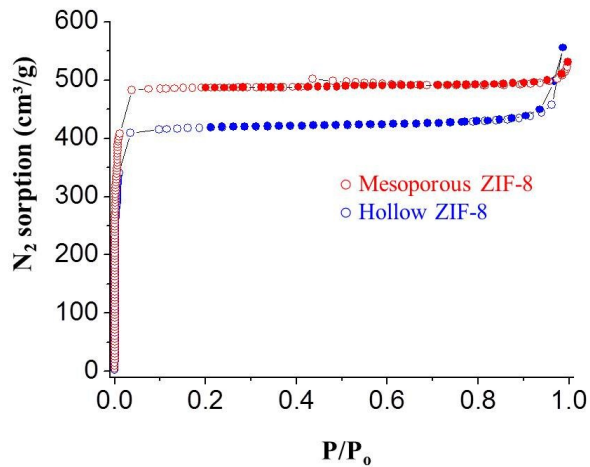
- (1) Hu, P.; Zhuang, J.; Chou, L.-Y.; Lee, H. K.; Ling, X. Y.; Chuang, Y.-C.; Tsung, C.-K. *Journal of the American Chemical Society* **2014**, *136*, 10561.
- (2) Zhuang, J.; Kuo, C.-H.; Chou, L.-Y.; Liu, D.-Y.; Weerapana, E.; Tsung, C.-K. *ACS Nano* **2014**, *8*, 2812.



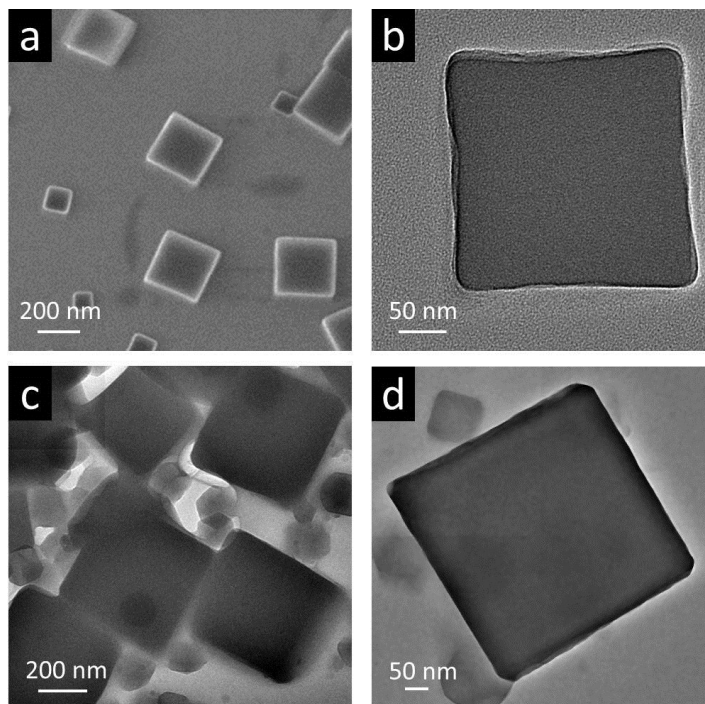
**Figure S1.** SEM images of example water synthesized (a) 150 nm ZIF-8 nanocubes, and (b) 200 nm ZIF-67 nanocubes. Size can be tuned between 100 nm and 500 nm.



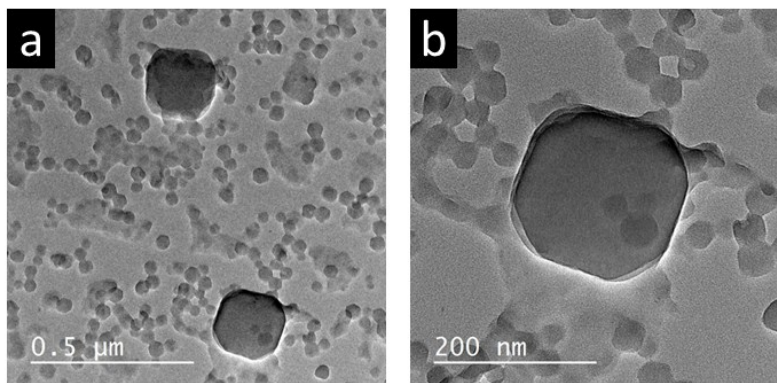
**Figure S2.** Powder X-Ray diffraction patterns of hollow ZIF-8 and mesoporous ZIF-8.



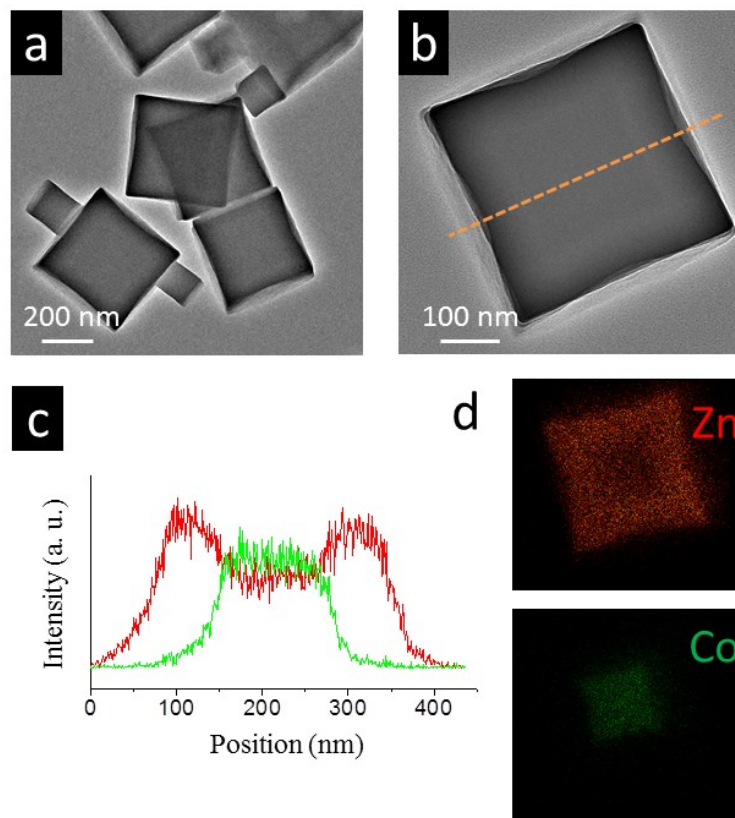
**Figure S3.** Nitrogen adsorption (○) and desorption (●) isotherms of hollow (blue) and mesoporous (red) ZIF-8.



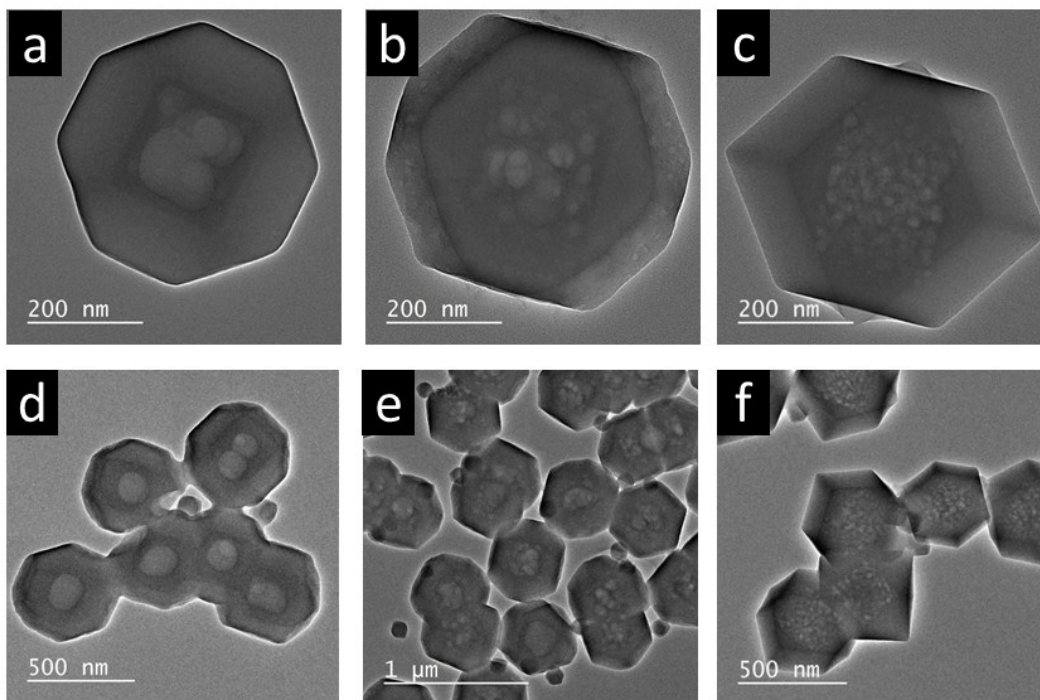
**Figure S4.** SEM images (a) and TEM images (b) of water synthesized ZIF-8 cores overgrown ZIF-8 nanocubes in water. (c-d) TEM images of methanol synthesized ZIF-8 core overgrown ZIF-8 nanocubes in water. As-synthesized ZIF-8 cores can be seen in both cases. Larger ZIF-8 crystals confirmed overgrowth. 150 nm of ZIF-8 nanocubes would be formed under the overgrowth condition if no additional ZIF-8 cores.



**Figure S5.** TEM images of water synthesized ZIF-8 cores overgrown with ZIF-8 nanocubes in methanol with the precursors 2-methylimidazole (2-mim) and  $\text{Zn}(\text{NO}_3)_2$  in a ratio of 55:1 (2-mim/Zn). About 20 nm of ZIF-8 nano-crystals were formed under the overgrowth condition because of the excess of 2-mim.



**Figure S6.** (a-b) TEM images of ZIF-67@ZIF-8 overgrowth in water. STEM/EDS line scan (c) and elemental mapping (d) of ZIF-67@ZIF-8 overgrowth in water. Green color represents Co and red color represents Zn



**Figure S7.** Time study of hollow MOF overgrowth in methanol. TEM images of (a and d) 1 hours overgrowth, (b and e) 3 hours overgrowth and (c and f) 6 hours overgrowth.