

MOF Membrane Synthesis in the Confined Space of a Vertically Aligned LDH Network

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Supporting Information

SI-1 Fabrication of LDH networks with diverse morphology

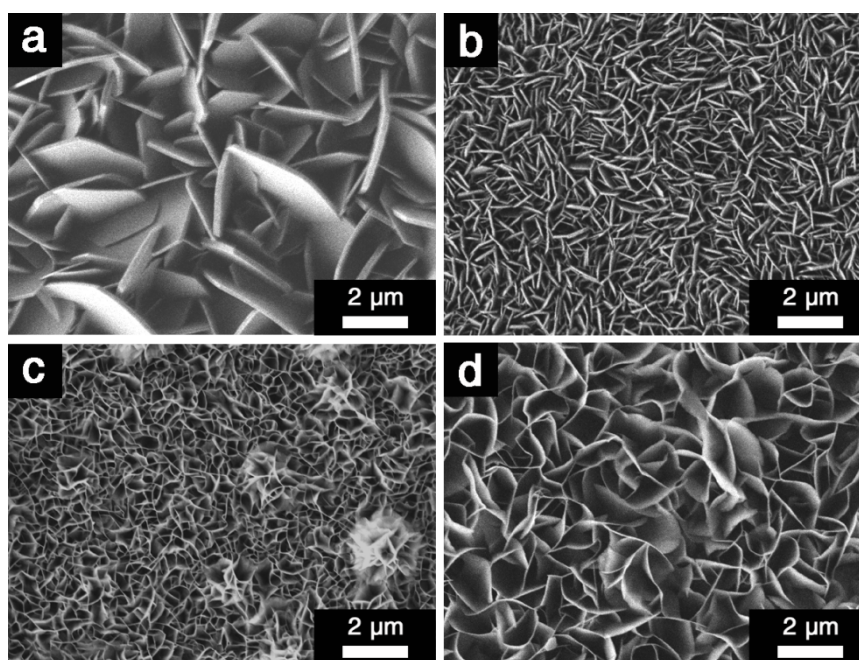


Fig. S1 SEM images of MgAl-CO₃ LDH networks prepared with a) α -Al₂O₃ as substrate, DDI water as solvent; b) γ -Al₂O₃ modified porous α -Al₂O₃ as substrate, DDI water as solvent; c, d) porous α -Al₂O₃ as substrate, methanol as solvent

Synthesis of supported LDH network shown in Fig. S1a

The precursor solution was prepared by adding 0.48 g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, 98%), 0.35 g $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa, 98%) and 1.6 g urea (Alfa, 98%) into 100 ml DDI water. Then the bare $\alpha\text{-Al}_2\text{O}_3$ substrate was vertically placed into a Teflon-lined stainless vessel, and methanol precursor solution was poured into the vessel and sealed. The vessel was put into convective oven with the temperature pre-heated to 120 °C. After an elapsed time of 24 h, the vessel was taken out and cooled to room temperature in air. Finally the membrane was taken out and washed with DDI water.

Synthesis of supported LDH network shown in Fig. S1b

Before in-situ growth, a $\gamma\text{-Al}_2\text{O}_3$ intermediate layer was deposited on a porous $\alpha\text{-Al}_2\text{O}_3$ substrate with a method well-known from the literature (*Thin Solid Films* 2008, **516**, 5020).

The precursor solution was prepared by adding 0.48 g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 1.6 g urea into 100 ml distilled deionized water (DDI water). Then a $\gamma\text{-Al}_2\text{O}_3$ modified substrate was vertically placed into a Teflon-lined stainless vessel, and precursor solution was poured into the vessel and sealed. The vessel was put into convective oven with the temperature pre-heated to 120 °C. After an elapsed time of 24 h, the vessel was taken out and cooled to room temperature in air. Finally the membrane was taken out and washed with DDI water.

Synthesis of supported LDH network shown in Fig. S1c

The precursor solution was prepared by adding 0.48 g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.35 g $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 1.6 g urea into 100 ml pure methanol. Then a bare $\alpha\text{-Al}_2\text{O}_3$ substrate was vertically placed into Teflon-lined stainless vessel, and methanol precursor solution was poured into the vessel and sealed. The vessel was put into convective oven with the temperature pre-heated to 120 °C. After an elapsed time of 24 h, the vessel was taken out and cooled to room temperature in air. Finally the membrane was taken out and washed with DDI water.

Synthesis of supported LDH network shown in Fig. S1d

The precursor solution was prepared by adding 1.92 g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 1.40 g $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 6.4 g urea into 100 ml pure methanol. Then the bare $\alpha\text{-Al}_2\text{O}_3$ substrate was vertically placed into Teflon-lined stainless vessel, and methanol precursor solution was poured into the vessel and sealed. The vessel was put into convective oven with the temperature pre-heated to 120 °C. After an elapsed time of 24 h, the vessel was taken out and cooled to room temperature in air. Finally the membrane was taken out and washed with DDI water.

Discussion and comparison on prepared LDH networks

As shown above, LDH networks with diverse microstructures could be in-situ grown on bare alumina substrates by proper manipulation of the synthetic parameters. For instance, in case H₂O was used as solvent, a vertically aligned LDH network with mutual distances $\sim 1 \mu\text{m}$ was formed on the bare $\alpha\text{-Al}_2\text{O}_3$ substrate (Fig. S1a and Fig. 1a), this LDH network-modified $\alpha\text{-Al}_2\text{O}_3$ substrate was then used in our experiment for the firm attachment of MOF seeds on the $\alpha\text{-Al}_2\text{O}_3$ substrate.

LDH networks became more densely packed (Fig. S1b) by surface modification of the bare $\alpha\text{-Al}_2\text{O}_3$ substrate with a $\gamma\text{-Al}_2\text{O}_3$ intermediate layer since $\gamma\text{-Al}_2\text{O}_3$ was more chemically active and provided more nucleation sites for LDH crystallites. Alternatively the use of methanol instead of H₂O as solvent of the precursor solution also favored the formation of densely packed LDH network since LDH crystallites tended to aggregate together spontaneously due to the low surface tension and hydrophobic nature of the methanol solvent (Fig. S1c, S1d). However, they were not the optimum choice as walls since the mass transfer resistance would increase and in turn may comprise the gas permeance of prepared MOF membranes.

Besides the substrate conditions and the type of solvent, chemical composition of the precursor solution and synthetic time also exerted influence on the morphology of prepared LDH networks. As shown in Fig. S2, increasing the concentration of reactants or prolonging the synthetic time would decrease the compactness of LDH networks, which in turn would negatively affect the quality of prepared ZIF-8 membranes.

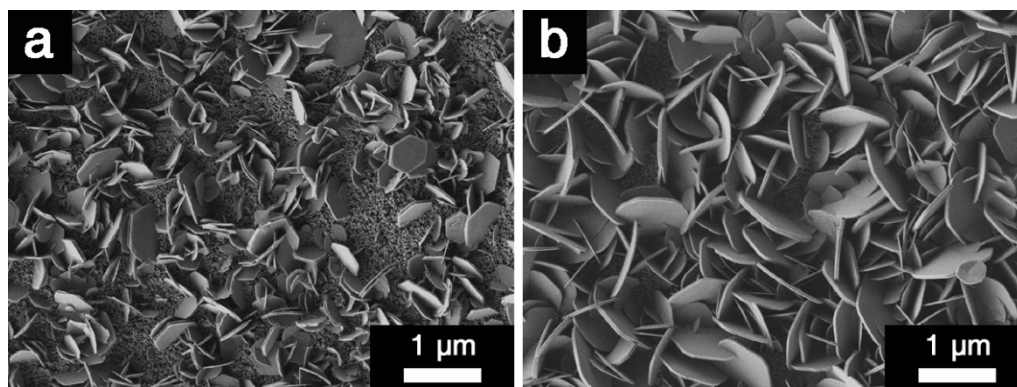


Fig. S2 SEM images of MgAl-CO₃ LDH networks prepared with $\alpha\text{-Al}_2\text{O}_3$ as substrate and DDI water as solvent. a) Concentrations of reactants were increased 4 times; b) the synthetic time was prolonged to 48 h.

Synthesis of supported LDH network shown in Fig. S2a

The precursor solution was prepared by adding 1.92 g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, 98%), 1.40 g $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa, 98%) and 6.4 g urea (Alfa, 98%) into 100 ml DDI water. Then the bare $\alpha\text{-Al}_2\text{O}_3$ substrate was vertically placed into a Teflon-lined stainless vessel, and precursor solution was poured into the vessel and sealed. The vessel was put into convective oven with the temperature pre-heated to 120 °C. After an elapsed time of 24 h, the vessel was taken out and cooled to room temperature in air. Finally the membrane was taken out and washed with DDI water.

Synthesis of supported LDH network shown in Fig. S2b

The precursor solution was prepared by adding 0.48 g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, 98%), 0.35 g $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa, 98%) and 1.6 g urea (Alfa, 98%) into 100 ml DDI water. Then the bare $\alpha\text{-Al}_2\text{O}_3$ substrate was vertically placed into a Teflon-lined stainless vessel, and precursor solution was poured into the vessel and sealed. The vessel was put into convective oven with the temperature pre-heated to 120 °C. After an elapsed time of 48 h, the vessel was taken out and cooled to room temperature in air. Finally the membrane was taken out and washed with DDI water.

SI-2 Experimental details

Preparation of substrate

Porous α -Al₂O₃ asymmetric porous substrates were supplied by Fraunhofer IKTS. Diameter and thickness of the substrate were 18mm and 1 mm, respectively. The mean pore diameter was 70 nm.

In-situ growth of LDH network

The precursor solution was prepared as shown in SI-1 (Fig. S1a).

Embedment of ZIF-8 seeds

ZIF-8 nanocrystals were prepared as previously reported. The seeding solution was prepared by dispersing 1.2 g ZIF-8 nanocrystals in 30 ml methanol, in which the LDH-modified α -Al₂O₃ substrate was immersed. Then the substrate was withdrawn from the solution and placed horizontally in air to facilitate the embedment of ZIF-8 seeds into the LDH network. After complete evaporation of methanol, the substrate was dried in a convective oven at 60 °C for 12 h. The process was repeated twice to warrant a complete coverage of ZIF-8 seeds on the substrate.

Secondary growth of ZIF-8 seed layer

The precursor solution was prepared similar to our previous recipe with slight modification. Briefly, 1.06 g zinc chloride (~99%, Merck), 0.98 g 2-methylimidazole (~99%, Sigma-Aldrich) and 0.54 g sodium formate (~99%, Sigma-Aldrich) were dissolved in 80 ml methanol (99.9%, Roth). After vigorous stirring for 2 h, the substrate covered with ZIF-8 seeds was vertically placed into a 50 ml Teflon-lined stainless vessel, and 35 ml of the precursor solution was poured into the vessel and sealed. The vessel was put into convective oven with the temperature pre-heated to 100 °C. After an elapsed time of 24 h, the vessel was taken out and naturally cooled to room temperature in air. Finally the membrane was taken out and washed with copious of methanol. Prepared ZIF-8 membrane was then dried in air.

SI-3 SEM and XRD characterization of ZIF-8 seeds

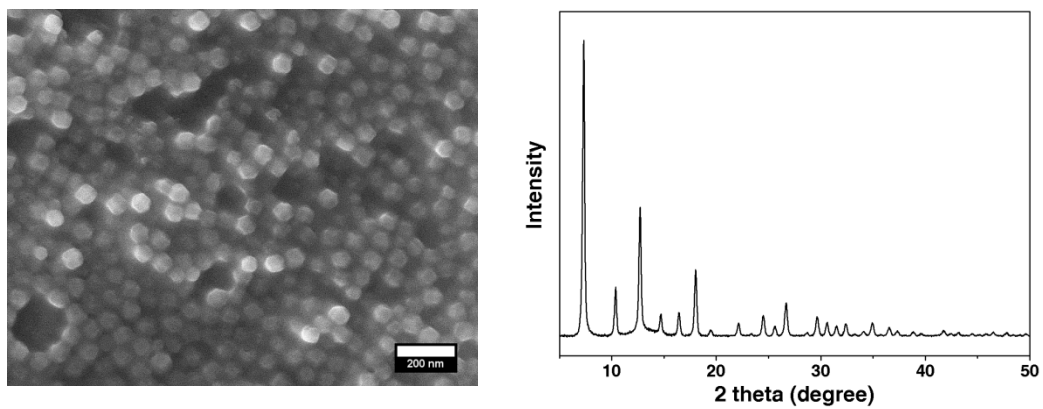


Figure S3 Left side: SEM image of prepared ZIF-8 seeds. Right side: XRD pattern of prepared ZIF-8 seeds.

SI-4 EDXS of the cross-section of ZIF-8-LDH membrane

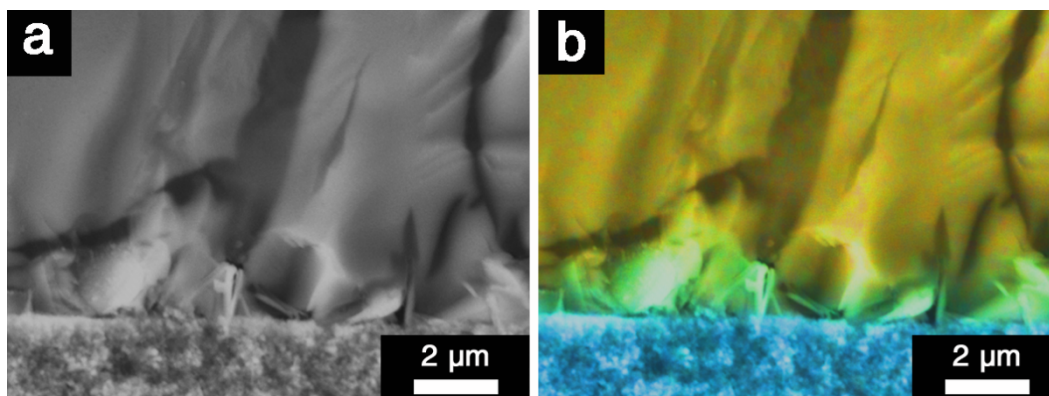


Figure S4 EDXS mapping of the cross-section of prepared ZIF-8 membrane. Color code: yellow = Zn; green = Mg; blue = Al.

SI-5 Demonstration of the gas separation equipment

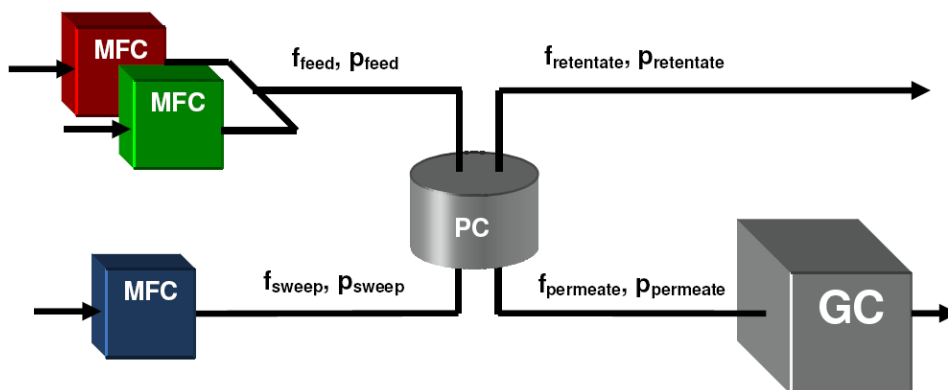


Fig. S5 Measurement equipment for single and mixed gas permeation. MFC: mass flow controller; PC: permeation cell with mounted membrane; GC: gas chromatograph; f : volumetric flow rate; p : pressure.

For the single gas permeation measurement, the prepared ZIF-8 membrane was fixed in a module sealed with O-rings. A volumetric flow rate of 50 ml min^{-1} gas was applied to the feed side of the membrane, and the permeate gas was removed from the permeate side by sweep gas. Pressures at both feed side and permeate side were kept at 1 bar. In most of the cases, N_2 was used as sweep gas, except in the N_2 single gas measurement, where CH_4 was employed as the sweep gas.

For the mixed gas permeation measurement, the prepared ZIF-8 membrane was fixed in a module sealed with O-rings. A 1:1 mixture of gas was applied to the feed side of the membrane, and the permeate gas was removed from the permeate side by sweep gas. The feed flow rate was kept constant with a total volumetric flow rate of 100 ml min^{-1} (each gas of 50 ml min^{-1}). Pressures at both feed side and permeate side were kept at 1 bar. In most of the cases, N_2 was used as sweep gas, except in the H_2/N_2 measurement, where CH_4 was employed as the sweep gas.

A calibrated gas chromatograph (HP7890a) is used to measure the concentration of single gases or mixed gases on the permeate side. The separation factor $\alpha_{i,j}$ of gas pairs is defined as the quotient of the molar ratios of the components (i, j) in the permeate side, divided by the quotient of the molar ratio of the components (i, j) in the feed side:

$$\alpha_{i/j} = \frac{x_{i,perm}/x_{j,perm}}{x_{i,feed}/x_{j,feed}}$$

SI-6 ZIF-8 layer grown on bare α -Al₂O₃ substrate by secondary growth

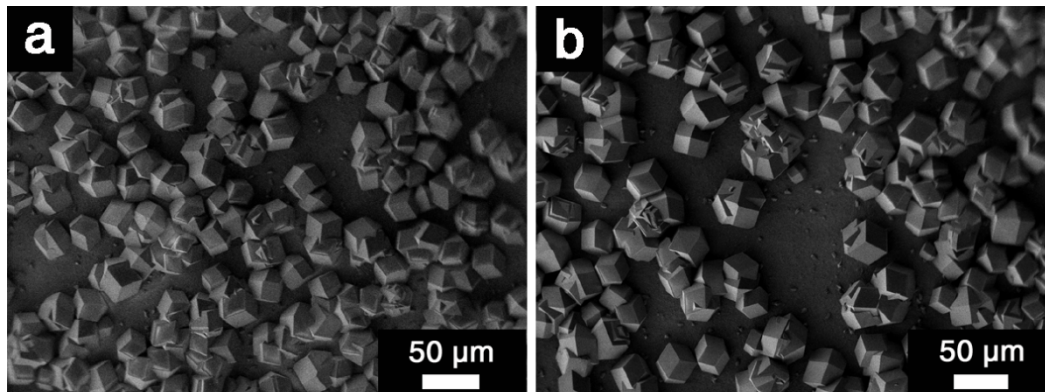


Fig. S6 SEM images of the ZIF-8 layer grown on bare α -Al₂O₃ substrate by secondary growth. The images were taken from the a) center and b) fringe of the membrane.

SI-7 ZIF-90 membrane prepared on LDH network-modified substrate by secondary growth

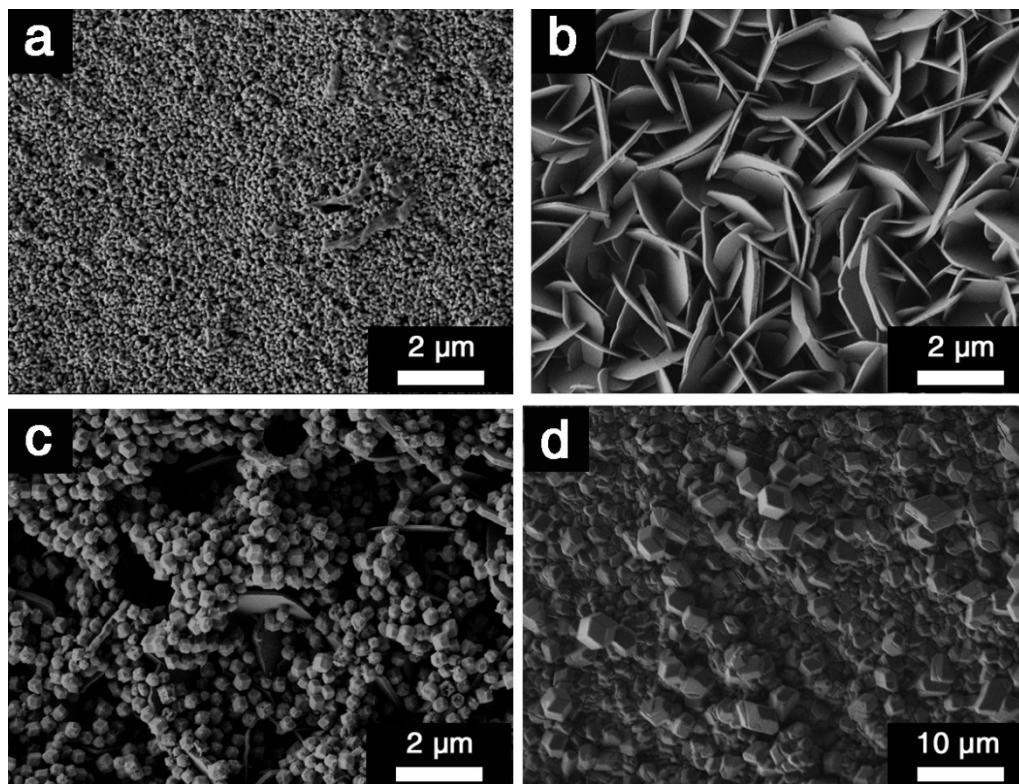


Fig. S7 SEM images of a) bare α - Al_2O_3 substrate, b) LDH network-modified α - Al_2O_3 substrate, c) ZIF-90 seeds attached on LDH network-modified α - Al_2O_3 substrate and d) ZIF-90 membrane after secondary growth.

ZIF-90 seeds with an average size of ~ 500 nm were prepared based on the work of S. Nair et al (A. J. Brown, J. R. Johnson, M. E. Lydon, W. J. Koros, C. W. Jones and S. Nair, *Angew. Chem. Int. Ed.*, 2012, **51**, 10615).

The seeding solution was prepared by dispersing 0.5 g ZIF-8 nanocrystals in 100 ml methanol, in which the LDH-modified α - Al_2O_3 substrate was immersed. Then the substrate was vertically withdrawn from the solution and placed horizontally in air to facilitate the embedment of ZIF-90 seeds into the LDH network. After complete evaporation of methanol, the substrate was dried in a convective oven at 60°C .

Secondary growth process was similar to the work of S. Nair et al. except that 1) the solvothermal synthesis was conducted at 65°C for 6 h, and 2) after solvothermal growth, the vessel was slowly cooled to room temperature in 6 h to minimize the formation of intercrystal cracks in the ZIF-90 layer.

SI-8 ZIF-90 layer prepared on the bare α -Al₂O₃ substrate by secondary growth

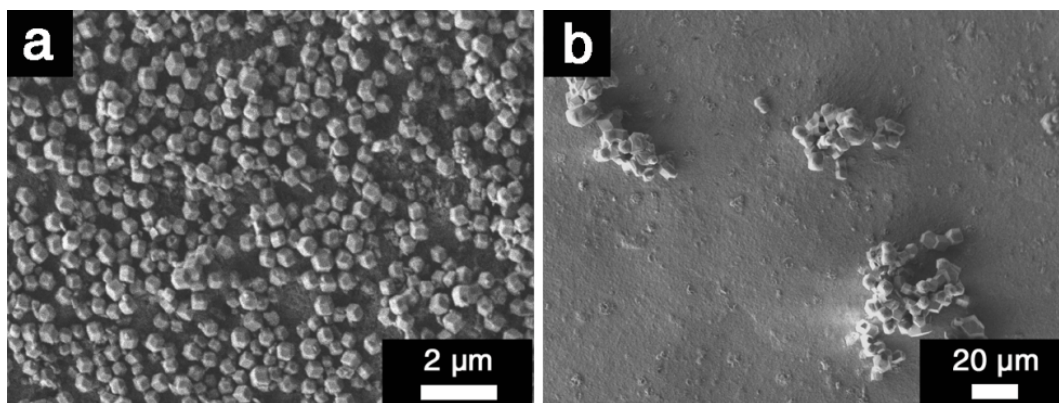


Fig. S8 SEM images of a) ZIF-90 seed layer dip-coated on a bare α -Al₂O₃ substrate and b) ZIF-90 layer after secondary solvothermal growth.