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Bio-Inspired Polydopamine: A Versatile and Powerful Platform for Covalent Synthesis of Molecular Sieve Membranes

Qian Liu,[†] Nanyi Wang,[‡] Jürgen Caro,[‡] and Aisheng Huang*,[†]

[†]Institute of New Energy Technology, Ningbo Institute of Material Technology and Engineering, CAS, 519 Zhuangshi Road, 315201 Ningbo, P. R. China

[‡]Institute of Physical Chemistry and Electrochemistry, Leibniz University Hannover, Callinstraße 3-3A, D-30167 Hannover, Germany

Supporting Information

ABSTRACT: Inspired by the bioadhesive ability of the marine mussel, a simple, versatile, and powerful synthesis strategy was developed to prepare highly reproducible and permselective molecular sieve membranes by using polydopamine as a novel covalent linker. Attributing to the formation of strong covalent and noncovalent bonds, ZIF-8 nutrients are attracted and bound to the support surface, thus promoting the ZIF-8 nucleation and the growth of uniform, well intergrown, and phase-pure ZIF-8 molecular sieve membranes. The developed ZIF-8 membranes show high hydrogen selectivity and thermal stability. At 150 °C and 1 bar, the mixture separation factors of H_2/CO_2, H_2/N_2, H_2/CH_4, and H_2/C_3H_8 are 8.9, 16.2, 31.5 and 712.6, with H_2 permeances higher than 1.8×10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1}, which is promising for hydrogen separation and purification.

Membrane-based separations offer great potential because of their lower energy consumption in comparison with conventional separation processes like distillation and adsorption.[1] Recently, metal–organic frameworks (MOFs), with highly diversified structures and pore size as well as specific adsorption affinities,[2−7] have emerged as a novel type of crystalline microporous material for the fabrication of superior molecular sieve membranes. In particular, MOFs are easier to activate than traditional porous materials like zeolites since no template/structure directing agent (SDA) is required for the MOF synthesis, and the occluded solvent molecules can be easily removed under mild conditions (e.g., vacuum, 150 °C). Therefore, in the case of MOF layers, cracks due to a harsh activation by thermal burning of the organic SDA at high temperature can be avoided. In the recent five years, more and more interests have focused on the preparation of supported MOF membranes/films as separators and sensors.[8−29] However, as highlighted recently,[30,31] there is still a long road ahead before robust synthetic strategies can be developed to prepare highly selective MOF membranes easily. It is often found that separate MOF islands rather than continuous MOF layers were formed on the native ceramic supports by a direct solvothermal synthesis route, because the heterogeneous nucleation of MOF crystals on support surface is very poor.[23,26] Therefore, seeds coating or chemical modification of the supports are usually indispensable to promote the heterogeneous nucleation of MOF crystals on supports. Recently, based on the chemical coupling between the aldehyde group of ZIF-90 and the amine group of 3-aminopropyltriethoxysilane (APTES), we have developed a novel synthesis strategy to prepare highly hydrogen selective ZIF-90 molecular sieve membranes by using APTES as covalent linker between the ZIF-90 layer and the Al_2O_3 support.[26] However, it should be noted that unlike ZIF-90, the organic linkers in most MOF materials can not provide additional linkage groups to form strong bonds with the introducing functional groups of the molecular linker. It is highly desired, therefore, to develop a novel and versatile molecular linker which can be used to attach the MOF nutrients onto supports for the facile synthesis of various MOF membranes regardless of the presence or absence of special linkage groups in the MOFs.

Inspired by the bioadhesion property of marine mussels, Messersmith et al. have demonstrated that dopamine (DPA) could polymerize and stick on all kinds of organic and inorganic surfaces through the formation of strong covalent and noncovalent bonds with surfaces.[32] The polymerization mechanism of DPA was proposed as interaction of a noncovalent self-assembly and a covalent polymerization through oxidation of catechol to dopaminequinone under an aerobic and alkaline condition and then further oxidizes and polymerizes through deprotonation and intermolecular Michael addition reaction to form a cross-linked homopolymer (Figure 1a).[32−34] The resultant polydopamine (PDA) has emerged as a versatile platform for secondary reactions. Recently, the PDA-

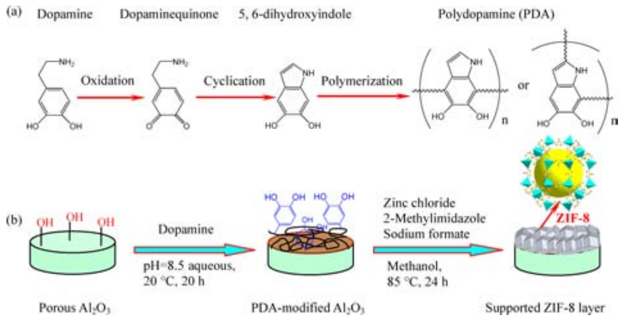

Figure 1. (a) Possible reaction mechanism for dopamine polymerization. (b) Scheme of preparation of ZIF-8 membranes by using PDA as covalent linker between ZIF-8 layer and Al_2O_3 support.

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based reaction platform has drawn great interest for application in cells adhesion, proteins immobilization, biominerals formation, and nanoparticles stabilization (Figure S1).[35−37] Attributing to its adhesive ability through noncovalent adsorption and a covalent reaction, PDA is very promising to be used as a molecular linker to attach MOF particles onto supports for the facile synthesis of dense molecular sieve membranes. However, to the best of our knowledge, there is no report on the preparation of molecular sieve membranes based on PDA reaction platform. In the present work, we report the preparation of highly permselective ZIF-8 membranes (one of the most promising MOF structures because of its outstanding thermal and hydrothermal stability) by using PDA as a molecular linker to promote the nucleation and crystal growth of the ZIF-8 membrane layer.

The preparation of ZIF-8 molecular sieve membranes on PDA-modified supports is shown schematically in Figure 1b. By simple immersion of the Al_2O_3 supports in buffered aqueous solution of DPA (pH = 8.5) for 20 h at room temperature, DPA spontaneously polymerizes into PDA and readily deposits on the Al_2O_3 support (Figure S2). The deposition of PDA on the Al_2O_3 support is also confirmed by XPS. As shown in Figure S3, after PDA modification of the Al_2O_3 support, the Al2p peaks from the Al_2O_3 support were completely shielded. Instead, the intensity of O1s and C1s peaks enhances, and a new N1s peak emerges, indicating the formation of a PDA layer on the Al_2O_3 surface.

After solvothermal reaction for 24 h at 85 °C (see Supporting Information), the surface of the PDA-modified Al_2O_3 support has been completely covered with well intergrown rhombic ZIF-8 crystals, and no cracks, pinholes or other defects are visible (Figure 2a). From the cross-section view shown in Figure 2b, the ZIF-8 membrane is well intergrown with a thickness of ~20 μm. On the contrary, no continuous layer can be formed if the support surface was not treated with DPA (Figure S4). Due to the weak interaction between the ZIF-8 precursor species and the support surface, the heterogeneous nucleation of ZIF-8 on the support surface is poor, which causes problems in the growth of a continuous ZIF-8 layer. In the present work, attributing to its noncovalent adsorption and covalent reaction ability,[32] PDA can be used as highly efficient molecular linker to attract and anchor the ZIF-8 nutrients onto the support surface for the formation of a homogeneous gel layer, thus promoting the nucleation and the growth of ZIF-8 membrane. XRD pattern of the ZIF-8 membrane (Figure S5) shows a high degree of crystallinity, and all of the peaks match well with those of ZIF-8 besides Al_2O_3 signals from the support.[17,38]

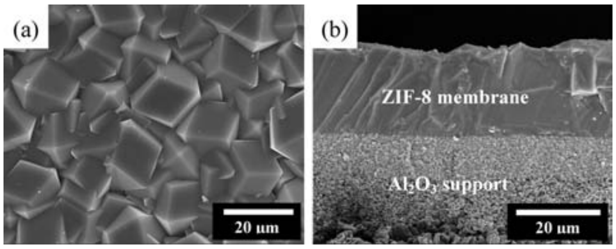

Figure 2. Top view (a) and cross-section (b) SEM images of the ZIF-8 membrane prepared on PDA-modified porous Al_2O_3 disk.

The volumetric flow rates of the single gases H_2, CO_2, N_2, CH_4, C_3H_6, and C_3H_8 as well as of the eqimolar binary mixtures of H_2 with CO_2, N_2, CH_4, C_3H_6, and C_3H_8 were measured by using the Wicke−Kallenbach technique as described elsewhere.[23,26] The permeances and separation factors are summarized in Table S1. Figure 3 shows the permeances of the single gases through the ZIF-8 membrane as a function of the kinetic diameters of the permeating molecules at 150 °C and 1 bar. As shown in Figure 3 and Table S1, the permeances clearly depend on the molecular size of the gases, and the H_2 permeance of 2.17 × 10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1} is much higher than those of the other gases. However, due to the well-known fact of lattice flexibility, also molecules with a kinetic diameter larger than the crystallographic pore size of ZIF-8 (0.34 nm) like CH_4 (0.38 nm) can pass the membrane.[17] At 150 °C and 1 bar, the ideal separation factors of H_2 from CO_2, N_2, CH_4, C_3H_6, and C_3H_8 are 10.3, 17.6, 34.8, 61.8, and 905.1, which by far exceed the corresponding Knudsen coefficients (4.7, 3.7, 2.8, 4.6, and 4.7), suggesting that the ZIF-8 membrane prepared on PDA-modified Al_2O_3 support displays high H_2 permselective molecular sieve performance.

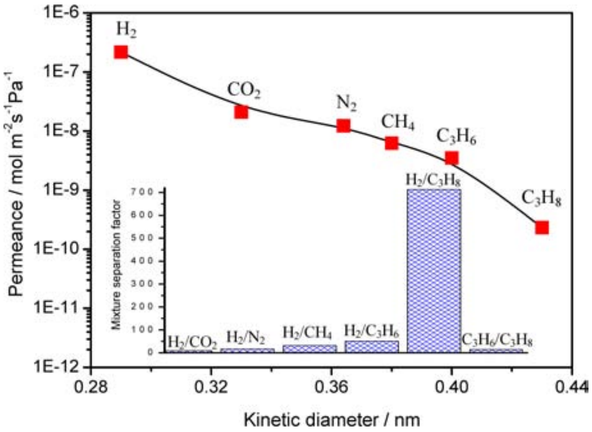

Figure 3. Single gas permeances of different gases through the ZIF-8 membrane prepared on PDA-modified Al_2O_3 disk at 150 °C as a function of their kinetic diameter. The inset gives the mixture separation factors.

The molecular sieve performance of the ZIF-8 membrane was also confirmed by the separation of equimolar mixtures at 150 °C and 1 bar. Comparing the H_2 single gas permeance with the H_2 permeance in mixtures, only a slight difference is found, suggesting that no competitive adsorption between the species plays a significant role at a high temperature (150 °C in this study), and the larger molecules (CO_2, N_2, CH_4, C_3H_6, and C_3H_8) only slightly hinder the permeation of the highly mobile H_2. As shown in the inset of Figure 3 and Table S1, for the 1:1 binary mixtures, the mixture separation factors of H_2/CO_2, H_2/N_2, H_2/CH_4, H_2/C_3H_6, and H_2/C_3H_8 are 8.9, 16.2, 31.5, 50.5, and 712.6, respectively, which also by far exceed the corresponding Knudsen coefficients. As reported recently,[20,22] ZIF-8 membranes can show a high propylene/propane selectivity. As shown in the inset of Figure 3 and Table S1, the present ZIF-8 membrane also displays high molecular sieve performance for propylene/propane separation with a separation selectivity of 13.6 at 150 °C. This mixture separation factor propylene/propane is in complete accordance with the findings of refs 20 and 22 for a temperature of 150 °C. Since the permeance of propylene decreases and that of propane increases with increasing temperature, at room temperature the propylene/propane separation factor is found to be higher (55 by ref 22, and 50 by ref 20).

ZIF-8 membranes belong to one of the most studied MOF membranes.[16−22] Recently, Lai and colleagues reported high-quality ZIF-8 membranes prepared on hollow YSZ ceramic fibers through secondary growth with seeding.[21] Comparing with literature data of mixed gas permeation on ZIF-8 membranes and other MOF as well as zeolite membranes (Table S2), the ZIF-8 membrane developed in this study shows higher separation selectivity. It is worth noting that the whole modification procedure of the support by PDA is simple and effective, and the modification takes place under a mild environment (simple immersion at room temperature, non-toxic) in comparison with the previously proposed seeding and chemical modification methods, which is helpful to prepare membranes at large-scale and reduce the costs of the membrane manufacturing. Further, it is found that the novel synthesis strategy through covalent functionalization by PDA is very helpful to enhance the reproducibility of membrane preparation (Table S3). The average H_2/CH_4 selectivity is 31.3 ± 0.55 (standard deviation) for three independent membrane preparations and tests in Table S3.

When the permeation temperature was increased from 25 to 150 °C at 1 bar, the H_2 permeance increases from 1.12×10^{-7} to 1.93×10^{-7} $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$, and the H_2/CH_4 mixture separation factor rises from 19.2 to 31.5 (Figure S6). This phenomenon can also be explained by an adsorption−diffusion model. At low temperature, mainly CH_4 is adsorbed in the ZIF-8 pores thus blocking the diffusion of the rarely adsorbed and highly mobile H_2. As temperature increases, less CH_4 is adsorbed and thus more H_2 can diffuse in the resulting free volume, leading to a greater enhancement of the H_2 permeance.[26] The ZIF-8 membrane has been tested for longer than one week at 150 °C, and the separation performance of the ZIF-8 membrane remains unchanged (Figure S7), indicating that the ZIF-8 membrane has a high thermal stability. Further, the ZIF-8 membrane can keep its high H_2 permselectivity when the H_2 partial pressure increases from 0.5 to 1.5 bar (Figure S8).

It is found that PDA modification also supports the facile preparation of other MOF membranes like ZIF-90 as well as zeolite membranes like LTA. Similar to the preparation of ZIF-8 membrane, with PDA modification of Al_2O_3 supports, dense ZIF-90 and zeolite LTA membranes can be formed easily (Figures S9, 10), while no continuous MOF or zeolite LTA membranes can be prepared on PDA-free supports. Further work is in progress to extend this synthesis approach to synthesis of other MOF and zeolite molecular sieve membranes.

In conclusion, inspired from the highly adhesive ability of the mussel adhesive protein, in the present work we have developed a simple, versatile, and powerful synthesis strategy to prepare dense MOF and zeolite molecular sieve membranes based on PDA reaction platform. Through the formation of strong covalent chemical bounds, MOF or zeolite nutrients are attracted and bound to the support surface, thus facilitating the nucleation and growth of uniform, well intergrown, and phase-pure MOFs and zeolites molecular sieve membranes. For ZIF-8 membrane, at 150 °C and 1 bar, the mixture separation factors of H_2/CO_2, H_2/N_2, H_2/CH_4, and H_2/C_3H_8 are 8.9, 16.2, 31.5, and 712.6, with H_2 permeances higher than 1.8×10^{-7} $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$. This high separation selectivity combined with its high thermal stability recommends the developed ZIF-8 membrane as a promising candidate for gas separation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

huangash@nimte.ac.cn

Notes

The authors declare no competing financial interest.

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