Supporting Information

MOFs synthesized in ionothermal method coping with leaching problem of IL-polymer composite membrane

Experimental Section

Materials

Zn $(NO_3)_2\cdot6H_2O$ (>98%, Sigma-Aldrich), 2-Methylimidazole (>99%, Acros Organics), Choline hydroxide (45% wt. % in water, TCI), Ethanol (Fischer Scientific), PVA (99% hydrolyzed, average Mw = 86,000–89,000, Sigma-Aldrich).

Synthesis of ZIF-8 nanocrystals in ionothermal method

Zinc nitrate (0.76g) and 2-methylimidazole (0.4g) were slowly added into choline hydroxide (10 ml) and stirred for about 2 hours at room temperature. After centrifuging and overnight drying, ZIF-8 nanocrystals were obtained.

Preparation of ZIF-8 and PVA composite membranes in situ crystallization method

PVA was fully dissolved in water to make a 10% solution at 90℃ (10 ml). Zinc nitrate (0.76g) and Hmim (0.4g) were slowly added into choline hydroxide (10 ml) to make ZIF-8 precursor. Different amount of precursor solution was slowly added into PVA solution. During stirring, the color of the solution changed from clear to white. This mixture was stirred for about 4 hours at room temperature. After removing the air under vacuum, the solution was poured into glass panes, water was evaporated at 60ºC. When visually dry, the membrane was peeled off from the glass substrate

and washed repeatedly with distilled water to remove unreacted reactants. A series of composite membranes were obtained named PVA-ZIF8-x (6, 13, 28, 48), x was the weight percentage ratio of the ZIF-8 nanoparticles to the composite membrane. We didn't mention composite membrane with more contents of ZIF-8, because the membrane is easy to be broken when ZIF-8 precursor was added more.

Structure characterization

The crystalline structures of ZIF-8 nanocrystals were determined by the X-ray diffraction (XRD) measurements using a Siemens D5005 diffractometer with Cu-Kα radiation (λ=1.5418 Å). The size and morphology of ZIF-8 nanocrystals were monitored by transmission electron microscope (TEM, JEOL 2000FX), operated at the accelerating voltage of 300 kV, morphology of composite membranes was tested by field-emission scanning electron microscope (FE-SEM: JEOS JSM 6700F). Fourier transform infrared (FT-IR) spectroscopy was performed using a Nicolet Impact 410 spectrometer. The samples were dispersed in dry KBr disks and measured over the range of 4000 to 500 cm^{-1}. The X-ray photoelectron spectroscopy (XPS) spectra were acquired using a Scienta ESCA200 spectrometer. N2 adsorption measurements were conducted on an ASAP 2010M porosimeter at 77K.

Hydroxide conductivity

Two-probe a.c. impedance spectroscopy was performed to explore the properties of the materials in anion conducting from 0.1 Hz to 100 kHz, 10 mV AC perturbation and 0.0 V DC rest voltage using a Princeton Applied Research Model 273A Potentiostat (Model 5210 frequency response detector, EG&G PARC, Princeton, NJ). Composite membranes were cut into square with a side length of 1cm. The hydroxide conductivity was calculated by the following formula:

$$\sigma = \dfrac{L}{RA}$$

(1)

where σ is the conductivity, L is the distance between the electrodes used to measure the potential,

R is membrane resistance and A is cross-sectional area of membrane.

Mechanical properties

The mechanical properties of the thin dry membranes were evaluated at room

temperature on SHIMADZU AG-I 1KN at a speed of 2 mm min^{-1}. The size of the samples was 15 mm

× 4 mm. Each sample was tested at least four times to reach an average value.
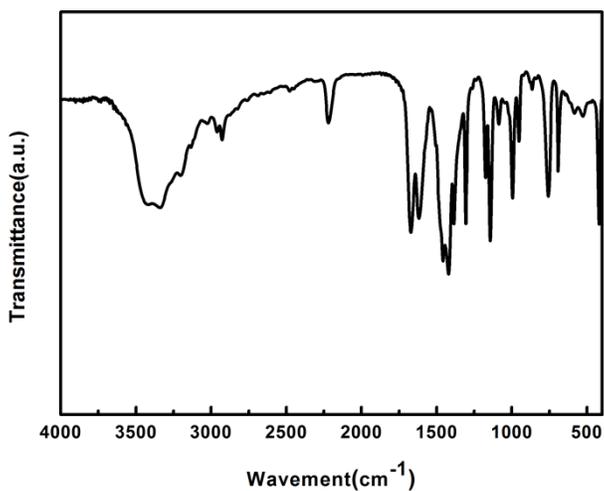
Fig. S1 FT-IR spectrum of the as-synthesized ZIF-8 samples
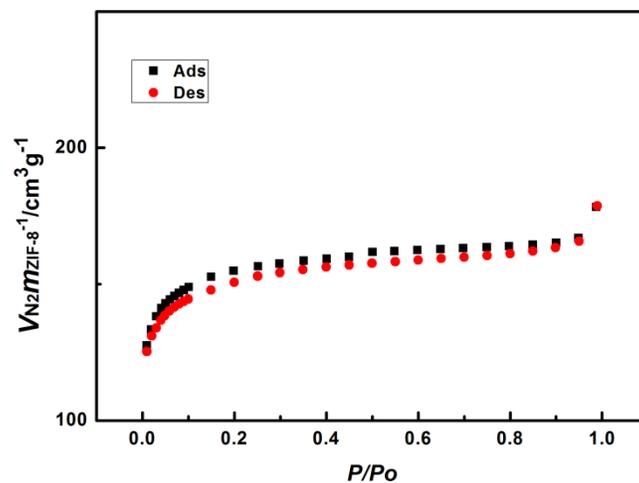
Fig. S2. N_2 adsorption (black symbols) and desorption (red symbols) isotherms of as-synthesized ZIF-8 at 77K.

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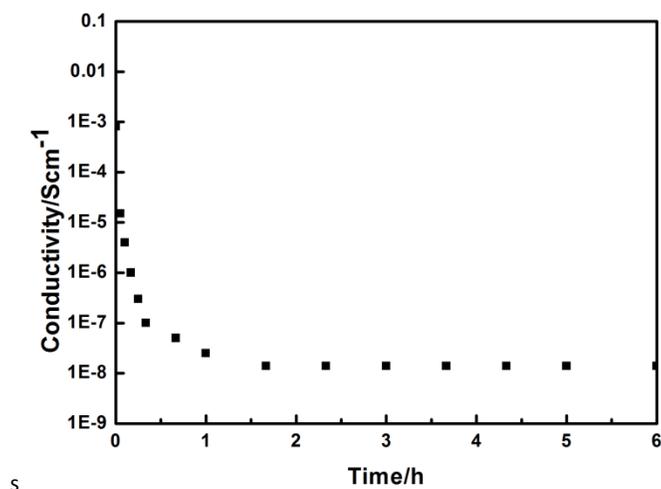
Fig. S3 Conductivities of the composite membrane with ZIF-8 fillers synthesized in methanol immersed in water for

different time
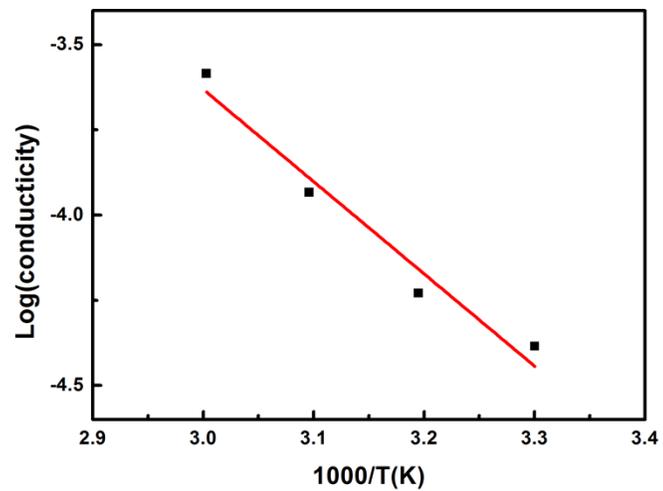
Fig. S4 Arrhenius-type plot of the conductivity of the PVA-ZIF8i-48 composite membrane at various temperatures