Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Facile fabrication of highly (110)-oriented ZIF-7 film with rod-shaped seeds

Sixing Chen,[a] Yanwei Sun,[a] Sikang Chen,[a] Yunlei Gao,[a] Fei Wang,[b] Hong Li,[c] and Yi Liu[a]*

[a.] State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Linggong Road 2, Ganjingzi District, Dalian 116024, China. E-mail: diligenliu@dlut.edu.cn

[b.] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China.

[c.] School of Optoelectronic Engineering and Instrumentation Science, Dalian University of Technology, Dalian 116024, China.

S1 Experimental section

Chemicals: Benzimidazole (98.5%), zinc chloride ($ZnCl_2$, 98%), zinc bromide ($ZnBr_2$, 99.9%), diethylamine (DEA, 99%), anhydrous ferric chloride ($FeCl_3$, 99%), polyvinylpyrrolidone (PVP, average M_W~58000), linoleic acid (LA, 99%), N-methylformamide (NMF, 99%), and polyethyleneimine (PEI, 99%, average M_W~10000) were purchased from Macklin, Shanghai; zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, 99%) was purchased from West Asia Chemical, Shandong; terephthalic acid (H_2BDC, 99%) was purchased from ALADDIN Reagent, Shanghai; N, N-dimethylformamide (DMF, 99.8%) was purchased from Kermel, Tianjin; and Al plates (99.9 wt.%) were purchased from Shenyang Chemicals. All reagents were directly used as received without further purification.

Synthesis of rod-shaped ZIF-7 seeds (aspect ratio: 7.66): 0.310 g benzimidazole, 0.265 g $ZnCl_2$, and 0.750 g DEA were dissolved in 30 mL DMF. After vigorous stirring for 15 min, the mixture was added into Teflon-lined autoclave and solvothermal treatment was conducted at 90 °C for 24 h under static conditions. After cooling, the solid product was centrifuged, washed with copious of ethanol, and finally dried at 70 °C for use.

Synthesis of rod-shaped ZIF-7 seeds (aspect ratio: 5.22) with $ZnBr_2$ as zinc source: 0.310 g benzimidazole, 0.438 g $ZnBr_2$ and 0.750 g DEA were dissolved in 30 mL DMF. After vigorous stirring for 15 min, the mixture was poured into a Teflon vessel and solvothermal reaction was carried out at 110 °C for 24 h. The product was centrifuged, washed with ethanol and dried in an oven at 70 °C.

Synthesis of rod-shaped MIL-88B (Fe) seeds: Rod-shaped uniform MIL-88B (Fe) seeds were prepared following the procedure reported in the literature with slight modification. 0.487 g $FeCl_3$ and 0.498 g H_2BDC were dissolved in 50 mL DMF. After stirring for 24h, the mixture was poured in to 80 mL glass reaction vessel and solvothermal reaction was carried out in a single-mode microwave oven (Discover, CEM) at 150 °C for 15 min. The product was sequentially centrifuged, washed with ethanol and dried in an oven at 70 °C.

Deposition of (110)-oriented ZIF-7 monolayer: Prior to deposition, 0.02 g rod-shaped ZIF-7 seeds were dispersed in 5 mL iso-propanol and vigorously stirred in a conical flask for at least 2 days. Afterwards, 10 µL 0.01 M PVP and 5 µL LA were added in the seed solution and stirred for more than 3 days. In the next step, a glass plate (2 × 2 cm) was horizontally placed under the air-liquid interface. The ZIF-7 seed-containing ethanol suspension was slowly injected at the turbulent air-liquid interface generated by a magnetic stirrer at a speed of 2 µL/min. The ZIF-7 seed monolayer was spontaneously formed at the air-liquid interface and then, transferred to the substrate surface. Obtained seed layer was dried at 70 °C overnight before use.

Deposition of rod-shaped ZIF-7 (aspect ratio: 5.22) and MIL-88B (Fe) monolayers: Above seed suspensions were prepared by dispersing 0.01 g ZIF-7 powders and 0.04 g MIL-88B powders in 5 mL iso-propanol and 5 mL ethanol, respectively. After vigorous stirring for 2 days, 10 µL 0.01 mM PVP and 5 µL LA were added in the above suspensions for another 3 days. Rod-shaped ZIF-7 and MIL-88B (Fe) seeds were deposited on the substrate surface following the procedure as described above.

Epitaxial growth of (110)-oriented ZIF-7 film: 0.103 g benzimidazole, 0.146 g $ZnBr_2$, and 0.250 g DEA were dissolved in a mixture comprising 27 mL DMF and 3 mL NMF. After vigorous stirring for 15 min, the mixture was poured into a 80 mL glass reaction vessel where the substrate pre-coated with (110)-oriented ZIF-7 monolayer was vertically placed. Solvothermal reaction was conducted in a single-mode microwave oven at 90 °C for 15 min. After cooling to room temperature, the ZIF-7 film was washed with methanol and dried overnight at 70 °C.

Epitaxial growth of (110)-oriented ZIF-7 film with varying zinc sources and heating modes: As comparative experiments, on the one hand, 0.088 g $ZnCl_2$ or 0.193 g $Zn(NO_3)_2{\cdot}6H_2O$, 0.103 g benzimidazole and 0.250 g DEA were dissolved in 30 mL DMF. After vigorous stirring for 15 min, the precursor solution was added in Teflon-lined autoclave where the (110)-oriented ZIF-7 monolayer-modified substrate was vertically placed. Solvothermal treatment was conducted at 100 °C for 24 h; on the other hand, the precursor solution was prepared by dissolving

0.146 g $ZnBr_2$, 0.103 g benzimidazole and 0.250 g DEA in 30 mL DMF. Both conventional solvothermal heating (at 100 °C for 24 h) and single-mode microwave heating (at 90 °C for 15 min) were carried out during epitaxial growth.

Fabrication of *c*-oriented ZIF-7 film: First, 0.446 g $Zn(NO_3)_2 \cdot 6H_2O$, 0.354 g benzimidazole, and 0.140 g PEI were dissolved in 200 mL DMF. After vigorous stirring for 24 h, obtained ZIF-7 nanoseeds were centrifuged, washed with ethanol, and redispersed in ethanol (2.5 wt.%). Second, the substrate surface was seeded by dip-coating in the above ZIF-7-containing ethanol suspension. Third, 0.204 g $ZnCl_2$ or 0.338 g $ZnBr_2$, 0.266 g benzimidazole, and 0.170 g DEA were dissolved in 30 mL DMF. After vigorous stirring for 15 min, the precursor solution was poured into a 80 mL glass reaction vessel where the seeded substrate was vertically placed. Solvothermal reaction was carried out under single-mode microwave heating at 100 °C for 30 min.

DC Polarization test: DC polarization tests were carried out at room temperature with three electrode system at the electrochemical interface of CHI660E. A gauze platinum and an Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. Bare Al plate, *c*-oriented ZIF-7 film-coated Al plate, and (110)-oriented ZIF-7 film-coated Al plate were used as working electrodes, respectively. A 3.5 wt.% sodium chloride aqueous solution was used as the corrosion medium. Prior to the experiment, the working electrode was immersed in the corrosive medium to warrant a stable open circuit potential. DC polarization test was carried out in the range of -2 V to -0.4 V and the scanning rate was set at 10 mV/s.

S2 ZIF-7 seed layers deposited under various conditions

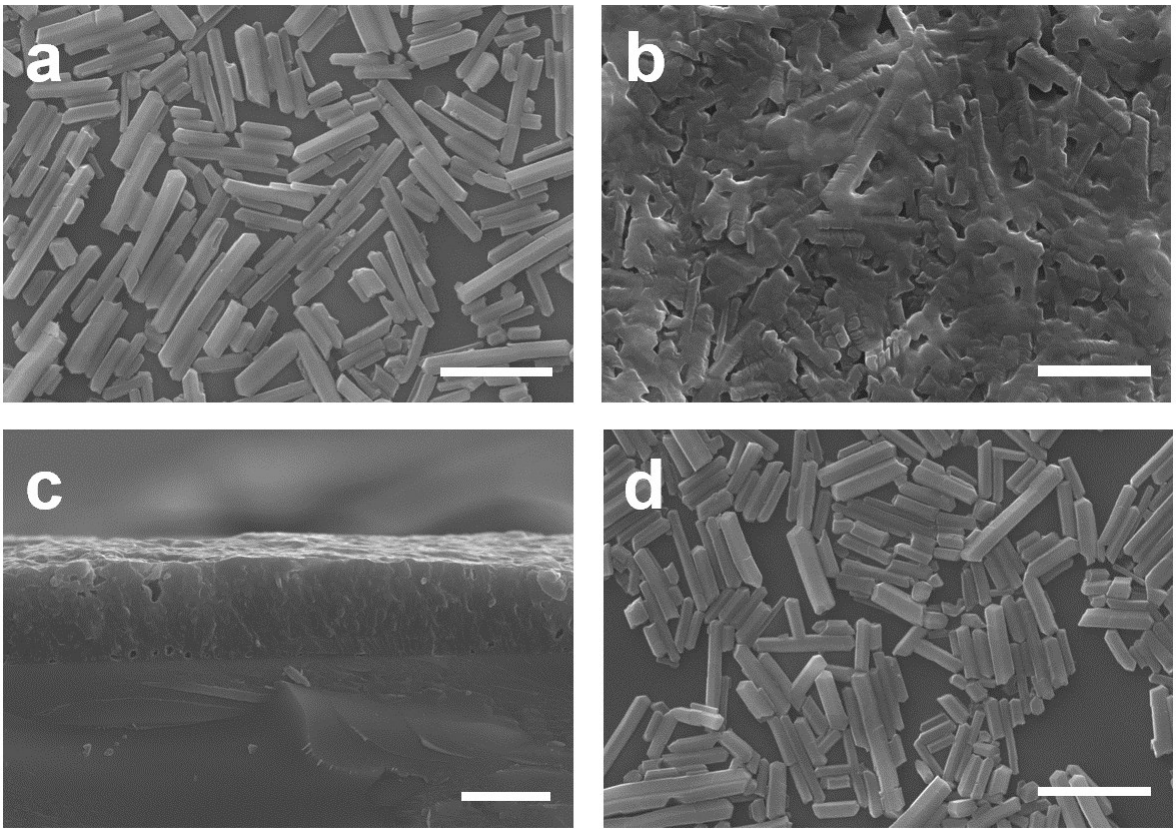

Fig. S1 SEM images of a) ZIF-7 seed layer deposited without any additives, b, c) ZIF-7 seed layer deposited with LA additives, and d) ZIF-7 seed layer deposited with PVP additives. Scale bar: 5 μm.

S3 XRD pattern of ZIF-7 seed layer prepared with the addition of only LA

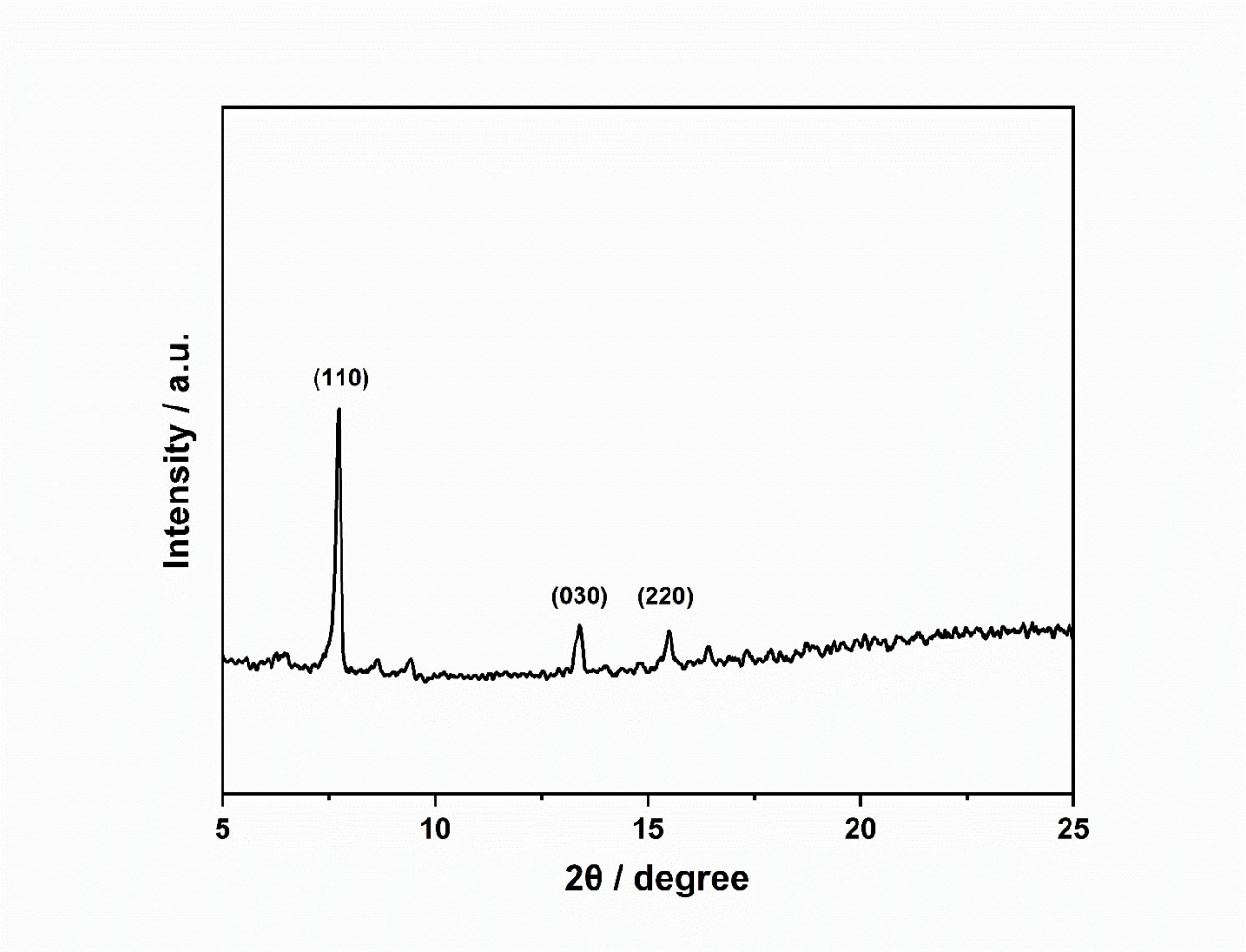

Fig. S2 The XRD pattern of ZIF-7 seed layer prepared with the addition of only LA.

S4 IR spectra of ZIF-7 seeds modified with different additives

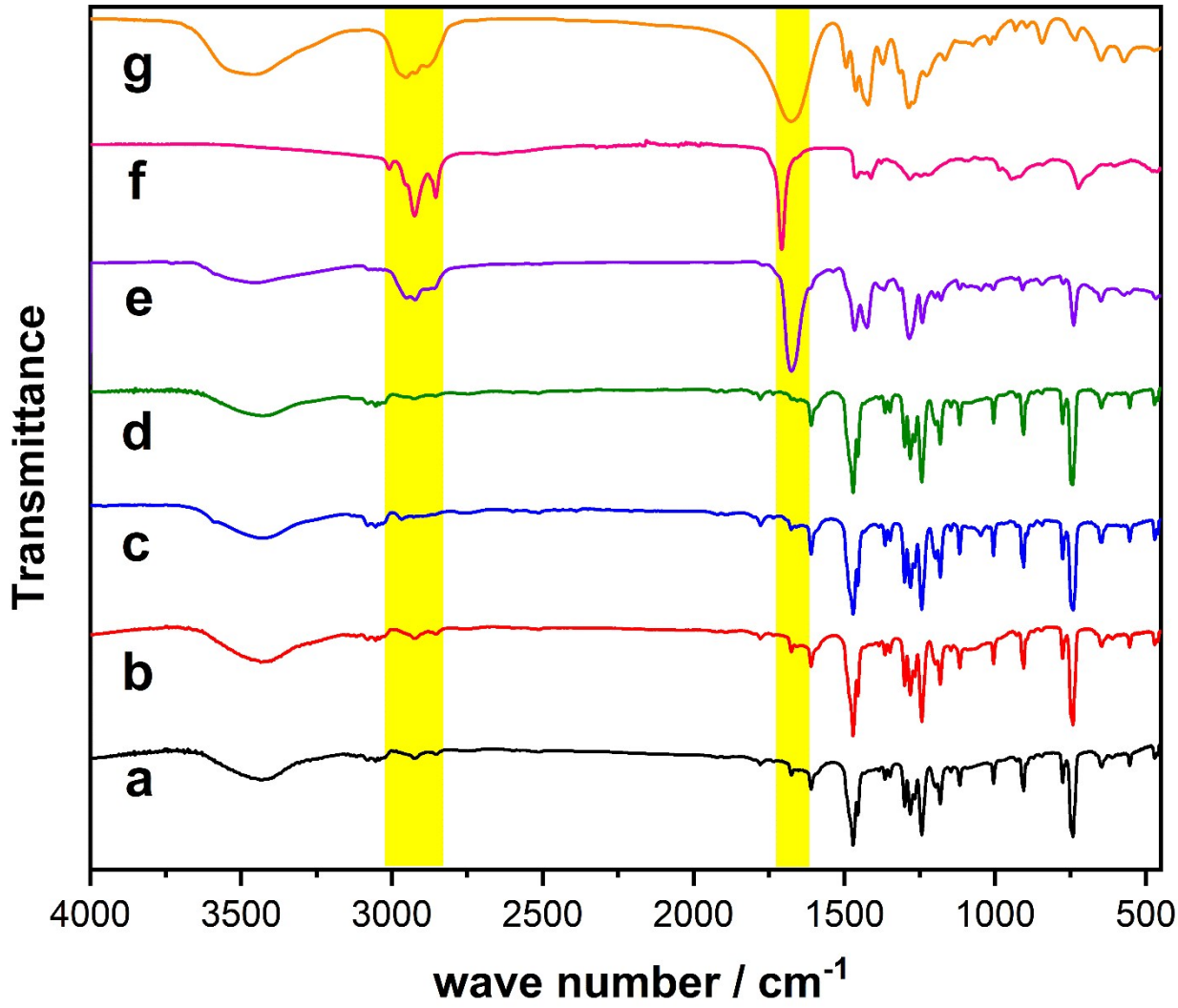

Fig. S3 IR spectra of a) ZIF-7 seeds, b) LA-modified ZIF-7 seeds washed with ethanol, c) PVP-modified ZIF-7 seeds washed with ethanol, d) LA and PVP-modified ZIF-7 seeds washed with ethanol, e) unwashed ZIF-7 seeds modified with LA-PVP binary additives, f) LA, and g) PVP.

S5 Morphology of ZIF-7 seeds and MIL-88B seeds

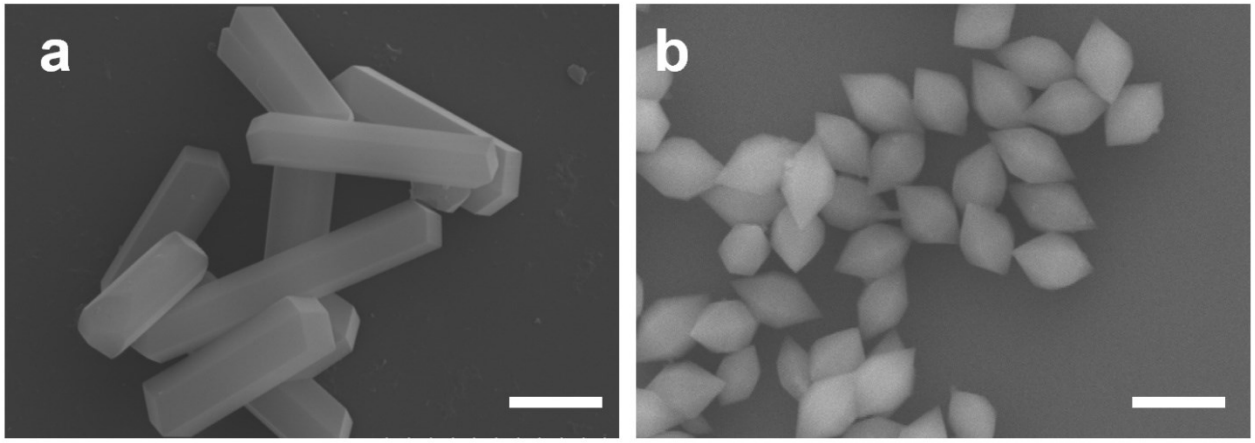

Fig. S4 SEM images of a) ZIF-7 seeds (aspect ratio: 5.22) synthesized with $ZnBr_2$ as zinc source and b) MIL-88B(Fe) seeds (aspect ratio: 1.70). Scale bar: 2 μm.

S6 ZIF-7 single seed layer with $ZnBr_2$ as zinc source

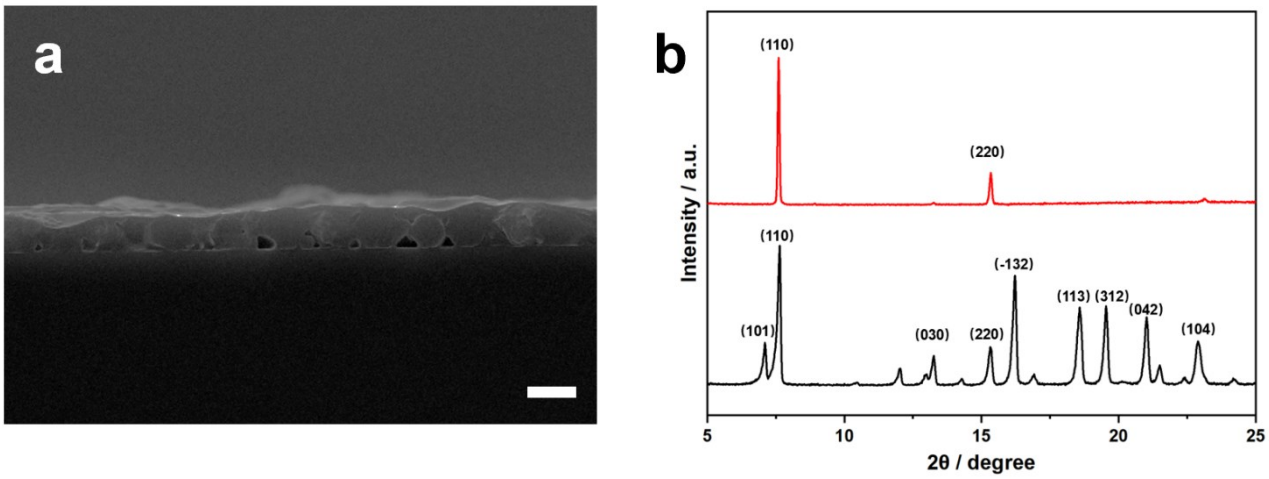

Fig. S5 a) SEM image of the cross section of ZIF-7 seed single seed layer (aspect ratio: 5.22); and b) XRD characterization of ZIF-7 powders and single seed layer prepared with $ZnBr_2$ as zinc source (aspect ratio: 5.22). Scale bar: 2 µm.

S7 HR-SEM image of MIL-88B seed layer

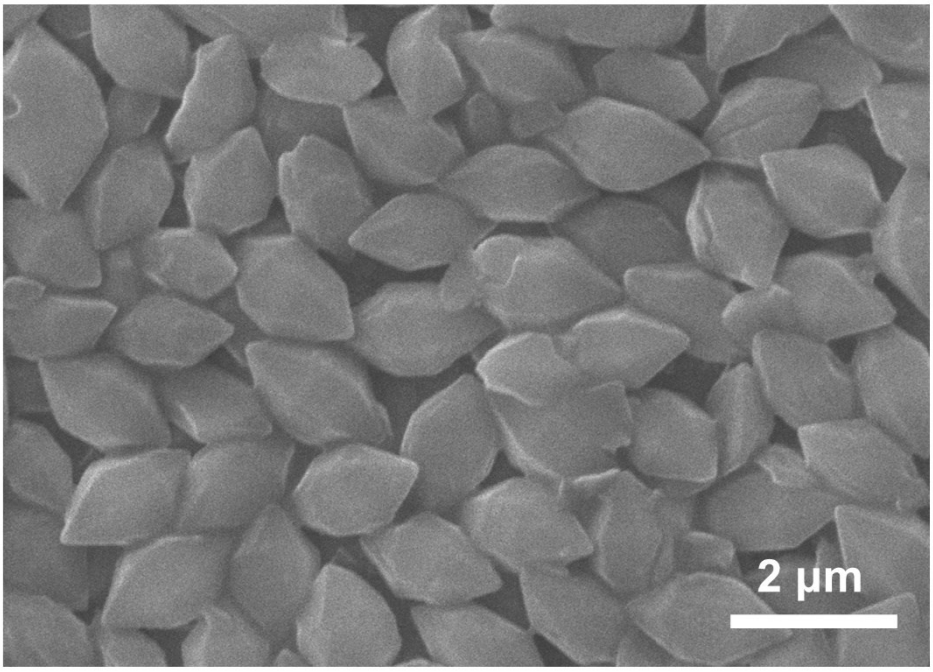

Fig. S6 HR-SEM image of MIL-88B single seed layer modified with LA-PVP binary additives.

S8 IR spectra of MIL-88B seeds

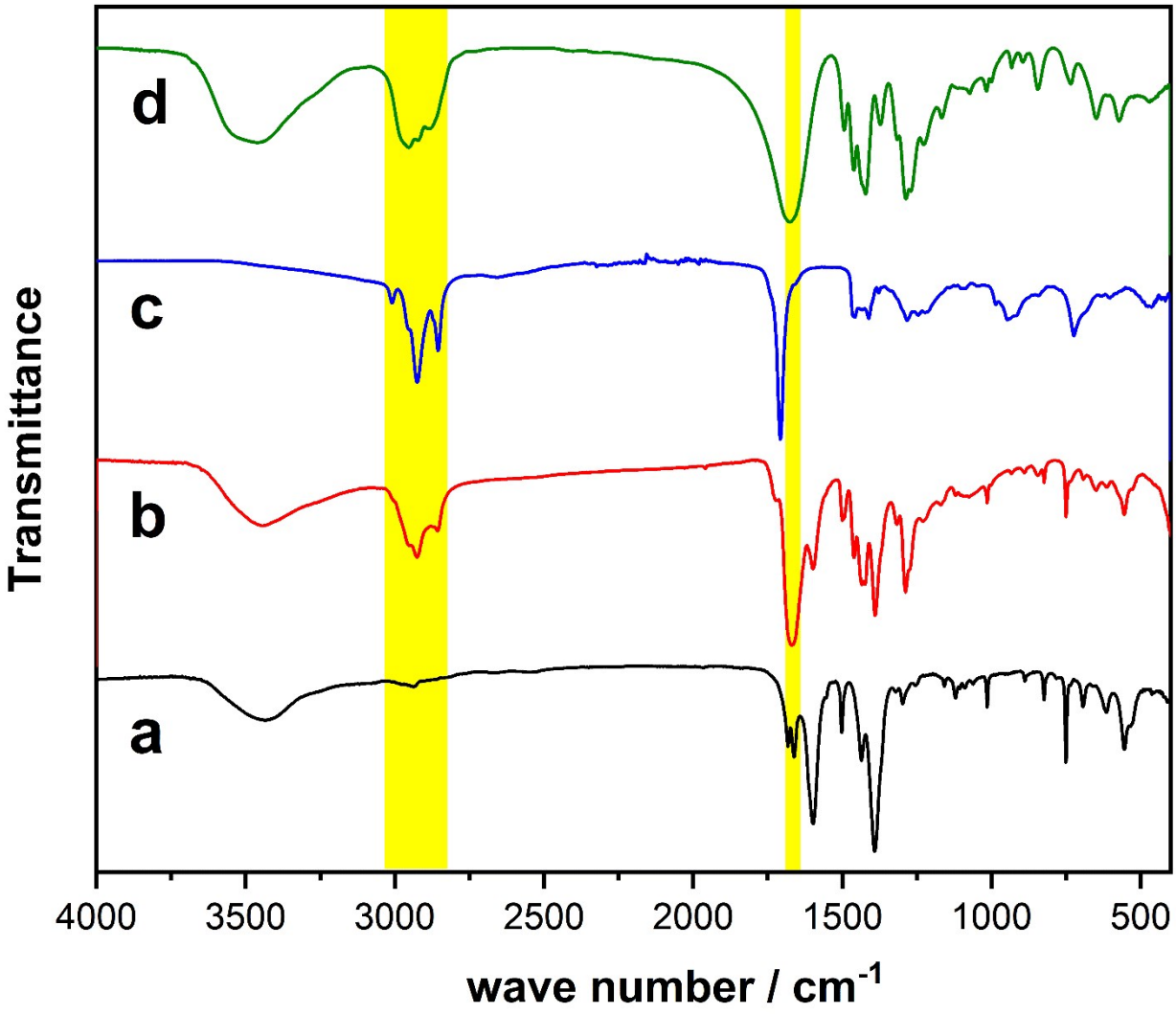

Fig. S7 IR spectra of a) MIL-88B seeds, b) unwashed MIL-88B seeds modified with PVP-LA binary additives, c) LA, and d) PVP.

S9 ZIF-7 films prepared under various conditions

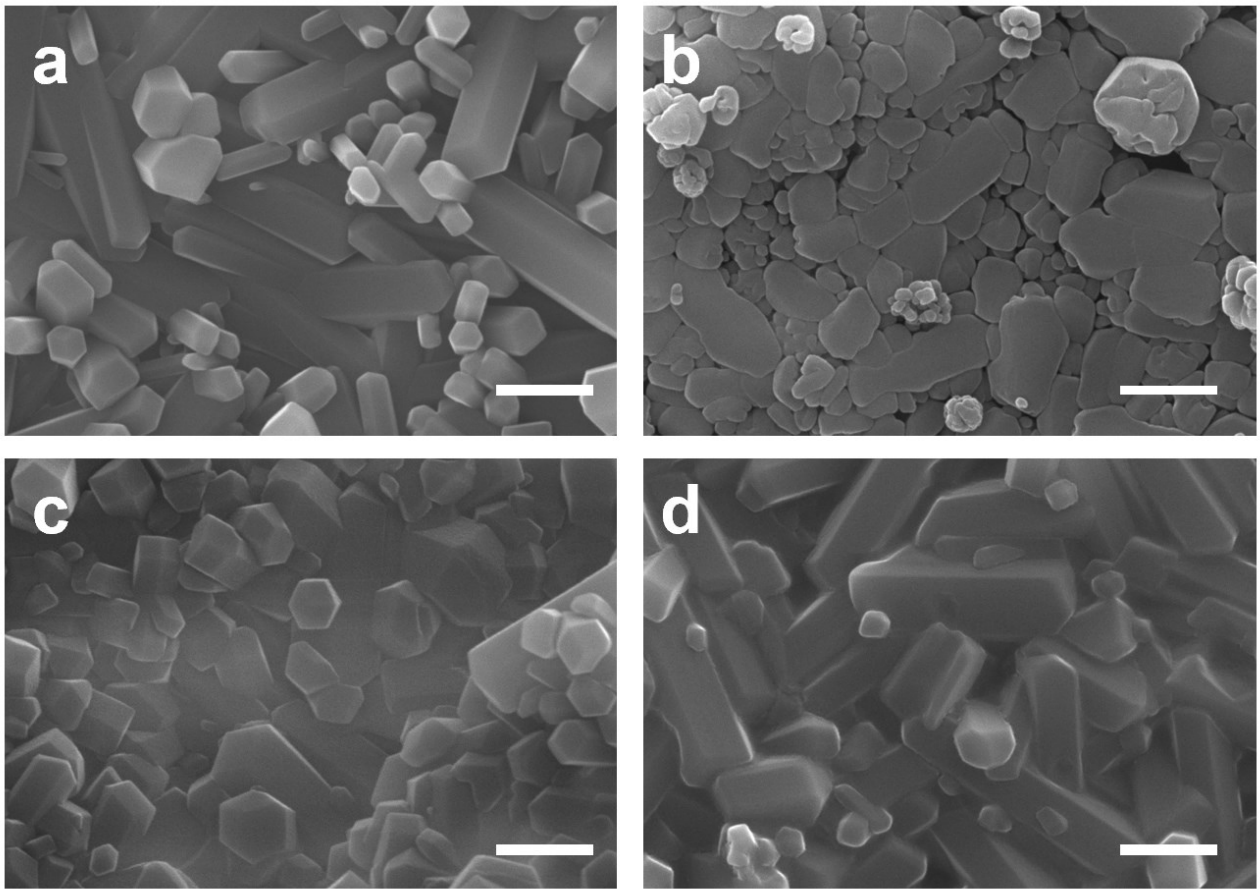

Fig. S8 SEM images of a) solvothermal epitaxial growth with $ZnCl_2$ as zinc source, b) solvothermal epitaxial growth with $Zn(NO_3)_2 \cdot 6H_2O$ as zinc source, c) solvothermal epitaxial growth with $ZnBr_2$ as zinc source, and d) single-mode microwave epitaxial growth with $ZnBr_2$ as zinc source and pure DMF as solvent. Scale bar: 2 μm.

S10 XRD patterns of ZIF-7 films prepared with different zinc sources

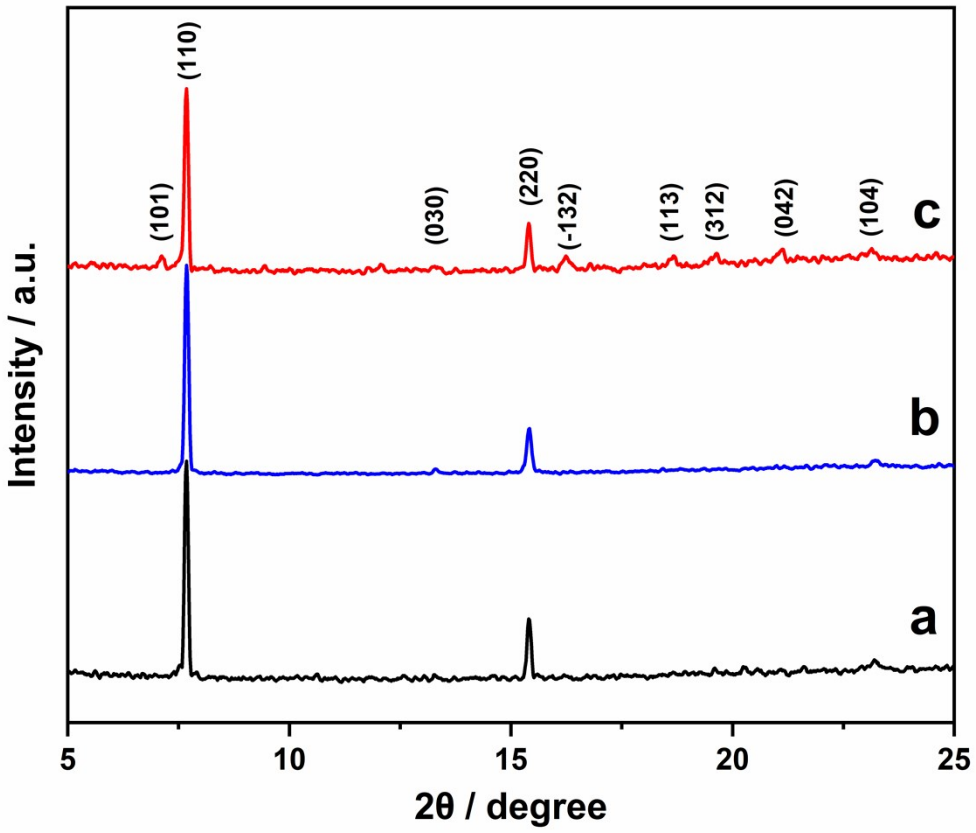

Fig. S9 XRD patterns of ZIF-7 films prepared by solvothermal epitaxial growth with a) $ZnCl_2$, b) $Zn(NO_3)_2 \cdot 6H_2O$, and c) $ZnBr_2$ as zinc sources.

S11 AFM images of ZIF-7 films with different orientations

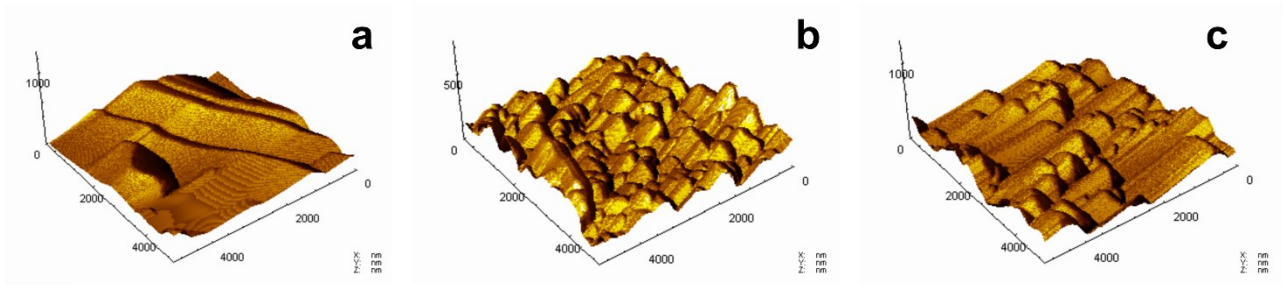

Fig. S10 AFM images of a) (110)-oriented ZIF-7 film (RMS roughness: 152.52 nm), b) *c*-oriented ZIF-7 film prepared with $ZnCl_2$ as zinc source (RMS roughness: 100.85 nm), and c) *c*-oriented ZIF-7 film prepared with $ZnBr_2$ as zinc source (RMS roughness: 243.47 nm).

S12 XRD patterns of *c*-oriented ZIF-films prepared with different zinc sources

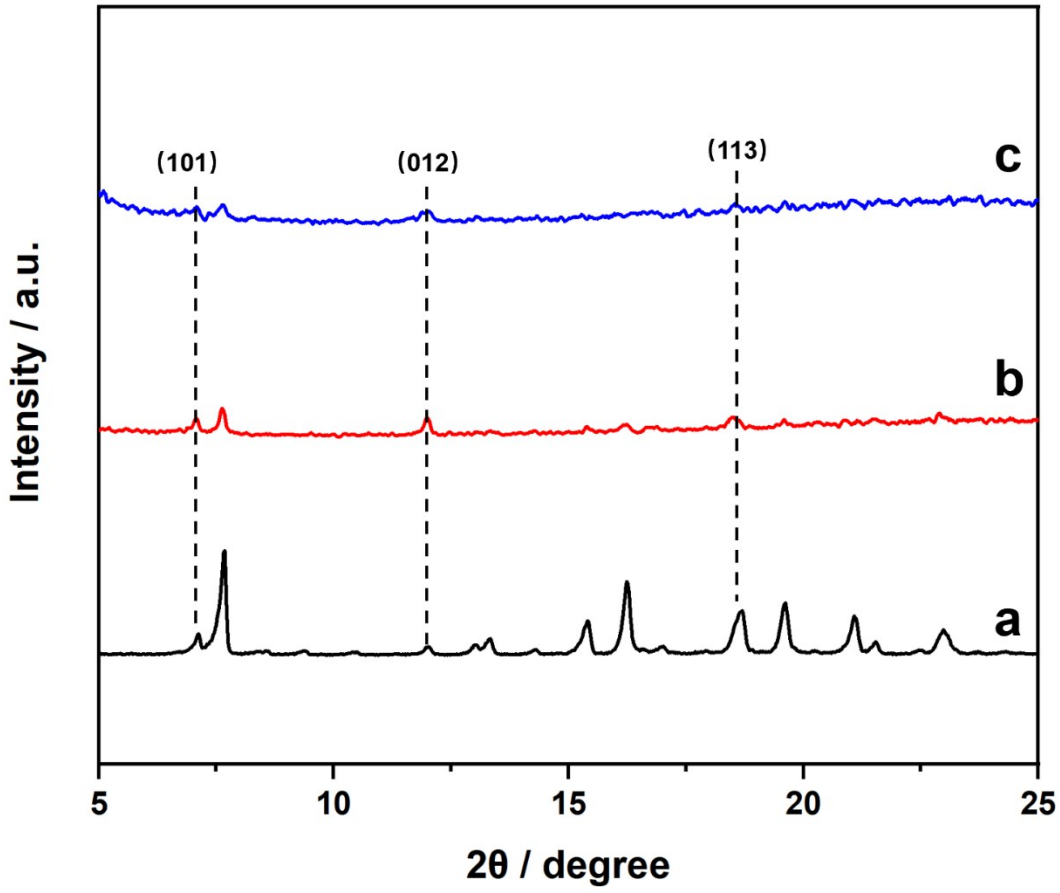

Fig. S11 XRD patterns of a) rod-shaped ZIF-7 seeds, b) *c*-oriented ZIF-7 film prepared with $ZnCl_2$ as zinc source, and c) *c*-oriented ZIF-7 film prepared with $ZnBr_2$ as zinc source.

S13 *c*-Oriented ZIF-films prepared with various zinc sources

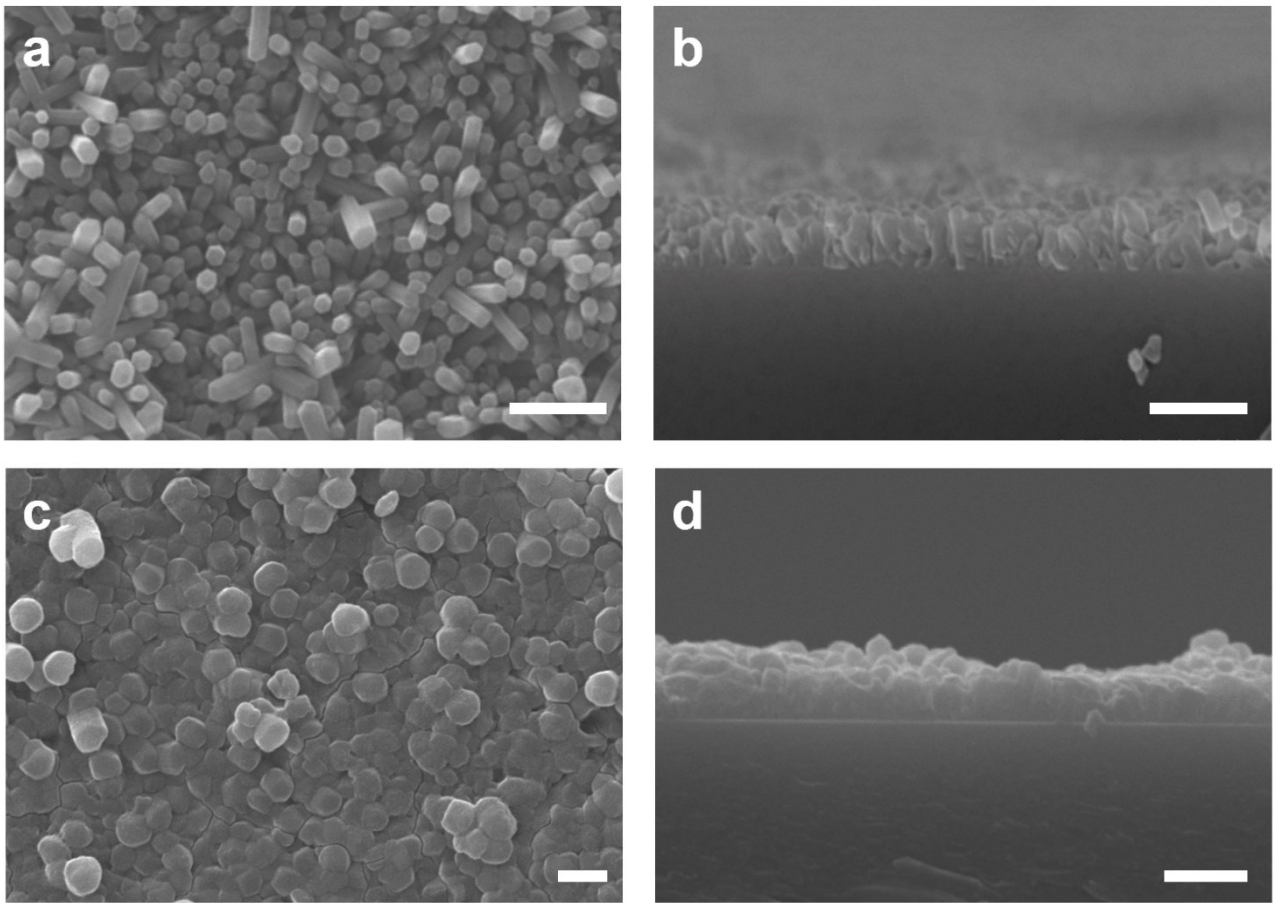

Fig. S12 SEM image of a, b) *c*-oriented ZIF-7 film prepared with $ZnCl_2$ as zinc source, and c, d) *c*-oriented ZIF-7 film prepared with $ZnBr_2$ as zinc source. Scale bar: 1 μm.