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Facile synthesis of a continuous thin $Cu(bipy)_2(SiF_6)$ membrane with selectivity towards hydrogen†

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$Cu(bipy)_2(SiF_6)$ is a highly porous metal–organic framework (MOF) and represents a prototypal "pillared sheet" platform offering opportunities to control the pore sizes. Its structural features, low cost and facile synthesis make it a great candidate to fabricate membranes for gas separation. The key to obtaining thin, continuous $Cu(bipy)_2(SiF_6)$ membranes is to control the $Cu(bipy)_2(SiF_6)$ crystal growth and enhance the binding between membrane and substrate. Here we explored a new route by direct synthesis and successfully obtained a continuous thin $Cu(bipy)_2(SiF_6)$ membrane on a macroporous glass-frit disk with high robustness. It is speculated that the SiF_6^{2-} used to construct the $Cu(bipy)_2(SiF_6)$ membrane came from the fluorinated substrate. The $Cu(bipy)_2(SiF_6)$ membrane shows the separation factors of H_2–CO_2, H_2–CH_4 and H_2–N_2 are 8.0, 7.5, and 6.8 respectively at 293 K and 1 bar with H_2 permeance of 2.7×10^{-7} mol m^{-2} s^{-1} Pa^{-1} as well as high thermal stability. We expect to explore more membranes of $Cu(bipy)_2(SiF_6)$ analogues with tuneable pore sizes using this route and to obtain membranes with higher gas separation performance.

Introduction

Metal–organic frameworks (MOFs), also known as porous coordination polymers (PCPs), as novel crystalline microporous materials have received much attention in the past decades due to their potentially useful properties in gas storage, selective molecular separation, and heterogeneous catalysis.[1,2] MOFs usually have diverse structures which are typically comprised of metal atoms or metal clusters coordinated to multi-functional organic ligands.[3,4] Their adjustable pore size, large porosity, and specific adsorption affinities make them candidates for fabrication of membranes for gas separation.[5–7] However, it still remains a challenge to prepare a continuous MOF membrane for practical gas separation applications, which requires the membranes to have high fluxes, high selectivities, stability, and large-scale facile synthesis as well as a low cost.[8,9] Accordingly, the MOFs with high porosity, suitable pore size, specific inner surface are favorable to be membranes with high gas fluxes and selectivities. Moreover, the stability to various environmental conditions, easy conditions to form and grow together, and low cost of MOFs are also preferred to fabricate a MOF membrane for practical gas separation applications. For instance, $Cu_3(BTC)_2$ is frequently seen as a membrane for gas separation due to its structural features, intergrowth properties and sorption properties.[5,10–12] Zeolitic imidazolate frameworks (ZIFs) which are with exceptional stability and adjustable pore sizes were commonly fabricated into membranes to separate H_2 from other bigger gas molecules.[13–19] $Cu(bipy)_2(SiF_6)$ (bipy = 4,4′-bipyridine) is a highly porous metal–organic framework (MOF) and represents a prototypal "pillared sheet" platform offering opportunities to control the pore sizes, which was firstly reported as one of the best sorbents for CH_4 in 2000.[20] The pore sizes of its Zn analog could be controlled from ultramicroporous to mesoporous dimensions.[21–23] Recently Zaworotko *et al.* reported the exhibition of highly selective CO_2 uptake over CH_4 and N_2 by $Cu(bipy)_2(SiF_6)$ for a MOF material that relies upon physisorption.[24] They also showed the optimal adsorption thermodynamics and kinetics for CO_2 separation by this kind of pillared material.[25,26] Additionally, the low cost and facile synthesis of these materials provide great potential in practical applications. The absence of open metal sites in their structures makes it easy to regenerate their porous structures and avoid the likelihood of high affinity toward H_2O. Therefore, these kinds of pillared MOF materials are great candidates for the fabrication of membranes for gas separation. However, to

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the best of our knowledge, so far no membranes by these kinds of MOFs have been prepared.

Owing to the low mechanical resistance, MOF membranes for gas separation are required to be fabricated on porous substrates such as metal nets, porous alumina, hollow ceramic fibers *etc.*[8] Usually, nano- or micro-crystals are used for the secondary growth which is from the zeolite membrane fabrication in order to control the crystal growth on the substrate surface. Seeds in the MOF membrane fabrication are also used because of the poor heterogeneous nucleation of many MOF crystals on inorganic supports.[27] However, $Cu(bipy)_2(SiF_6)$ is a kind of MOF that is easy to grow up but hard to obtain small crystals suitable as seeds to grow thin membranes. Compared to secondary growth, direct synthesis is considered to be more powerful and facile with apparent simplicity, in which the preparation and deposition of seed crystals were eliminated and this is significant for industrial production. Thus, how to control the $Cu(bipy)_2(SiF_6)$ crystal growth and enhance the binding between membrane and substrate by direct synthesis is the biggest challenge to obtain thin, continuous $Cu(bipy)_2(SiF_6)$ membranes for gas separation. There are some pretreatment strategies to increase the heterogeneous nucleation and obtain a continuous thin MOF membrane by direct synthesis. Our group has reported a method called "twin metal source" and demonstrated the successful fabrication of a $Cu_3(BTC)_2$ membrane on a Cu net[5] and slice,[28] and a $Zn_3(BTC)_2$ film on a Zn wafer.[29] Huang *et al.* treated a porous titania support with 2-aminopropyltriethoxysilane which was able to bind to the support surface and to act as a linker for binding of ZIF-22 crystals. They subsequently obtained a high quality ZIF-22 membrane.[14] In this study, we explored a new route and successfully obtained a continuous thin $Cu(bipy)_2(SiF_6)$ membrane on a glass-frit disk with high robustness. In this route, the glass-frit disk as a substrate was firstly modified by $(NH_4)_2SiF_6$, in which the F atom was integrated into the substructures of substrate surface. The $Cu(bipy)_2(SiF_6)$ membrane on the modified substrate was formed without a SiF_6^{2-} source after solvothermal treatment (Fig. 1). It is assumed that the limited amount of produced SiF_6^{2-} under solvothermal conditions and its source from the substrate lead to the thinness of the membrane and high binding between the membrane and the substrate.

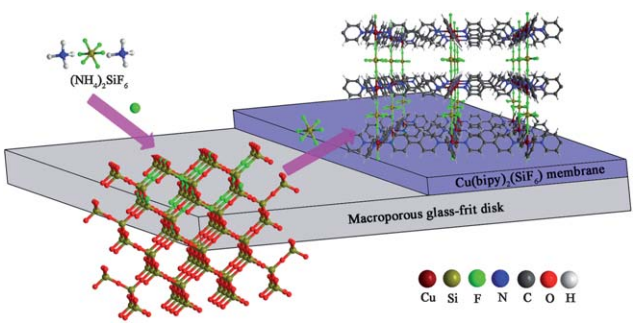

Fig. 1 Schematic diagram of the $Cu(bipy)_2(SiF_6)$ membrane fabricated on fluoridated glass-frit disk.

Experimental

Materials

Ammonium fluosilicate ($(NH_4)_2SiF_6$) and copper fluoroborate hexahydrate ($Cu(BF_4)_2\cdot(H_2O)_6$, 45% aqueous solution) were provided by Aladdin Chemistry Co. Ltd. 4,4′-bipyridine, deionized water and ethylene glycol was used as received. Macroporous glass frits (P4 or G5, 25 mm in diameter, pore size 2–4 mm) were provided by Science and Education Equipment Co. Ltd., Taixing City, China. The used supports have been polished using 1200-mesh sand paper to get a smooth surface.

Synthesis

The glass-frit disks as the substrate were treated in a solution of H_2SO_4 and H_2O_2 ($H_2SO_4 : H_2O_2 = 7 : 3$, v/v) and heated at 383 K for 5 h, and then washed with deionized water several times until the pH value of the water was about 7. The substrate was dried at 353 K and immersed in 20 mL of $(NH_4)_2SiF_6$ aqueous solution (0.1 M). The solution and substrate were transferred to a teflon-lined stainless-steel autoclave keeping the substrate perpendicular to the bottom of the autoclave. The autoclave was heated in an oven under 423 K for 22 h. After cooling to room temperature, the substrate was taken out of the autoclave, thoroughly washed with deionized water, and then dried at 353 K.

To synthesize the membrane, $Cu(BF_4)_2\cdot(H_2O)_6$ (45% aqueous solution) was diluted to 20% and 0.76888 g (5 mmol) of 4,4′-bipyridine was first dissolved in a mixed solution of 15 mL of ethylene glycol and 5 mL of deionized water. And then 3.4524 g of the $Cu(BF_4)_2\cdot(H_2O)_6$ solution and the bipy solution were mixed with stirring at room temperature for 1 h and loaded in a 30 mL teflon-lined stainless-steel autoclave. The modified glass-frit disk was placed vertically in the autoclave using a home-made teflon holder. The autoclave was heated at 358 K for 24 h. After cooling to room temperature, the substrate with the $Cu(bipy)_2(SiF_6)$ membrane on both sides was taken out of the autoclave, thoroughly washed with DMF and CH_3OH. Finally, the membrane was soaked in 100 mL of CH_3OH for 12 h which was then repeated five times every 12 h. The membrane was activated under vacuum for 7 h at 373 K to remove the solvent in the pores of the crystals before the gas separation measurement.

Characterization

X-ray diffraction (XRD) patterns were collected by a Siemens D5005 diffractometer using Cu kα radiation (λ = 1.5418 Å). Scanning electron microscopy (SEM, FE-SEM: JEOS JSM6700F) was applied to characterize the morphology of the membrane. X-ray photoelectron spectroscopy (XPS, ESCALAB250) was applied to study the surface of the substrate. To test the gas separation, the activated membrane was sealed in a membrane module which has been introduced in our earlier report.[5,30] The volume ratio of the mixture of gases was controlled by a soap film flow meter. The flow rate of the sweep gas Ar was controlled at 50 mL min^{-1}. The feed flow rate was set to 100 mL min^{-1} for the single gas measurements. The total volumetric flow in the feed for binary gas measurements was 100 mL min^{-1} with each

gas of 50 mL min^{-1}. Then the mixture gases in the feed side were introduced into one side of the membrane from the inlet and the feed pressure is measured by a pressure gauge, while the outlet is connected with a vacuum valve. By controlling the vacuum valve we can regulate the permeation pressure. The permeate component through the membrane was taken by Ar into an on-line HP6890 gas chromatograph.

Results and discussion

To prepare the $Cu(bipy)_2(SiF_6)$ membrane, the macroporous glass-frit disk was firstly treated in a solution of H_2SO_4 and H_2O_2 to remove organic impurities and activate its surface. Afterwards, the substrate was immersed in $(NH_4)_2SiF_6$ solution and hydrothermally treated. The fluoridated substrate after being washed was used to synthesize the $Cu(bipy)_2(SiF_6)$ with the mixed solution of $Cu(BF_4)_2 \cdot (H_2O)_6$ and bipy under solvothermal conditions. The blue polycrystalline $Cu(bipy)_2(SiF_6)$ membrane with uniform and continuous coverage is formed on the substrate (Fig. 2a). The membrane would turn light blue after being activated under vacuum and 373 K for 7 h. It is worth noting that the $Cu(bipy)_2(SiF_6)$ crystals were anchored very firmly on the substrate. The MOF membrane only fell off when scratched by knife (Fig. 2b).

The peak positions in the X-ray diffraction (XRD) pattern of the as-prepared membrane match well with those of the simulated pattern, indicating the phase purity and homogeneity of the prepared crystalline membrane (Fig. S1†). The relative peak intensities of the membrane indicate the random orientation of $Cu(bipy)_2(SiF_6)$ crystals. Scanning electron microscopy (SEM) was used to check the morphology of the as-prepared membrane. It can be seen in Fig. 3b and c that the membrane is defect-free and the $Cu(bipy)_2(SiF_6)$ crystals with a size less than 10 μm are merged tightly with each other. The cross-section image in Fig. 3d demonstrates the compact anchor of $Cu(bipy)_2(SiF_6)$ crystals on the substrate and the thickness of the membrane is estimated to be about 8–10 μm.

X-ray photoemission measurements (XPS) were applied to study the formation mechanism of the robust $Cu(bipy)_2(SiF_6)$ membrane. It is known that the binding energy of the XPS peaks is relevant to the ionization energy of the core electrons. A specific chemical shift in binding energy values indicates one specific chemical state. The core-level F 1s XPS spectra of the raw glass-frit disk surface, the disk treated by H_2SO_4 and H_2O_2, and the disk after treatment with $(NH_4)_2SiF_6$ as well as the $(NH_4)_2SiF_6$ powder are shown in Fig. 4. As expected, the XPS spectra of the raw substrate and that treated by H_2SO_4 and H_2O_2 show no F 1s signal. The appearance of a peak at 687.3 eV in the XPS spectra of the fluoridated glass-frit disk indicates the F atoms in the substructures of the substrate surface. The chemical shift of about 1.7 eV in binding energy between the substrate and pure $(NH_4)_2SiF_6$ powder demonstrates the difference of chemical environment of F atoms. From the results above, it is speculated that $(NH_4)_2SiF_6$ would decompose to produce F^- anions which could react with the substrate surface (mainly composed of SiO_2) under hydrothermal conditions. Additionally, the F atoms came into the SiO_2 (glass) substructures of the substrate surface. The reverse reactions would occur on the surface of the substrate under the subsequent solvothermal conditions and produce SiF_6^{2-} anions to form the $Cu(bipy)_2(SiF_6)$ crystalline layers. It is assumed that the

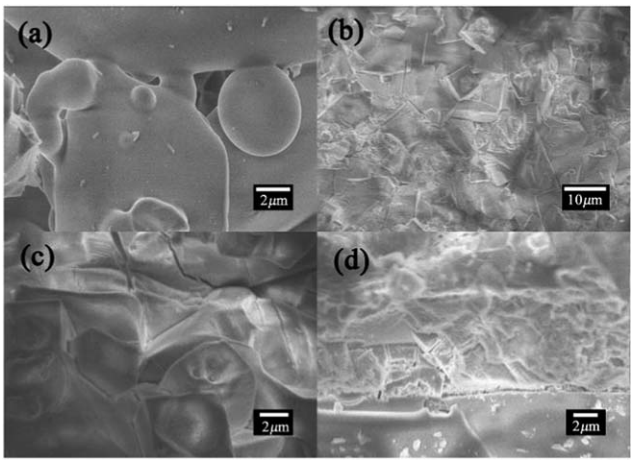

Fig. 3 SEM images of the supported $[Cu(bipy)_2(SiF_6)]$ membrane: (a) the substrate (macroporous glass-frit disk); (b and c) top-view; (d) cross-section of the MOF membrane.

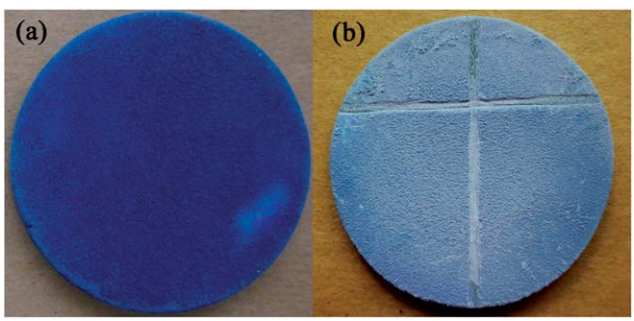

Fig. 2 Optical images of the supported $[Cu(bipy)_2(SiF_6)]$ membrane: (a) as-synthesized; (b) activated and scraped out in a cross.

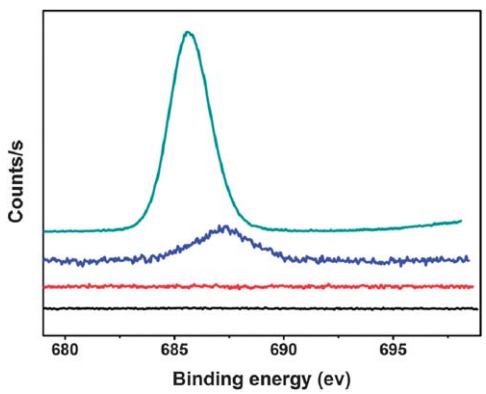

Fig. 4 F 1s XPS spectra of the raw glass-frit disk surface (black); glass frit disk treated in a solution of H_2SO_4 and H_2O_2 (red); glass frit disk treated in $(NH_4)_2SiF_6$ solution (blue); $(NH_4)_2SiF_6$ (green).

fluorination reaction to modify the substrate occurred very limitedly and could only produce a small amount of SiF_6^{2-} anions, which would lead to the thinness of the formed membrane. It can also explain the compact anchor of $Cu(bipy)_2(SiF_6)$ layers on the substrate, since the SiF_6^{2-} anions which formed the $Cu(bipy)_2(SiF_6)$ crystalline on the surface of the substrate were from the substrate.

Encouraged by the successful synthesis of the $Cu(bipy)_2(SiF_6)$ membrane, we tested the volumetric flow rates of the single gases H_2, CO_2, CH_4 and N_2 as well as the binary gases of H_2–CO_2, H_2–CH_4 and H_2–N_2 using home-made gas permeation equipment to study the gas permeability and selectivity of the membrane. The test results are summarized in Table S1.† Fig. 5a represents the permeances and separation factors at room temperature (293 K). It is found that the permeances show a decreasing trend in the order $H_2 > CH_4 \approx N_2 > CO_2$ for both single- and binary-gas permeation and the permeance of H_2 is much higher than those of the other gases. As shown in Table S1,† the ideal separation factors of H_2 and other gases, determined as the ratio of the single component permeances, are much higher than the Knudsen constant, which indicates the good quality of the membrane. However, the ideal separation factors of CO_2/CH_4 and CO_2/N_2 is only 0.90 and 0.88 respectively which are a little higher than the Knudsen constant. This result is surprising at first and very disappointing, considering the high selectivity of CO_2/CH_4 by $Cu(bipy)_2(SiF_6)$ powder samples (10.5 by IAST calculations based on the adsorption isotherms).[24] As well known, both the diffusion and adsorption will govern the permeance of small gas molecules in micropores. Therefore, the discrepancy of the permeances can be explained by the differences in the intrinsic diffusion properties of different gases and their interactions with the pore surface.[31] The permeances of the gases mentioned above in the $Cu(bipy)_2(SiF_6)$ membrane could be in contrast to the molecular sieving effect because of the large pores (7.8 Å) which is far beyond the gas molecules.[32–34] The lowest permeance of CO_2 could be explained by the higher molecular weight, and the relatively strong interaction between CO_2 and the inner surface, which would also weaken their mobility in large pores. The H_2 selectivities over CO_2, CH_4 and N_2 were confirmed by binary-gas permeation tests. The mixture separation factors of H_2–CO_2, H_2–CH_4 and H_2–N_2 are 8.0, 7.5, and 6.8 respectively (at 293 K and 1 bar) with a H_2 permeance of 2.7×10^{-7} mol m^{-2} s^{-1} Pa^{-1}. In comparison, Bux *et al.* reported a H_2/CH_4 separation factor of 11.2 for a supported ZIF-8 membrane but with relatively low fluxes (5.08×10^{-8} mol m^{-2} s^{-1} Pa^{-1}).[6] Hertäg *et al.* reported a higher selectivity of 16 through the developed ZIF-8 membrane with H_2 permeance in the same range 1.3×10^{-7} mol m^{-2} s^{-1} Pa^{-1}.[35]

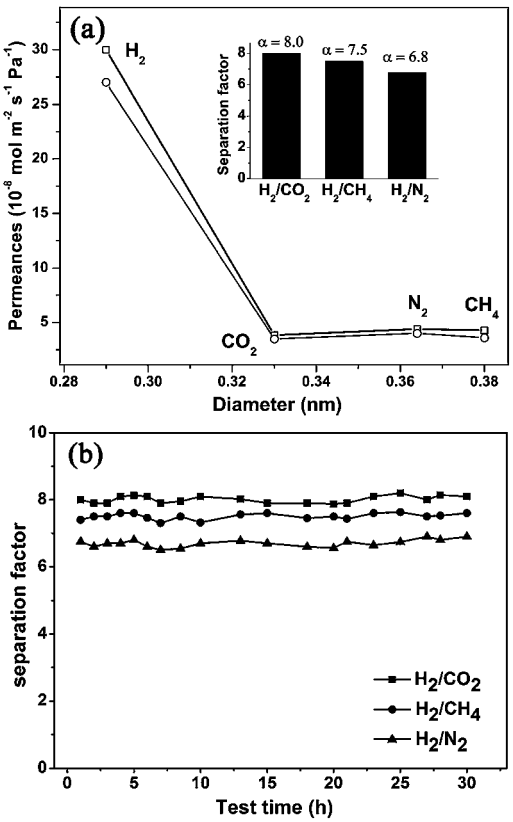

Fig. 5 (a) Single- (□) and binary- (○) gas permeances of different gases on the $Cu(bipy)_2(SiF_6)$ membrane at 293 K as a function of the kinetic diameter (inset: the separation factor for H_2 over other gases by binary gases tests). (b) Plot of H_2–CO_2, H_2–CH_4 and H_2–N_2 separation factors of the $Cu(bipy)_2(SiF_6)$ membranes (average values of five different membranes) at different test times. Permeation temperature = 293 K, feed pressure = 1×10^5 Pa.

Thermal stability is important for practical gas separation performance of membranes. The $Cu(bipy)_2(SiF_6)$ membrane was also tested in single- and binary-gas permeations at 313 K and 343 K (Table S2†). It can be found that the permeances increased when the temperatures were increased to 313 and 343 K indicating an activated diffusion process. However, a declining trend in separation factors is observed. This phenomenon which is different from the case of ZIF-7,[36] could be caused by the difference in the improved diffusion rates in magnitudes between H_2 and other gases along with the increasing temperature. Owing to the high mechanical stability and robustness of the membrane, the reproducibility and durability of the $Cu(bipy)_2(SiF_6)$ membrane were also examined. As shown in Fig. 5b, the membranes retain high separation factors over 30 hours. The membranes also demonstrate high gas separation performance after standing under ambient conditions for more than three months. Moreover, in order to validate the reproducibility, gas separation studies of binary gases (H_2–CO_2, H_2–CH_4 and H_2–N_2) were also implemented among twenty membranes synthesized by the same method. The separation factor averages of the three kinds of binary gases are 8.0, 7.2 and 6.4 with variances of 0.283, 0.233 and 0.248 respectively. The excellent reproducibility and durability shows that the membrane has significant stability and has a broad application prospect.

Conclusions

In conclusion, we developed a novel seeding-free route and successfully obtained a continuous thin $Cu(bipy)_2(SiF_6)$ membrane on a glass-frit disk with high robustness. The fluoridation of the substrate by $(NH_4)_2SiF_6$ could be supposed as the

"storage" of SiF_6^{2-}, which controls the growth of the $Cu(bipy)_2(SiF_6)$ crystals and enhances the binding between the membrane and the substrate. The $Cu(bipy)_2(SiF_6)$ membrane shows high separation factors of H_2–CO_2, H_2–CH_4 and H_2–N_2 of 8.0, 7.5, and 6.8 respectively at 293 K and 1 bar with a H_2 permeance of 2.7×10^{-7} mol m^{-2} s^{-1} Pa^{-1} as well as high thermal stability. We intend to explore more membranes of $Cu(bipy)_2(SiF_6)$ analogues with tuneable pore sizes using this route and to obtain membranes with a higher gas separation performance.

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