Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.


## Electronic Supplementary Material

# Flexible Route to Crisp-like Metal–Organic Frameworks Derivatives by Crystalline Transformation

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**General information.** Powder X-ray diffraction measurements were carried out on a Bruker AXS D8 Advance diffractometer with nickel-filtered Cu Kα radiation (λ = 1.5406 Å). The morphology of each sample was observed using scanning electron microscopy (SEM) on a JEOL JSM-7600 filed-emission SEM with an accelerating voltage of 5 KV and 15 KV. Internal structures of the samples were observed by transmission electron microscope (TEM, JEOL JEM-2010). The Brunauer-Emmett-Teller (BET) surface area, pore volume and pore size were performed at 77 K with a Micromeritics ASAP 2020 adsorption apparatus and at pressure up to 1 bar.

**Preparation of ZIF-8 particles.** Specifically, 15 mL methanol solution of zinc nitrate hexahydrate (111.558 mg, 25 mM), 15 mL methanol solution of 2-methylimidazole (30.7875 mg, 25 mM) were mixed briefly and added in a 40 mL glass vial. After reacting at room temperature and standing for 24 h, the solid product was centrifuged at 8,000 rpm for 5 min and washed with methanol three times. The recovered product was further dried at room temperature overnight.

**Preparation of ZIF-67 particles.** Typically, 25 mL of methanol solution containing $Co(NO_3)_2 \cdot 6H_2O$ (0.87 g) was introduced into 25 mL of methanol solution containing 2-methylimidazole (1.97 g) and the reaction was kept still at room temperature for 24 h. The purple product was collected by centrifugation at 8,000 rpm for 5 min and washed with ethanol for at least 3 times to remove excess ions. For further application, the obtained precipitate was vacuum dried at 70 °C overnight.

**Transformation of ZIF-8 to complex (crisp-like) in deionized water.** Typically, 8 mg of as-synthesized ZIF-8 particles were mixed with 40 mL deionized water. 2 mL solution was added in a 4 mL glass vial, and heated at 120 °C for 5 h. Then, the solution was cooled to room temperature and washed with methanol solution. The white powders were obtained, which were dried at room temperature overnight.

**Transformation of $Zn_2(bim)_4$ to ZIF-8 in double solvent.** The as-prepared $Zn_2(bim)_4$ (20 mg) and 2-methylimidazole(165 mg) were added into a 40 mL capped glass vial containing a 16 mL mixture of deionized water and DMF ($V_{DI\ water}$:$V_{DMF}$ = 1:3). After that, the solution was sonicated for 10 min. The vial was heated to 70 °C for 24 h. Then the product was collected by centrifugation and washed with methanol several times to obtain the product.

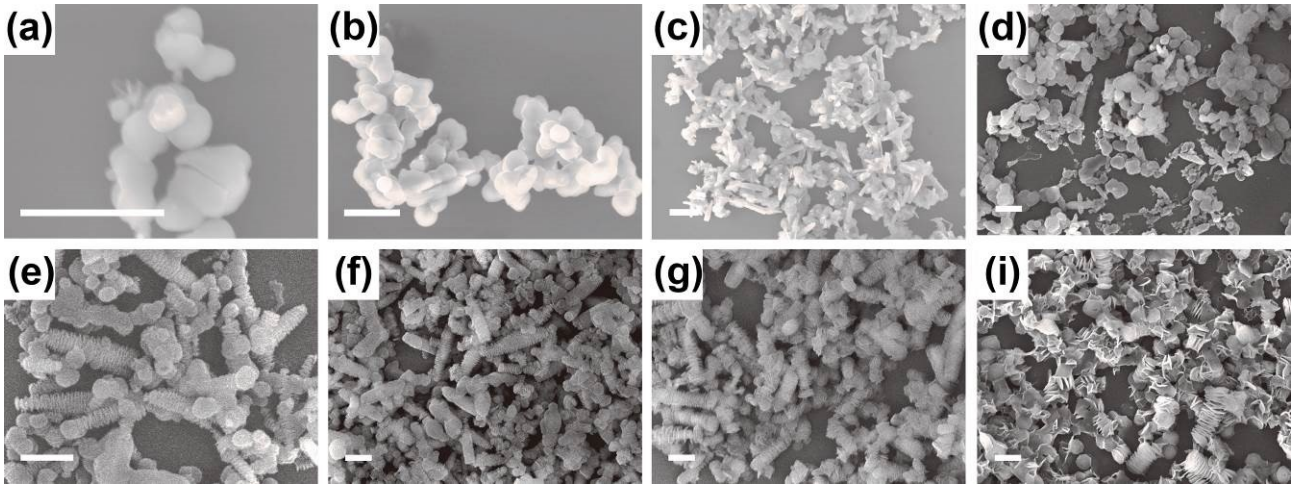



**Figure S1** SEM images of crystalline transformation of ZIF-7 at 120 °C at: (a) 30 min, (b) l h, (c) 2 h, (d) 4 h, (e) 6 h, (f) 11 h, (g) 17 h, (h) 24 h. Scale bars: 1 μm.

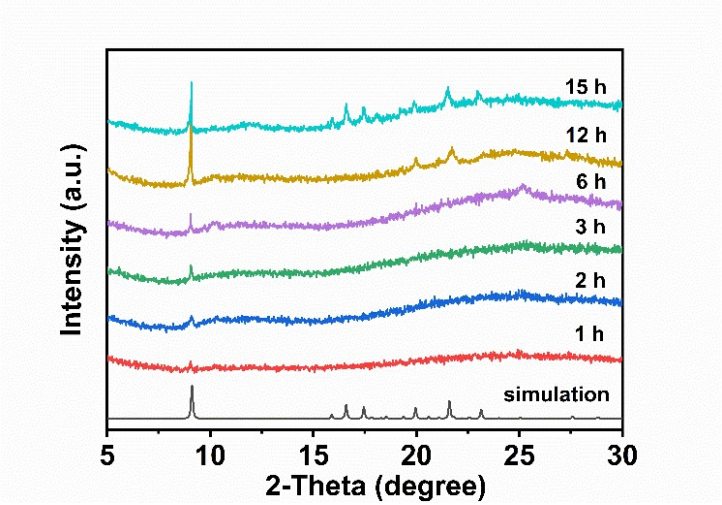
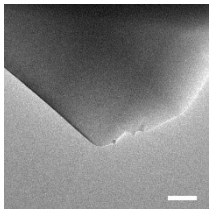
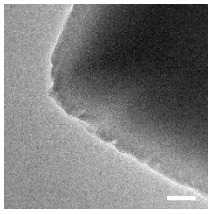
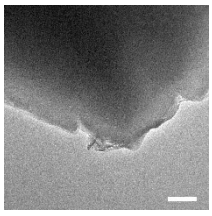



**Figure S2** Time dependent XRD patterns of products during the ZIF-7 transformation process.

**Table S1.** Control experiment of direct growth of zn/bim coordinations.

| Concentrations (mmol/L) of $Zn(NO_3)_2 \cdot 6H_2O$: benzimidazole | 1.25: 2.5 | 0.625: 1.25 | 0.313: 0.625 | 0.156: 0.313 |
|---|---|---|---|---|
| TEM images |  |  |  | |
| Notes | The concentration was adjusted in accordance with the mole ratio in ZIF-7 | | | No products |

* All the control experiments were done in the same conditions. The precursors were dispersed in DI water and heated at 120 °C for 15 h. Scale bars in TEM images: 200 nm.

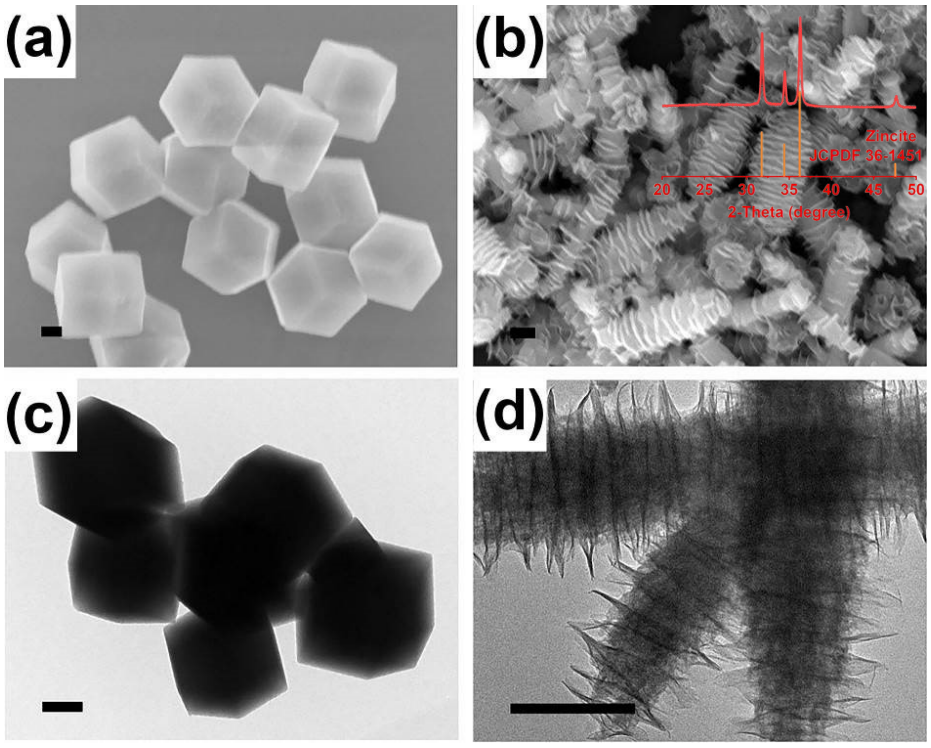



**Figure S3** SEM, TEM images of crystalline transformation of ZIF-8. (a, c) ZIF-8; (b, d) ZIF-8 in water at 120 °C for 5 h.

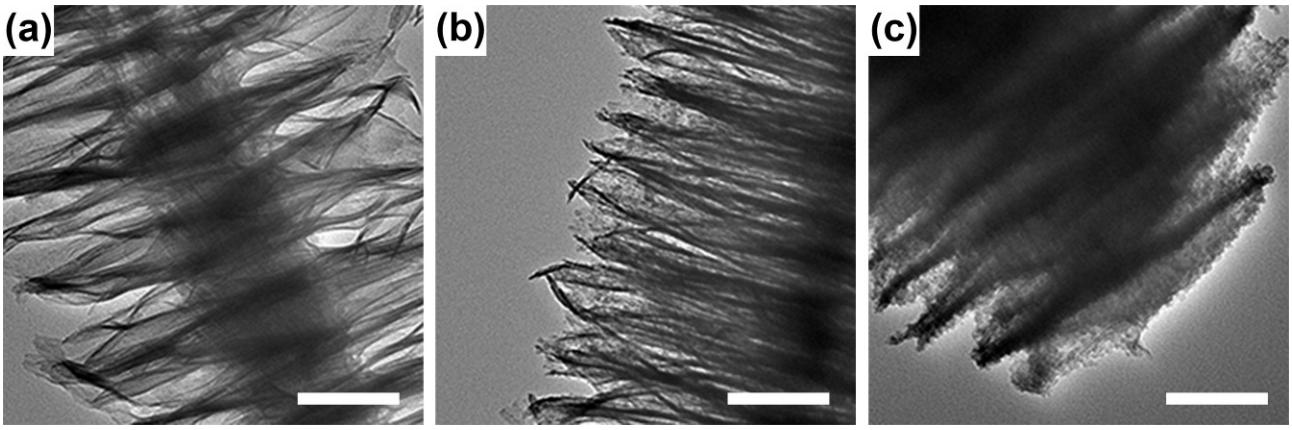



**Figure S4** TEM images of (a) $Zn_2(bim)_4$, (b) $Zn_2(bim)_4$@ZnS, and (c) $Zn_2(bim)_4$@CoS. Scale bars are 100 nm.

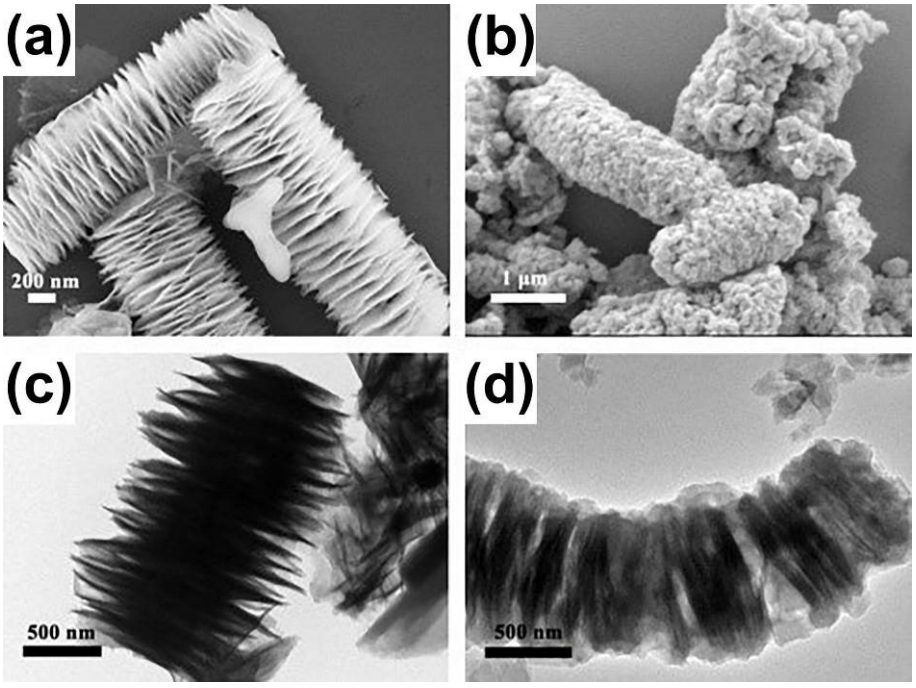



**Figure S5** SEM, TEM images of (a, c) $Zn_2(bim)_4$, and (b, d) $Zn_2(bim)_4$@ZIF-8, respectively.

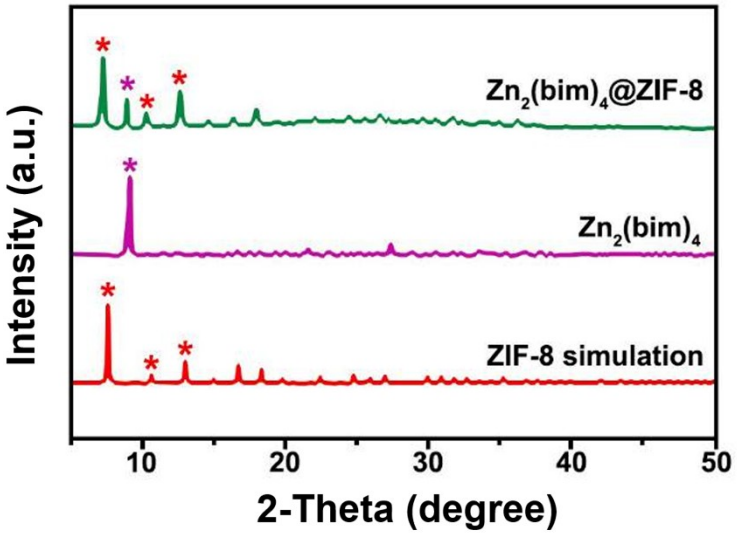



**Figure S6** XRD patterns of $Zn_2(bim)_4$ and $Zn_2(bim)_4$@ZIF-8.

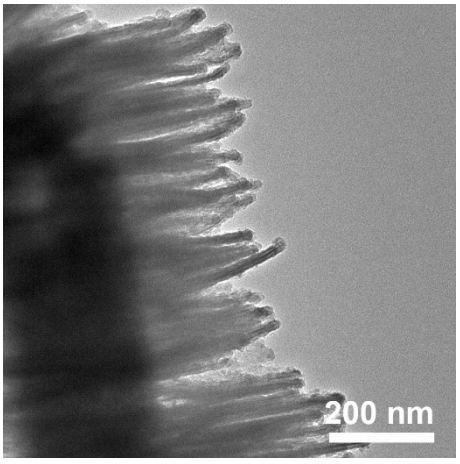



**Figure S7** TEM image of $Zn_2(bim)_4$@CoS after OER reactions for 10 h.