Supplementary Information

Concentration gradient induced in-situ formation of MOFs tubes

Yiliang Wang,*[ab] Hui Peng[c] and Yingying Zhang*[a]

[a.] *Department of Chemistry, Tsinghua University, Beijing, 100084, P. R. China.*
   E-mail: wangyiliang1988@163.com, yingyingzhang@tsinghua.edu.cn
[b.] *Analysis and Testing Center, Shandong University of Technology, Zibo, 255000, P. R. China.*
[c.] *Group Applied Mechanics (AME), Institute for Mechanical Process Engineering and Mechanics, Karlsruhe Institute of Technology, Karlsruhe, 76131, Germany.*

1. Experimental Section

Chemicals. The sodium alginate (SA, 200 mPa·s), 2-methylimidazole (99%), and rhodamine B (479.01 g/mol) were purchased from Sigma-Aldrich. Boric acid, cobalt nitrate hexahydrate ($Co(NO_3)_2\bullet 6H_2O$), sodium formate were purchased from Sinopharm Chemical Reagent Co. Ltd. All chemicals were of analytical grade without further purification.

Preparation of cobalt alginate fibers. The cobalt alginate (CoA) fibers with different diameters were prepared with the same methods. Firstly, 5 wt% sodium alginate (SA) solutions were prepared by mechanical stirring for 12h at room temperature (RT). Then we extruded the SA solutions into $Co(NO_3)_2$ solutions (0.5 mol/L) with different nozzles and crosslinked them for 24 h.

The prepared fibers were washed in different ways. The CoA-1 fibers for preparing A-ZIF1 were immersed in large quantities of water for 1h and then washed with ethanol one time, which keeps a little water in the fiber. The CoA-2 fibers for synthesizing A-ZIF2 were washed with water one time and then immersed in large quantities of ethanol for 1h, removing the excess Co^{2+} and water. The CoA-3 fibers for A-ZIF3 were immersed in large quantities of water for 1h, removing the excess Co^{2+}. The CoA-4 fibers for A-ZIF4 were obtained by rinsing CoA-3 fibers with ethanol one time, resulting in a dense shell without extra Co^{2+}.

Preparation of A-ZIF1 fibers, A-ZIF2 fibers, A-ZIF3 fibers, and A-ZIF4 tubes. A-ZIF1 fibers. The CoA-1 fibers were transferred into 20 mL of a methanol solution containing 3 mmol of 2-methylimidazolate (2-M) and 1.58 mmol of sodium formate (SF) for 24 h. ***A-ZIF2 fibers.*** The CoA-2 fibers were transferred into 20 mL of a methanol solution containing 3 mmol of 2-M and 1.58 mmol of SF for 24 h. ***A-ZIF3 fibers.*** The CoA-3 fibers were transferred into 20 mL of a methanol solution containing 3 mmol of 2-M for 24 h. ***A-ZIF4 tubes.*** The CoA-4 fibers were transferred into 20 mL of a water solution containing 3 mmol of 2-M and 1.58 mmol of SF for 6 h, then the pink fibers convert into purple tubes (A-ZIF4st). After that, the tubes were washed with water and ethanol separately for one time. Then, the obtained tubes were transferred into 20 mL of a methanol solution containing 3 mmol of 2-M and 1.58 mmol of SF for 24 h.

The obtained A-ZIF fibers and tubes were immersed in large quantities of ethanol for 1h and then washed with ethanol three times. These fibers and tubes were stored in ethanol before the test.

Dye Absorption of A-ZIF4 tubes.

The 20 mg A-ZIF4 tube was placed in 3 mL of a 50 mg/L rhodamine B ethanol solution for a different time, then the UV−vis spectra of the solution would be tested immediately. The 30 mg cobalt alginate was also tested for dye absorption under the same condition for comparison. The adsorption amount was calculated utilizing the following equation:

$$Q_t = \frac{(C_0 - C_t) * V}{M}$$

where C_0 and C_t are the dye concentration at initial and time t (mg/L), M is the mass of adsorbent (g), and V is the volume of the solution (0.003 L).

Characterization.
The morphology of the fibers and tubes were characterized using SEM (Quanta 450 FEG and JSM IT300), TEM (Hitachi H-7650), and optical microscope (JEM-2010). Brunauer−Emmett−Teller (BET) analysis was performed on Accelerated Surface Area and Porosimetry System (ASAP 2460). Fourier transform infrared (FTIR) spectra were performed with an ATR IR spectrometer (Nicolet 6700) in detection mode, and the spectra were collected from 400 cm^{-1} to 4000 cm^{-1}. The binding energy of elements in different samples was characterized by X-ray photoelectron spectroscopy (XPS, PHI QUANTERA-II SXM). Powder X-ray diffraction patterns (XRD) were recorded on an X-ray diffractometer (Bruker D8) with a Cu Kα radiation (λ = 1.5418A). The pyrolysis behaviors were performed on a Mettler-Toledo thermogravimetric analysis (TGA)/DSC-1 (Greifensee) at a heating rate of 20 °C min^{-1} from 50 °C to 800 °C. The adsorption capacity of alginate and A-ZIF4 tube were characterized by UV-Vis with a DU 800 UV/vis spectrophotometer.

2. Synthesis Mechanism

The synthesis mechanism of different A-ZIF composites has been summarized in Fig. 4. The chemical structures and morphologies are influenced by the H_2O in CoA, the SF, and the solvent. The H_2O enables the move of alginate chains, producing the

rough surface of A-ZIF1 fibre. As for SF, the function is supplying enough cations for balancing the water ionization and releasing the chelated Co^{2+}, which could create necessary conditions for the growth of ZIF-67 particle (A-ZIF2 fibre). Besides, the solvent also shows an obvious influence on the A-ZIF composites. In the methanol, the alginate chains were frozen and can't move freely. So all the A-ZIF prepared in the methanol could keep the fibrous state. In the H_2O, the released Co^{2+} would bridge with 2-M and form ZIF-67 in the out layer of CoA fibre, creating a tough shell. As the reaction goes on, more and more Na^+ and $HCOO^-$ transfer to the fibre core, producing a high solute concentration. Meanwhile, the CoA hydrogel would de-crosslink into soluble Na alginate. Consequently, the core would swell and come out from the fibre, then the A-ZIF4st tube forms. To improve the surface area of MOFs tubes, another synthesis process of ZIF-67 in methanol solution containing $Co(NO_3)_2$, 2-M, and SF had been conducted. The unique MOFs tubes would create more possible applications.
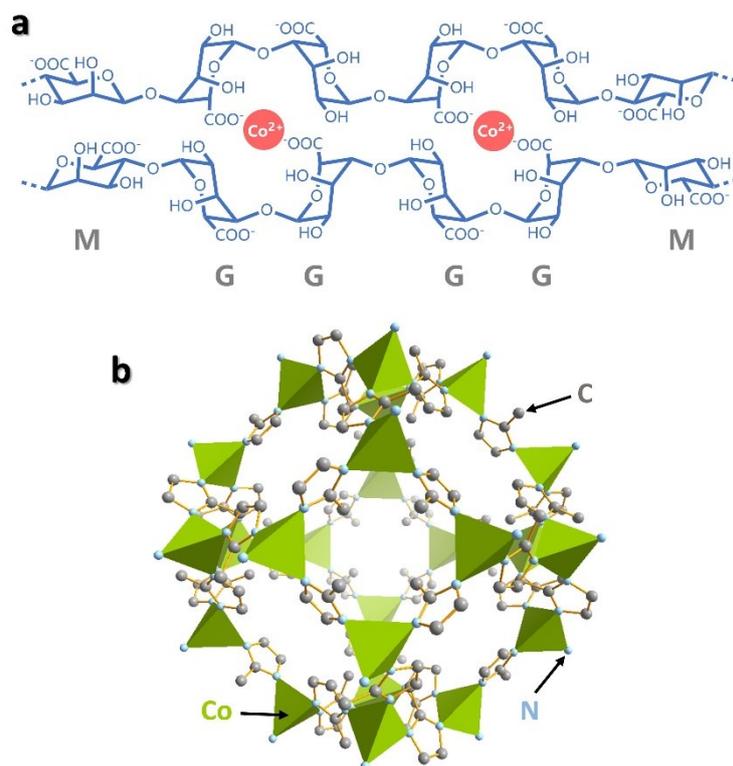
Fig. S1 (a) The chain structure of CoA fiber. (b) The chemical structure of ZIF-67.
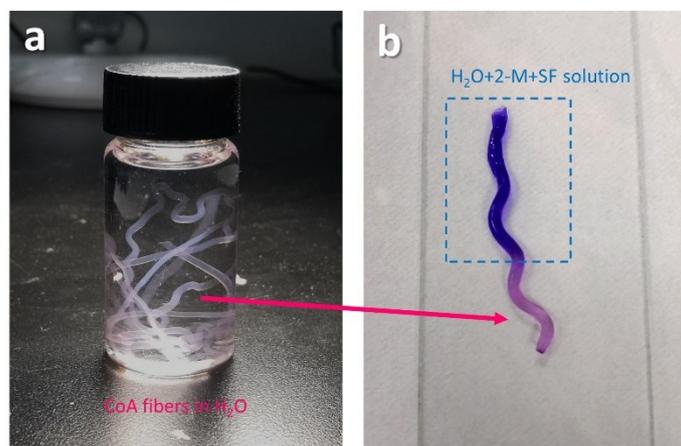
Fig. S2 (a) The photograph CoA fibers in H_2O. (b) the photograph of CoA fiber partly immersed in water solution containing 2-methylimidazolate (2-M) and sodium formate (SF) for the 30s.
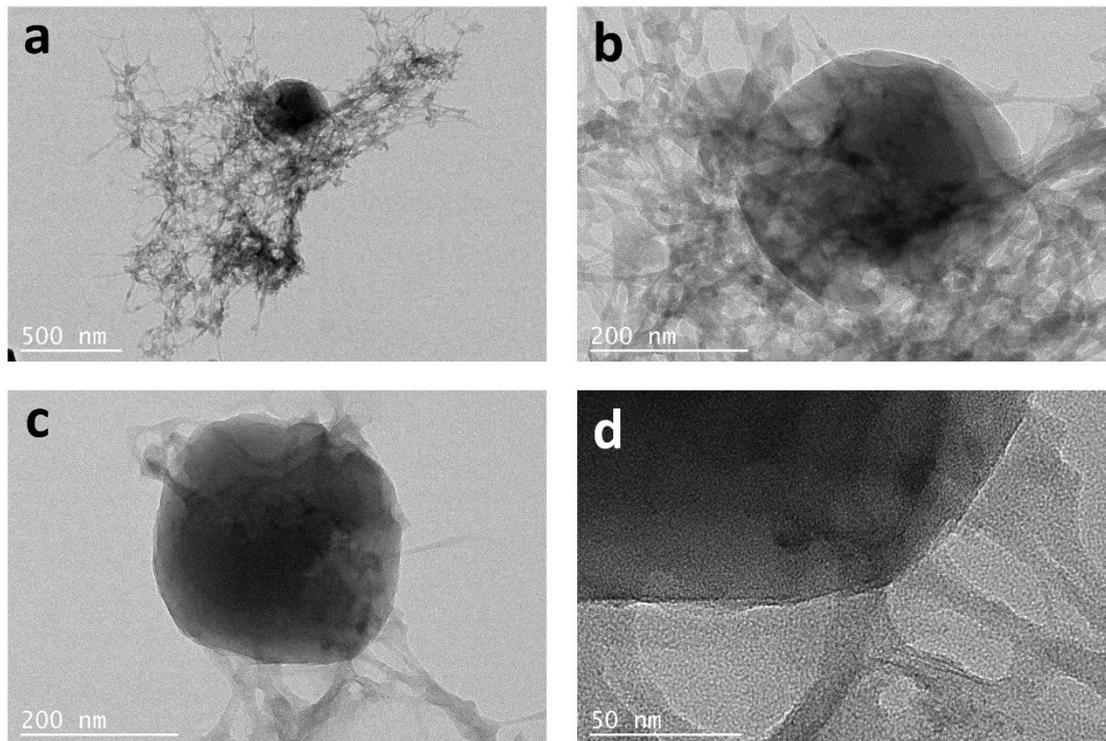
Fig. S3 TEM images of the A-ZIFst tube.
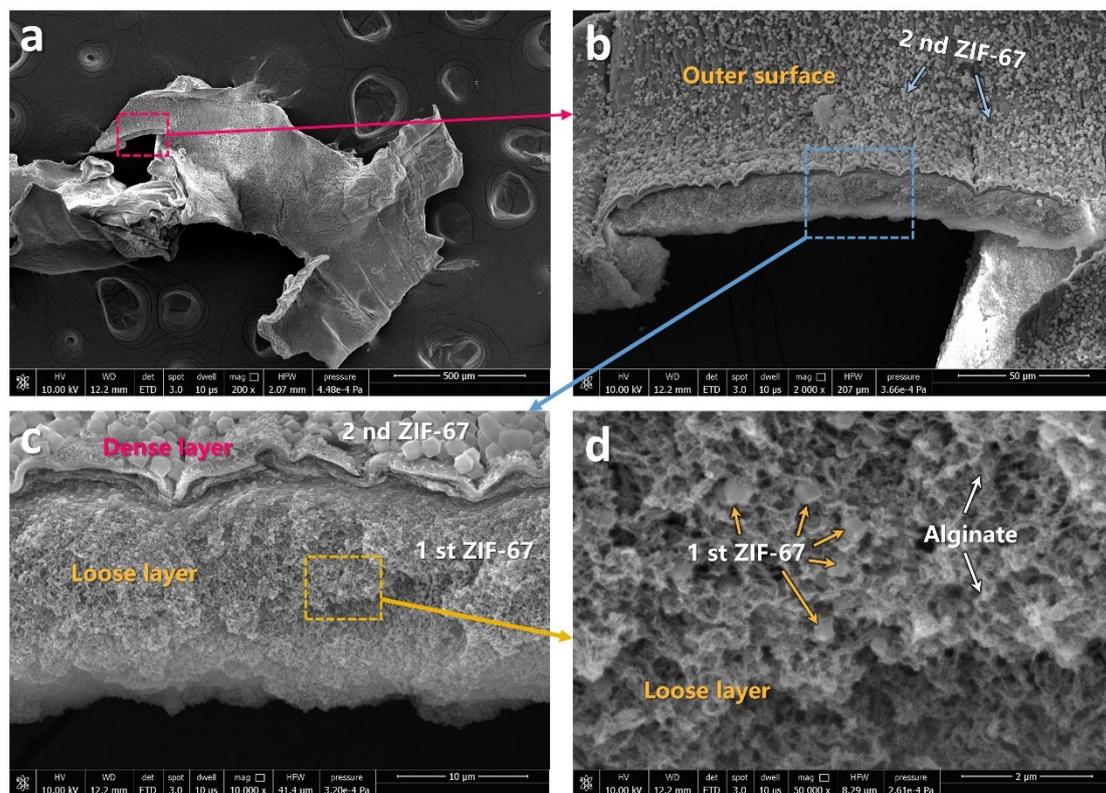
Fig. S4 (a) SEM image of the broken A-ZIF4 tube. (b-d) The cross-section of the tube wall. The difference between the outer dense layer with big 2 nd ZIF-67 particles and the inner loose layer containing small 1 st ZIF-67 particles is easy to distinguish.
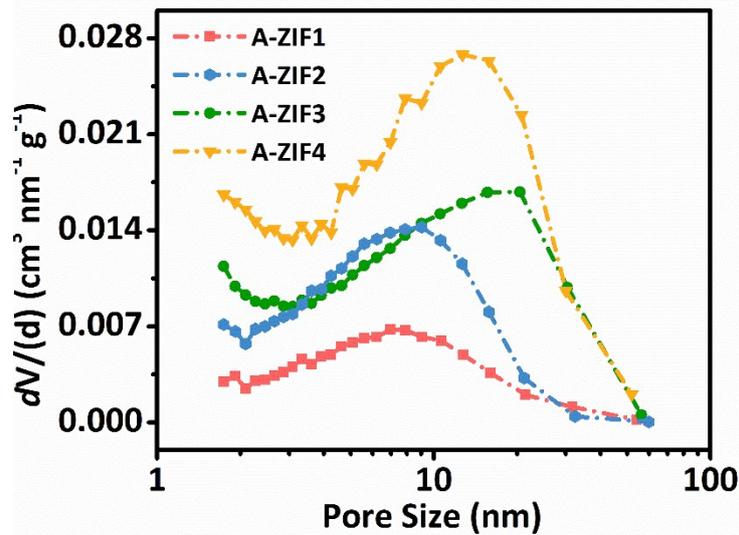
Fig. S5 The pore size distribution.
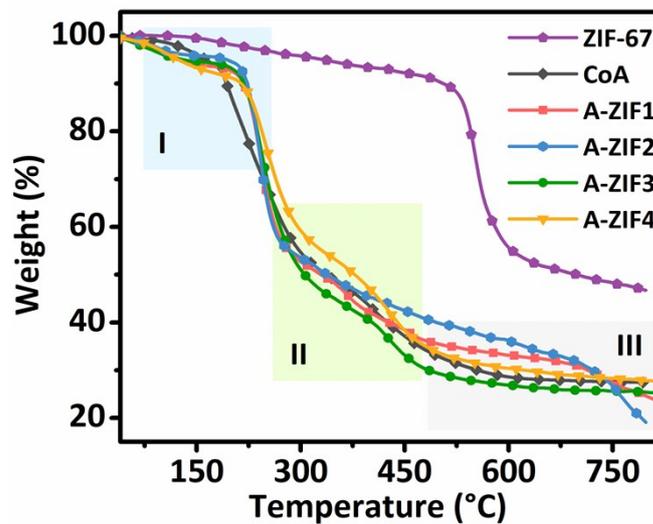
Fig. S6 The TGA curves of ZIF-67, CoA, and A-ZIF in N_2.

The ZIF-67 has good thermal stability, which could extend the first decomposition step of A-ZIF to 220 °C.[1] The second degradation step is mainly caused by the dehydration of alginate and the formation of the intermediate materials.[2] When the temperature increases to 475 °C, the weight loss is associated with the pyrolysis of ZIF-67 and intermediate materials. For A-ZIF1 and A-ZIF2, the last weight loss from 750 °C should be attributed to the big ZIF-67 particles and the firm alginate, which delay the decomposition of carbonates arising from the SF and the generation of Co_2O_3.[3]
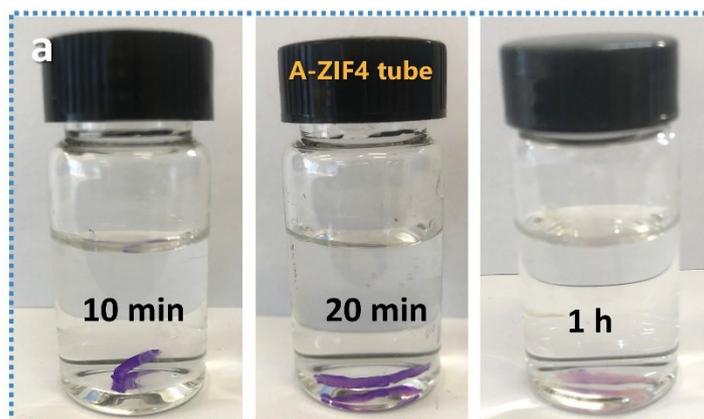
Fig. S7 The photograph of A-ZIF4 tube in water for 10 min, 20 min, and 1 h.

The disappearance of ZIF-67 particles in the water-treated A-ZIF4 tube was mainly caused by the lack of cations in alginate, which drives the decomposition of ZIF-67. The alginate would bind with the Co^{2+}, producing the pink cobalt alginate hydrogel.
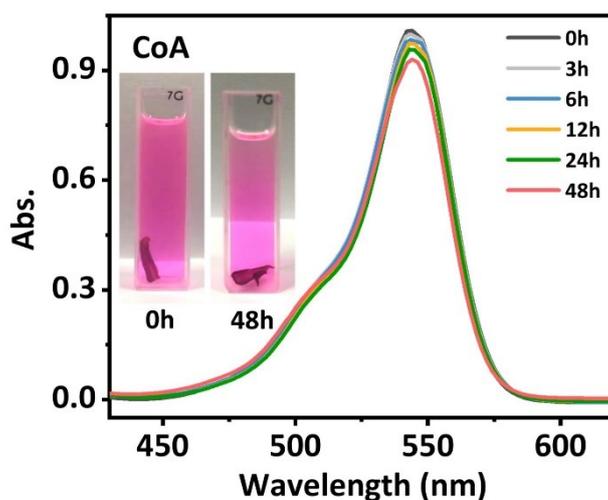
Fig. S8 The UV-Vis absorption spectra of Rhodamine B by adsorption on CoA at a given time.

References

1   J. Meng, C. Niu, L. Xu, J. Li, X. Liu, X. Wang, Y. Wu, X. Xu, W. Chen, Q. Li, Z. Zhu, D. Zhao and L. Mai, *J. Am. Chem. Soc.*, 2017, **139**, 8212-8221.

2   Y. Wang, X. Yang, H. Peng, F. Wang, X. Liu, Y. Yang and J. Hao, *ACS Appl. Mater. Interfaces*, 2016, **8**, 9925-9935.

3   L. Wang, Z. Wang, L. Xie, L. Zhu and X. Cao, *ACS Appl. Mater. Interfaces*, 2019, **11**, 16619-16628.