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Facile synthesis of continuous thin Cu(bipy)₂(SiF₆) membrane with selectivity towards hydrogen

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Cu(bipy)₂(SiF₆) 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 great candidates to fabricate membranes for gas separation. The key to obtain thin, continuous Cu(bipy)₂(SiF₆) membranes is to control the Cu(bipy)₂(SiF₆) crystal growth and enhance the binding between membrane and substrate. Here we explored a new route by direct synthesis and successfully obtained continuous thin Cu(bipy)₂(SiF₆) membrane on macroporous glass-frit disk with high robustness. It is speculated that SiF₆²⁻ to construct the Cu(bipy)₂(SiF₆) membrane were came from the fluorinated substrate. The Cu(bipy)₂(SiF₆) membrane shows the separation factors of H₂/CO₂, H₂/CH₄ and H₂/N₂ are 8.0, 7.5, and 6.8 respectively at 293 K and 1 bar with H₂ permeance of 2.7×10^{-7} mol·m⁻²·s⁻¹·Pa⁻¹ as well as high thermal stability. It is expected to explore more membranes of Cu(bipy)₂(SiF₆) analogues with tuneable pore sizes using this route and obtain membranes with higher gas separation performance.

Introduction

Metal-organic frameworks (MOFs), also known as porous coordination polymers (PCPs), as a novel crystalline microporous materials have received much attention due to their potentially useful properties in gas storage, selective molecular separation, and heterogeneous catalysis in the past decades.^{1,2} MOFs usually have diverse structures which are typically comprised of metal atoms or metal clusters coordinated to multifunctional 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 with high fluxes, high selectivities, stability, and large-scale facile synthesis as well as 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, Cu₃(BTC)₂ were frequently seen to be membranes for gas separation duo 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 H₂ from other bigger gas molecules.¹³⁻¹⁹ Cu(bipy)₂(SiF₆) (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 CH₄ in 2000.²⁰ The pore sizes of its Zn analog could be controlled from ultramicroporous to mesoporous dimensions.²¹⁻²³ Recently Zaworotko, M. J. et al. reported the exhibition of highly selective CO₂ uptake over CH₄ and N₂ by Cu(bipy)₂(SiF₆) for a MOF material that relies upon physisorption.²⁴ They also showed the optimal adsorption thermodynamics and kinetics for CO₂ separation by this kind of pillared materials.^{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 H₂O. Therefore, this kind of pillared MOF materials are great candidates for the fabrication of membranes for gas separation. However, to the best of our knowledge, so far no membranes by these kind of MOFs could be 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 and 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 substrate surface. The use of seeds in the MOF membrane fabrication is also because of the poor heterogeneous nucleation of many MOF crystals on inorganic support.²⁷ However, Cu(bipy)₂(SiF₆) is kind of MOFs that are easy to grow up but hard to obtain their 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 $\text{Cu}(\text{bipy})_2(\text{SiF}_6)$ crystal growth and enhance the binding between membrane and substrate by direct synthesis is a biggest challenge to obtain thin, continuous $\text{Cu}(\text{bipy})_2(\text{SiF}_6)$ membrane 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 $\text{Cu}_3(\text{BTC})_2$ membrane on Cu net⁵ and slice²⁸, and $\text{Zn}_3(\text{BTC})_2$ film on Zn wafer²⁹. Huang et al. treated a porous titania support with 2-aminopropyltriethoxysilane which is able to bind to the support surface and to act as a linker for binding of ZIF-22 crystals, subsequently obtained a high quality ZIF-22 membrane.¹⁴ In this study, we explored a new route and successfully obtained a continuous thin $\text{Cu}(\text{bipy})_2(\text{SiF}_6)$ membrane on glass-frit disk with high robustness. In this route, the glass-frit disk as substrate was firstly modified by $(\text{NH}_4)_2\text{SiF}_6$, in which the F atom was supposed into the substructures of substrate surface. The $\text{Cu}(\text{bipy})_2(\text{SiF}_6)$ membrane on the modified substrate was formed without 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 membrane and the substrate.

Fig. 1 Schematic diagram of $\text{Cu}(\text{bipy})_2(\text{SiF}_6)$ membrane fabricated on fluoridated glass-frit disk

Experimental

Material

Ammonium fluosilicate $(\text{NH}_4)_2\text{SiF}_6$ and copper fluoroborate hexahydrate $\text{Cu}(\text{BF}_4)_2 \cdot (\text{H}_2\text{O})_6$ (45% aqueous solution) were provided by Aladdin Chemistry CO. Ltd., 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 substrate were treated in a solution of H_2SO_4 and H_2O_2 ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2 = 7:3$, 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 $(\text{NH}_4)_2\text{SiF}_6$ 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, $\text{Cu}(\text{BF}_4)_2 \cdot (\text{H}_2\text{O})_6$ (45% aqueous solution) was diluted to 20% and 0.76888 g (5 mmol) 4,4'-bipyridine were dissolved in 15 mL ethylene glycol and 5 mL deionized water mixed solution firstly. And then 3.4524 g of the $\text{Cu}(\text{BF}_4)_2 \cdot (\text{H}_2\text{O})_6$ solution and the bipy solution were mixed with stirring under 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 by home-made teflon holder. The autoclave was heated under 358 K for 24 h. After cooled to room temperature, the substrate with $\text{Cu}(\text{bipy})_2(\text{SiF}_6)$ 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 CH_3OH for 12 h with 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 $\text{K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Scanning electron microscopy (SEM, FE-SEM: JEOS JSM6700F) were 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 mixture gases were controlled by a soap film flow meter. The flow rate of the sweep gas Ar was controlled at 50 mL/min. The feed flow rate was set to 100 mL/min for the single gas measurements. The total volumetric flow in the feed for binary gas measurements was 100 mL/min with each gas of 50 mL/min. 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 were taken by Ar into an on-line HP6890 gas chromatograph.

Results and discussion

To prepare the $\text{Cu}(\text{bipy})_2(\text{SiF}_6)$ membrane, 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 $(\text{NH}_4)_2\text{SiF}_6$ solution and hydrothermally treated. The fluoridated substrate after being washed was used to synthesize the $\text{Cu}(\text{bipy})_2(\text{SiF}_6)$ with the mixed solution of $\text{Cu}(\text{BF}_4)_2 \cdot (\text{H}_2\text{O})_6$ and bipy under solvothermal conditions. The blue polycrystalline $\text{Cu}(\text{bipy})_2(\text{SiF}_6)$ membrane with uniform and continuous coverage is formed on the substrate (Fig. 2a). The membrane would turn light blue after activated under vacuum and 373 K for 7 h. It is worth to note that the $\text{Cu}(\text{bipy})_2(\text{SiF}_6)$ crystals were anchored very firmly on the

substrate. The MOF membrane only fell off when scratched by knife (Fig. 2b).

Fig. 2 Optical images of the supported $[\text{Cu}(\text{bipy})_2(\text{SiF}_6)]$ membrane: a, as-synthesized; b, activated and scraped out in the cross.

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 $\text{Cu}(\text{bipy})_2(\text{SiF}_6)$ crystals. Scanning electron microscopy (SEM) was used to check the morphology of the as-prepared membrane. It can be seen in Fig. 3b and 3c that the membrane is defect-free and the $\text{Cu}(\text{bipy})_2(\text{SiF}_6)$ crystals with a size less than $10\ \mu\text{m}$ are merged tightly with each other. The cross-section image in Fig. 3d demonstrates the compact anchor of $\text{Cu}(\text{bipy})_2(\text{SiF}_6)$ crystals on the substrate and the thickness of the membrane is estimated about $8\text{--}10\ \mu\text{m}$.

Fig. 3 SEM images of the supported $[\text{Cu}(\text{bipy})_2(\text{SiF}_6)]$ membrane: (a) the substrate (macroporous glass-frit disk); (b, c) top-view; (d) cross-section of the MOF membrane.

X-ray photoemission measurement (XPS) was applied to study the formation mechanism of the robust $\text{Cu}(\text{bipy})_2(\text{SiF}_6)$ membrane. It is known that the binding energy of 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 treated by $(\text{NH}_4)_2\text{SiF}_6$ as well as the $(\text{NH}_4)_2\text{SiF}_6$ powder were shown in Fig. 4. As expected, the XPS spectra of raw substrate and that treated by H_2SO_4 and H_2O_2 show no F 1s signals. The appearance of peak at $687.3\ \text{eV}$ in XPS spectra of

fluoridated glass-frit disk indicates the F atoms in the substructures of substrate surface. The chemical shift about $1.7\ \text{eV}$ in binding energy between the substrate and pure $(\text{NH}_4)_2\text{SiF}_6$ powder demonstrates their difference of chemical environment of F atoms. From the results above, it is speculated that $(\text{NH}_4)_2\text{SiF}_6$ would decompose 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 $\text{Cu}(\text{bipy})_2(\text{SiF}_6)$ crystalline layers. It is assumed that the 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 be explained the compact anchor of $\text{Cu}(\text{bipy})_2(\text{SiF}_6)$ layers on the substrate since the SiF_6^{2-} anions to form the $\text{Cu}(\text{bipy})_2(\text{SiF}_6)$ crystalline on the surface of the substrate was from the substrate.

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 $(\text{NH}_4)_2\text{SiF}_6$ solution (blue); $(\text{NH}_4)_2\text{SiF}_6$ (green).

Encouraged by the successful synthesis of $\text{Cu}(\text{bipy})_2(\text{SiF}_6)$ membrane, we test 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 ($293\ \text{K}$). It is found that the permeances show a decreasing trend in an order $\text{H}_2 > \text{CH}_4 \approx \text{N}_2 > \text{CO}_2$ 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 a 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 results is surprising at first and very disappointing, considering the high selectivity of CO_2/CH_4 by $\text{Cu}(\text{bipy})_2(\text{SiF}_6)$ 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 with the difference of intrinsic

diffusion properties of different gases and their interactions with pore surface.³¹ The permeances of the gases mentioned above in Cu(bipy)₂(SiF₆) membrane could be contrast to the molecular sieving effect because of the large pores (7.8 Å) which is far beyond gas molecules.³²⁻³⁴ The lowest permeance of CO₂ could be explained by the higher molecular weight, and the relative strong interaction between CO₂ and inner surface would also weaken their mobility in large pores. The H₂ selectivities over CO₂, CH₄ and N₂ were confirmed by binary-gas permeation tests. The mixture separation factors of H₂/CO₂, H₂/CH₄ and H₂/N₂ are 8.0, 7.5, and 6.8 respectively (at 293 K and 1 bar) with H₂ permeance of 2.7×10^{-7} mol·m⁻²·s⁻¹·Pa⁻¹. In comparison, Bux, H. reported a H₂/CH₄ separation factors 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 Loreen, H. et al. reported a higher selectivity 16 through developed ZIF-8 membrane with H₂ permeance in the same range 1.3×10^{-7} mol·m⁻²·s⁻¹·Pa⁻¹.³⁵

Thermal stability is important on the practical gas separation performance of membranes. The Cu(bipy)₂(SiF₆) membrane was also tested in single- and binary-gas permeation 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, declining trend of separation factors is observed. This phenomenon which is different from the case of ZIF-7,³⁶ could be caused by the different improved diffusion rates in magnitudes between H₂ and other gases along with the increasing temperature. Owing to the high mechanical stability and robustness of the membrane, the reproducibility and durability the Cu(bipy)₂(SiF₆) membrane were also examined. As shown in Fig. 5b, the membranes retain high separation factors over 30 hours. The membrane 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 (H₂/CO₂, H₂/CH₄ and H₂/N₂) 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(SiF₆) membrane on glass-frit disk with high robustness. The fluoridation of the substrate by (NH₄)₂SiF₆ could be supposed as the “storage” of SiF₆²⁻, which control the growth of the Cu(bipy)₂(SiF₆) crystals and enhance the binding between membrane and substrate. The Cu(bipy)₂(SiF₆) membrane shows high separation factors of H₂/CO₂, H₂/CH₄ and H₂/N₂ are 8.0, 7.5, and 6.8 respectively at 293 K and 1 bar with H₂ permeance of 2.7×10^{-7} mol·m⁻²·s⁻¹·Pa⁻¹ as well as high thermal stability. It is expected to explore more membranes of Cu(bipy)₂(SiF₆) analogues with tuneable pore sizes using this route and obtain membranes with higher gas separation performance.

Fig. 5 Caption(a) Single- ($\square$) and binary- ($\circ$) gas permeances of different gases on the Cu(bipy)₂(SiF₆) membrane at 293 K as a function of the kinetic diameter (inset: the separation factor for H₂ over other gases by binary gases tests); (b) Plot of H₂/CO₂, H₂/CH₄ and H₂/N₂ separation factors of the Cu(bipy)₂(SiF₆) membranes (average values of five different membranes) at different test time. Permeation temperature =293 K, Feed pressure = 1×10^5 Pa.

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