

Supplemental Information

Superhydrophobic Zeolitic Imidazolate Framework ZIF-90 with High Steam Stability for Efficient Recover of Bioalcohols

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Experimental details:

Chemicals were used as received: Imidazole-2-carboxyaldehyde (ICA, >99%, Alfa Aesar), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (>99%, Merck), sodium formate (99.99% metals basis, Aladdin), methanol (>99.5%, Sinopharm Chemical Reagent Co. Ltd), diethyl ether (>99.7, Sinopharm Chemical Reagent Co. Ltd), 2,3,4,5,6-Pentafluorobenzonitrile (>99%, Sigma-Aldrich), $\text{BH}_3 \cdot \text{THF}$ (1.0 M, Sigma-Aldrich), THF (anhydrous, >99.9%, Sigma-Aldrich), HCl (>99%, Aladdin), NaOH (>97%, Aladdin), Na_2SO_4 (>99%, Aladdin), ethanol (>97%, Aladdin).

Preparation of pentafluorobenzylamine: Pentafluorobenzylamine was synthesized according to the chemical reaction shown in **Fig. S2** with the procedure reported elsewhere with minor modification.¹ Typically, $\text{BH}_3 \cdot \text{THF}$ (1 M; 25 ml, 25 mmol) was carefully added into pentafluorobenzonitrile (1 g, 5.18 mmol) anhydrous THF (80 ml) solution in a round bottom flask at 293 K under stirring condition. Then the resulting mixture was refluxed (373 K) and stirred for 10 h. After reaction, the mixture was cooled to 273 K, and 2.6 M HCl (100 ml) was carefully added into the mixture. And then, the resulting mixture was continued to reflux for 1 h. The resultant solution was evaporated under vacuum to remove THF with conventional rotary evaporation method. Excessive HCl solution was added to the residue and then extracted with diethyl ether (200 ml) for 3 times. The water phase was treated with 10% NaOH aqueous until the pH reached to 10 ~ 11, and then extracted with excessive diethyl ether (100 ml) for 3 times. The combined organic phase was washed thoroughly with sodium chloride solution, and then dried over with Na_2SO_4 . The solvent was removed under vacuum and light yellow liquid was obtained, which was used without further purification. The formation of pentafluorobenzylamine was confirmed by fourier transform infrared (FT-IR) spectroscopy and ^1H -NMR nuclear magnetic resonance (NMR) spectroscopy. The FT-IR spectroscopy was achieved in the absorbance mode in a Bruker Tensor 27 spectro photometer. The NMR spectroscopy was obtained at ambient temperature using a Bruker 400 MHz instrument (NMR

Switzerland Bruker 400MHz AVANCE III). The signals are presented relative to TMS as 0 ppm, and CDCl₃ was used for solvent.

Synthesis of ZIF-90: ZIF-90 crystals were synthesized by solvothermal method in a Teflon-lined autoclave according to the procedure reported elsewhere.² Normally, a solid mixture of 0.296 g (1.00 mmol) zinc nitrate hexahydrate, 0.384 g (4.00 mmol) imidazole-2-formaldehyde and 0.068 g (1.00 mmol) sodium formate was dissolved in 40 ml methanol by ultrasonic treatment. The as-prepared solution was placed in a Teflon-lined stainless steel autoclave, and heated at 85 °C in an air-circulating oven for 24 h. After solvothermal reaction and cooling to 20 °C, the ZIF-90 crystals was filtered and washed with methanol three times, and then dried in air for 24 h at room temperature.

Synthesis of superhydrophobic ZIF-90: The as-synthesized ZIF-90 crystals (0.15 g, 0.59 mmol) and 10 mL pentafluorobenzylamine (0.347g, 1.76 mmol) were suspended in methanol solution, and refluxed at 100 °C for 24 h. And then the solid was filtered and washed with fresh methanol (20 mL) three times to obtain superhydrophobic ZIF-90 crystals. Finally, the superhydrophobic ZIF-90 crystals were dried under vacuum (10^{-2} Torr) for 24 h at room temperature.

Characterization of as-synthesized ZIF-90 and superhydrophobic ZIF-90: The morphology of the as-synthesized ZIF-90 and superhydrophobic ZIF-90 was characterized by field emission scanning electron microscopy (FESEM). FESEM micrographs were taken on an S-4800 (Hitachi) with a cold field emission gun operating at 4 kV and 10 μ A. The phase purity and crystallinity of the as-synthesized ZIF-90 and superhydrophobic ZIF-90 was confirmed by X-ray diffraction (XRD). The XRD patterns were recorded at room temperature under ambient conditions with Bruker D8 ADVANCE X-ray diffractometer with Cu K α radiation at 40 kV and 40 mA. FT-IR spectra of the as-synthesized ZIF-90 and superhydrophobic ZIF-90 were obtained by using Bruker TENSOR27 Impact spectrometer. The superhydrophobic performance of the as-synthesized ZIF-90 and superhydrophobic ZIF-90 was evaluated by water contact angle (CA). The water contact angle was measured with a Dataphysics OCA20 contact-angle system at room temperature under ambient conditions. Water droplets (about 5 μ L) were dropped

carefully onto the surface of the as-synthesized ZIF-90 and superhydrophobic ZIF-90 crystals. The contact angle value for each sample was obtained by measuring four different positions of the same sample and averaging them to get the final contact angle value.

Thermal and hydrothermal stability measurement of the as-synthesized ZIF-90 and superhydrophobic ZIF-90: The thermal stability of the as-synthesized ZIF-90 and superhydrophobic ZIF-90 was measured by Thermogravimetric analyses (TGA). TGA was carried out using a Mettler Toledo TGA/STDA 851e. Samples (10 mg) placed in 70 μ L alumina pans were heated in an air flow from 0 to 900 $^{\circ}$ C with a heating rate of 5 $^{\circ}$ C/min.

The as-synthesized ZIF-90 and fluorinated ZIF-90 crystals were boiled in water for testing their thermal stability. The as-synthesized ZIF-90 and fluorinated ZIF-90 crystals (0.06 g) were respectively added into water (1 g), and then were placed in a Teflon-lined stainless steel autoclave and heated at 100 $^{\circ}$ C in an air-circulating oven for 24 h. After the treatment in boiling water, the as-prepared ZIF-90 and fluorinated ZIF-90 crystals were separated by filtration.

Adsorptive separation of alcohols/water mixture by using the as-synthesized ZIF-90 and superhydrophobic ZIF-90: To evaluate the adsorption capacity of the as-synthesized ZIF-90 and superhydrophobic ZIF-90 for the recovery of alcohols from alcohol/water mixtures, the as-synthesized ZIF-90 and superhydrophobic ZIF-90 powders (0.2 g) were added into 10 wt% ethanol/water mixture (5.0 g) which was dyed by red oil for clarity, and then keeping stirring for 2 h. After a following selective adsorption of ethanol for 20 h, the as-synthesized ZIF-90 and superhydrophobic ZIF-90 powders which have adsorbed ethanol were separated by a simple filtration. After filtration, the obtained supernatants was analyzed by liquid chromatography to determine the relative content of ethanol. Before and after adding the superhydrophobic ZIF-90 powders, the compositions of the alcohol/water mixture were analyzed by gas chromatography (GC-1690T, Jiedao). The alcohol removal percentage was used to evaluate the adsorptive separation performance of the the superhydrophobic ZIF-90. The alcohol removal percentage was calculated using the following equation:

$$R_{alcohol} = \left(1 - \frac{Wt(alcohol)_{final}}{Wt(alcohol)_{initial}}\right) \times 100\%$$

Where $Wt(alcohol)_{initial}$ and $Wt(alcohol)_{final}$ are the initial alcohol weight and final alcohol weight of the alcohol/water mixture, respectively.

Reference

- 1 B. Kumar Das, N. Shibata and Y. Takeuchi, *J. Chem. Soc. Perkin Trans*, 2002, **1**, 197–206.
- 2 Q. Liu, N. Wang, J. Caro and A. Huang, *J. Am. Chem. Soc.*, 2013, **135**, 17679-17682.

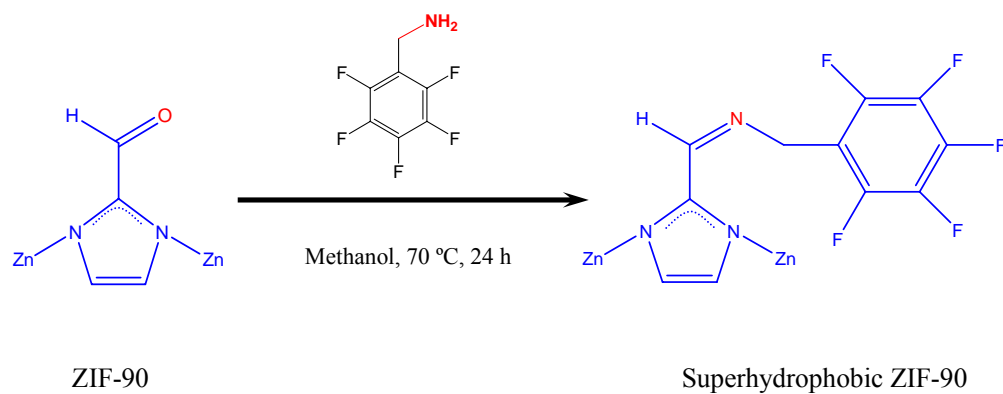


Fig. S1. Schematic diagram of covalent post-functionalization of ZIF-90 via imines condensation reaction to prepare superhydrophobic ZIF-90.

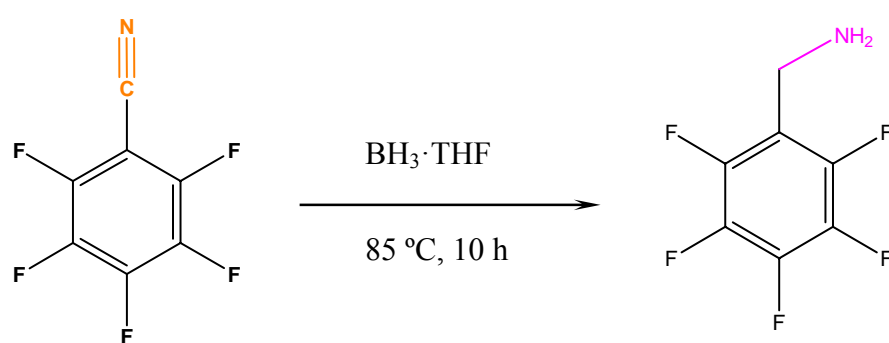


Fig. S2. Schematic diagram of the preparation of pentafluorobenzylamine.

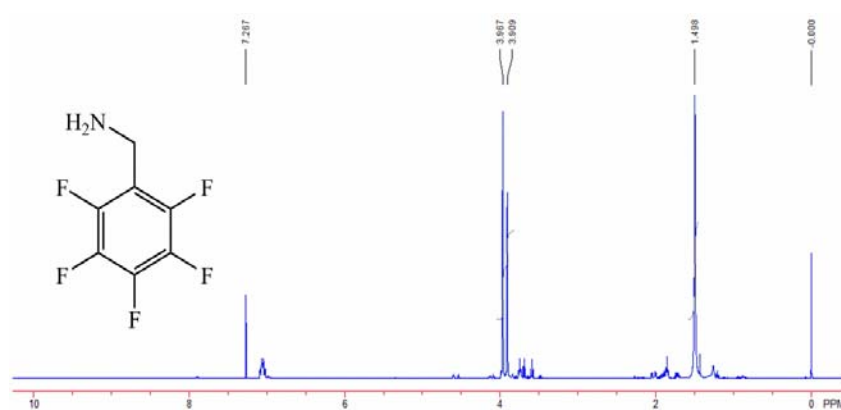
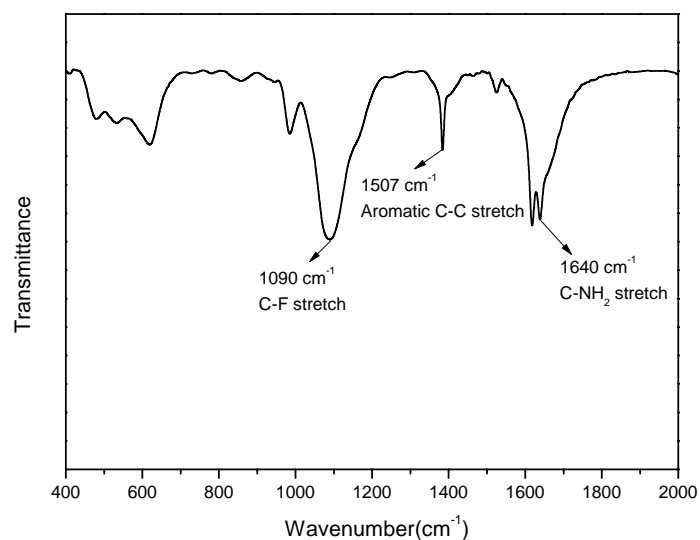


Fig. S3. (a) FT-IR spectra of pentafluorobenzylamine amino stretch at 1640 cm^{-1} , C-F (aromatic) covalent bond at 1100 cm^{-1} highlighted for clarity, (b) ^1H NMR spectrum for the as-synthesized pentafluorobenzylamine (400 MHz, CDCl_3 , 298K, TMS): 7.26 ppm (2H, s, CDCl_3), 3.96 ppm (2H, s, ArCH_2), 1.50 ppm (2H, s).

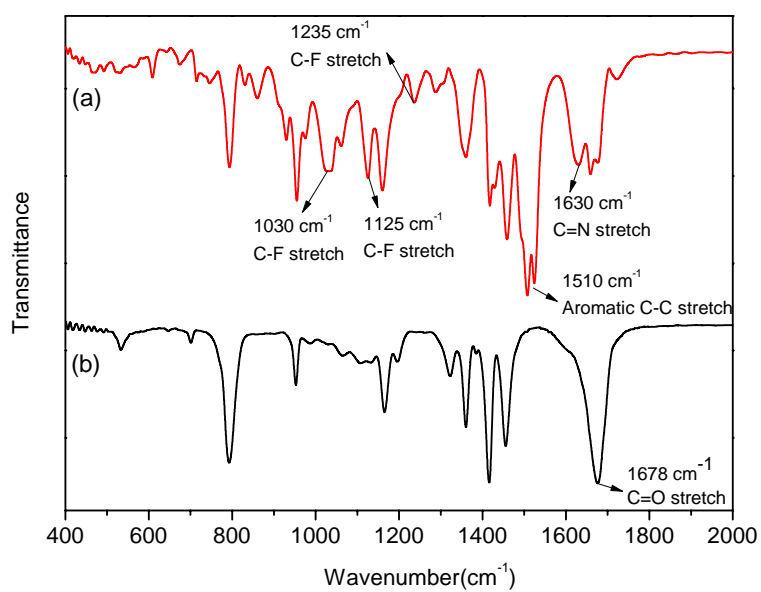


Fig. S4. FT-IR spectrums of the as-prepared ZIF-90 (a) and superhydrophobic ZIF-90 (b).

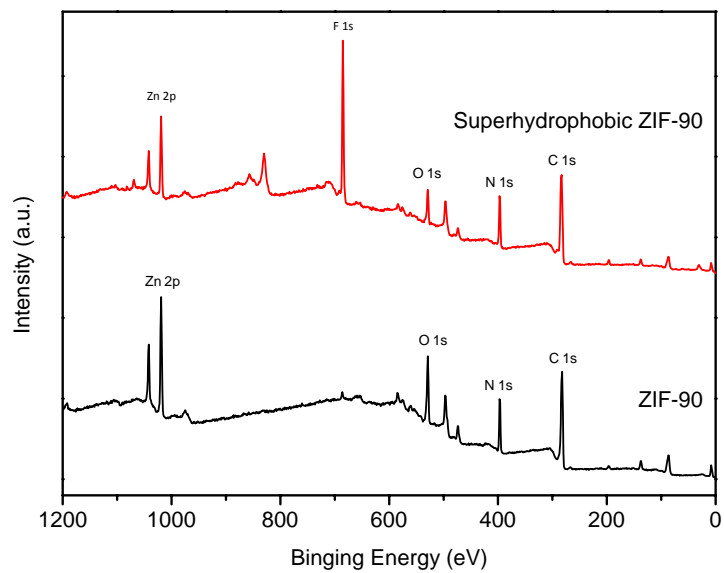


Fig. S5. XPS spectra of the ZIF-90 and superhydrophobic ZIF-90.

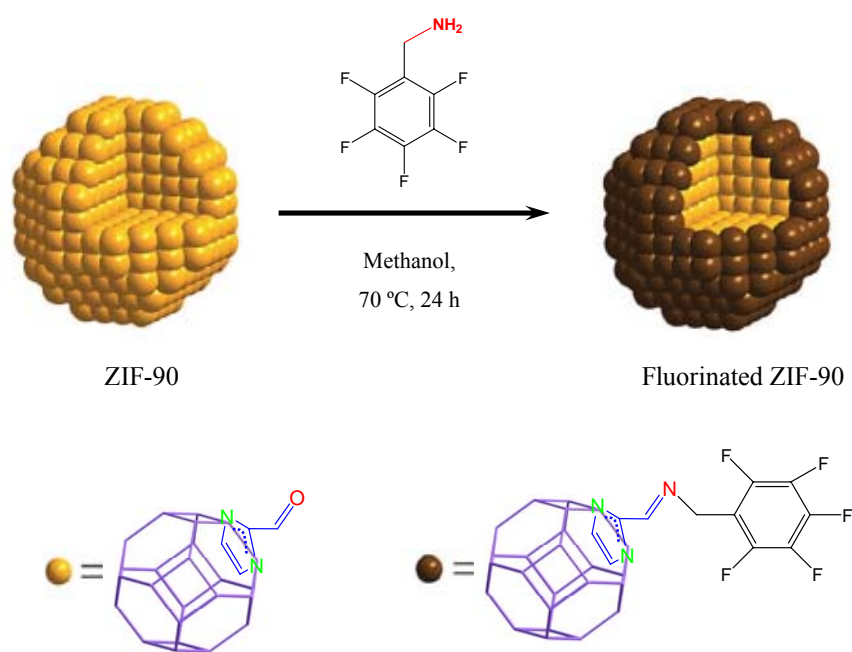


Fig. S6. Schematic diagram of covalent post-functionalization of ZIF-90 at the external surface of ZIF-90 crystals (X. Liu, et al., Chem. Commun., 2013, 49, 9140).

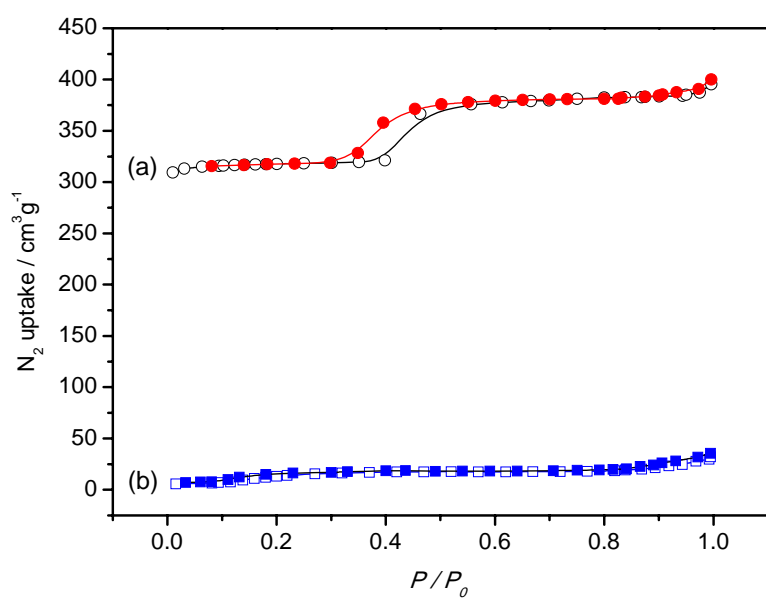


Fig. S7. N₂ isotherms for the as-synthesized ZIF-90 (a) and superhydrophobic ZIF-90 (b) measured at 77 K. Open and filled circles represent adsorption and desorption branch, respectively.

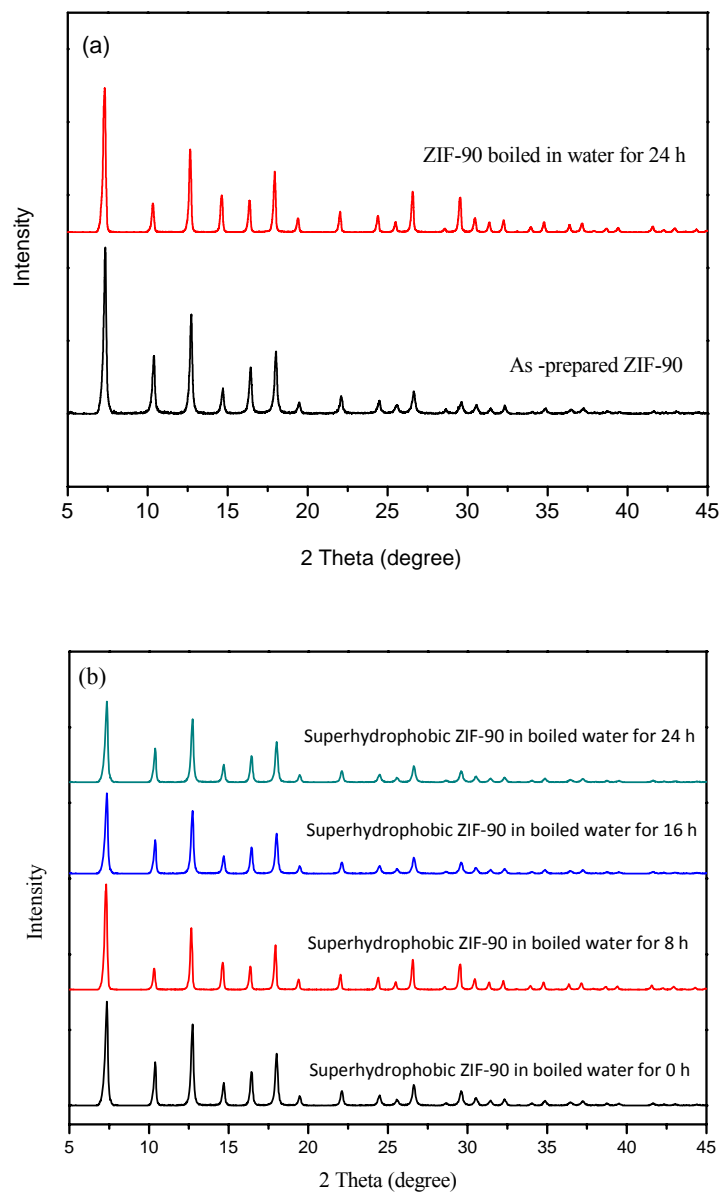


Fig. S8. XRD patterns of the as-prepared ZIF-90 before or after being boiled in water for 24 h (a), and superhydrophobic ZIF-90 after being boiled in water for different time (b).

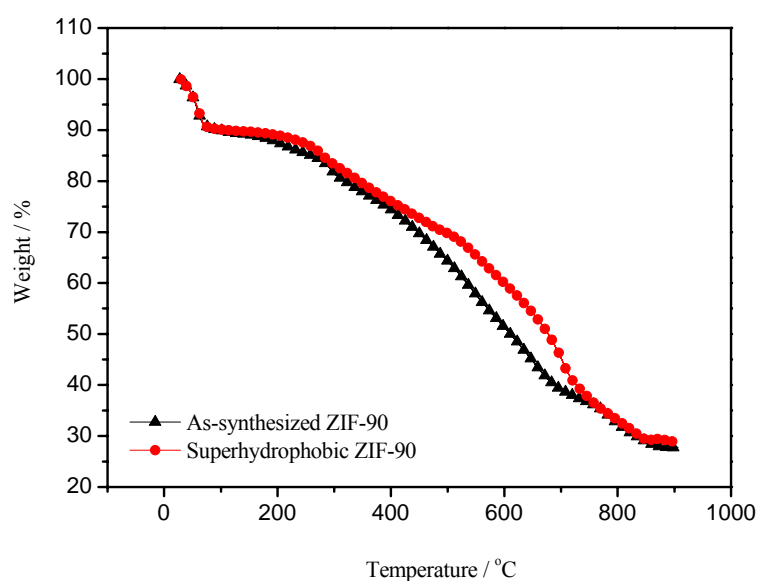


Fig. S9. TGA trace of the as-synthesized ZIF-90 and superhydrophobic ZIF-90. The initial weight loss 30-90 °C is due to methanol trapped within the pores. The loss of weight 20-80 °C is most likely due to strongly associated solvent within the framework.

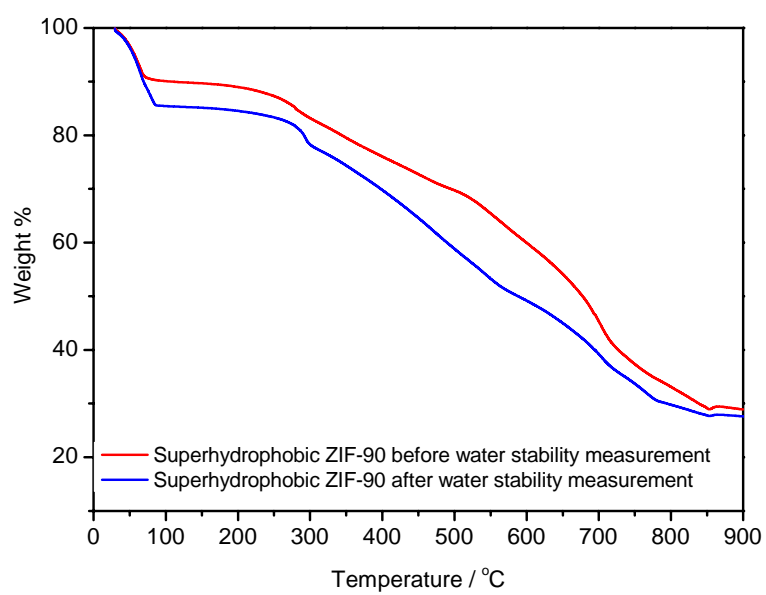


Fig. S10. TGA of the superhydrophobic ZIF-90 before and after the measurement of water stability.

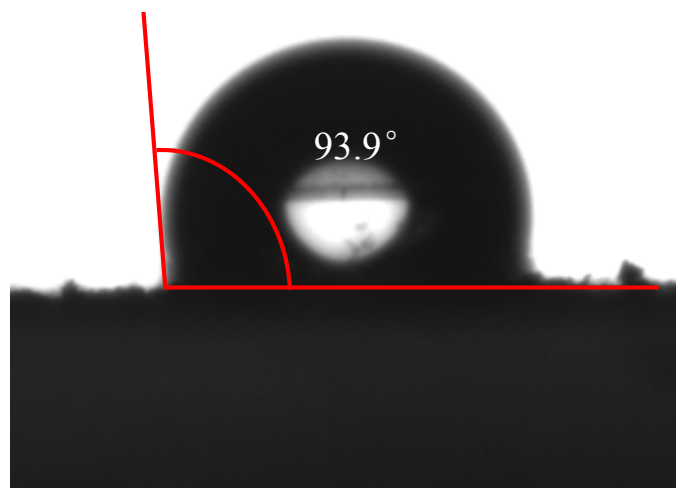


Fig. S11. Measurement of water contact angle (CA) for the as-prepared ZIF-90.

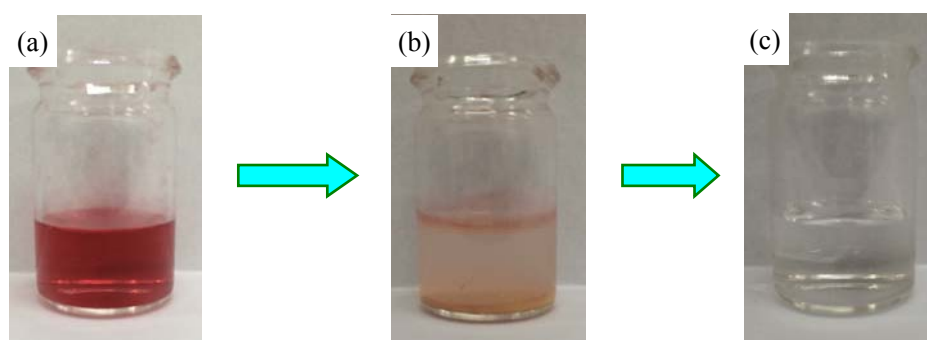


Fig. S12. Snapshots showing the adsorption and removal of ethanol (the ethanol was dyed by red oil for clarity) from 10 wt% ethanol/water solution by using the superhydrophobic ZIF-90. (a) ethanol/water solution before adding the superhydrophobic ZIF-90 particles; (b) ethanol/water solution after adding the superhydrophobic ZIF-90 particles and standing for 20 h at 20 °C; (c) ethanol/water solution after filtering and removing the superhydrophobic ZIF-90 particles which have adsorbed ethanol.

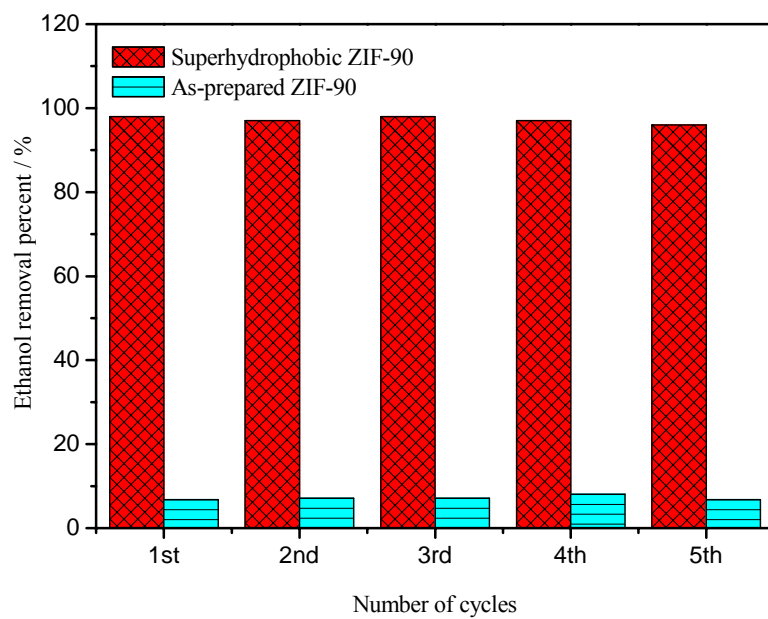


Fig. S13. Comparison of ethanol removal percent between the superhydrophobic ZIF-90 and as-synthesized ZIF-90.

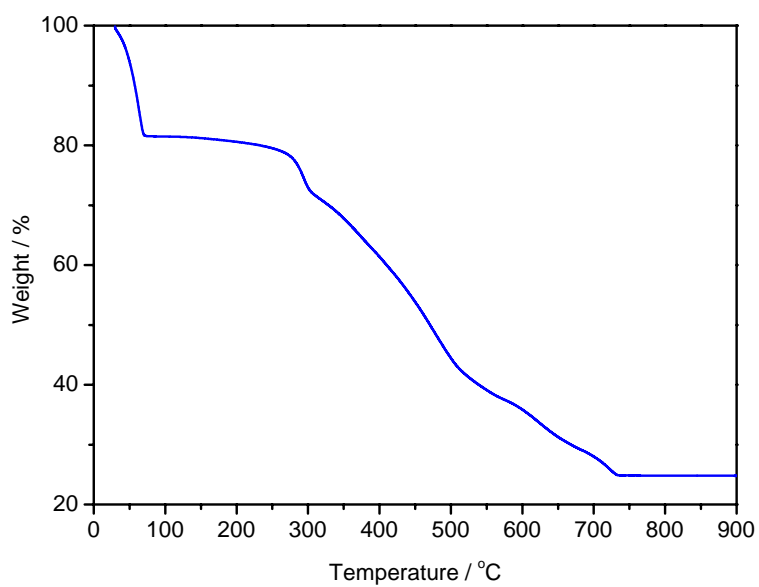


Fig. S14. TGA trace of the superhydrophobic ZIF-90 which has fully adsorbed ethanol.

Table S1

Table S1. Element composition of the ZIF-90 and superhydrophobic ZIF-90.

Samples	Element composition (Wt%)				
	Zn	F	O	N	C
ZIF-90	23.22	0	15.23	14.55	47
Superhydrophobic ZIF-90	13.87	24.55	5.39	12.78	43.4