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Rapid synthesis of ultrathin, defect-free ZIF-8 membranes via chemical vapour modification of polymeric support

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Ultrathin ZIF-8 membranes with a thickness of around 200 nm were prepared by chemical vapour modification of surface chemistry and nanopores of asymmetric bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) substrate. The resulting ZIF-8 membranes exhibited exceptional H_2 permeance as high as 2.05×10^{-6} mol.m^{-2}.s^{-1}.Pa^{-1} with high H_2/N_2 and H_2/CO_2 selectivities (9.7 and12.8, respectively).

Zeolitic imidazolate frameworks (ZIFs), a subclass of metal organic frameworks (MOFs), are hybrid porous crystalline materials composed of metal ions (e.g., Zn, Co) bridged by imidazolates.[1] Remarkably, they exhibit permanent porosity and relatively high chemical and thermal stability,[2] which make them very promising candidate materials for numerous applications such as catalysis, molecular separation, chemical sensing, gas adsorption and storage.[3] In particular, the preparation of MOFs into membranes and thin films is desirable for gas separation.[4] The well-defined porous structures of ZIFs allow them to achieve gas separation with high selectivity via molecular sieving. ZIF membranes are prepared by growing a thin ZIF layer on porous substrate via two general techniques, i.e. in situ (direct) growth and secondary (seeded) growth.[5] In situ growth, a method used for direct growth of a ZIF layer on a bare porous substrate, has been widely studied for the fabrication of ZIF membranes. However, due to limited heterogeneous nucleation sites on the support and poor compatibility between ZIF and support, this method may result in defective ZIF films with intercrystalline voids.[6] Chemical modification can effectively overcome the issue by providing anchors to ligands or metal ions. Compared to other methods such as microwave-assisted solvothermal synthesis,[7] rapid thermal deposition (RTD),[8]

layer-by-layer deposition of crystal,[9] and liquid-phase epitaxy (LPE),[10] chemical modification not only provides a faster and energy-efficient route but also indirectly improves the thermal stability and chemical resistance of the composite.

So far, most supports for growing a ZIF layer are ceramic-based materials such as alumina.[5c, 11] To favour ZIF formation and adhesion, these supports are functionalized with organosilane molecules or other functional groups.[5c, 11] Caro and co-workers[11e] prepared a continuous ZIF-90 membrane by using 3-aminopropyltriethoxysilane (APTES) as a covalent linker. The amine groups of the APTES were shown to react with the aldehyde groups of the ZIF precursor and promote the nucleation and growth of the ZIF-90 at these fixed sites on the surface of the porous ceramic substrate. A similar surface modification method and its influence on heterogeneous nucleation have been also demonstrated with other MOF materials by other groups.[12] However, the poor scalability and high cost of the inorganic materials limit the applications of ZIF membranes.[13] Growing ZIF on a polymer substrate, on the other hand, has great potential to achieve high-quality membranes at a low cost. To date, there have been only a few reports on successful in situ growth of ZIF on a polymer surface.[6, 9-10] To effectively use a polymer membrane as a substrate, the polymer membrane needs to be chemically modified. Li et al. successfully grew a continuous and well integrated ZIF-8 layer on a polyvinylidene fluoride (PVDF) substrate treated in ammonia or ethanediamine solution.[6b] The same group also successfully prepared ZIF-8-polyacrylonitrile(PAN) membrane by hydrolyzing PAN substrate to produce deprotonated carboxyl groups.[14] The modified polymer substrates exhibited increased stiffness due to cross-linking.[6b, 14] Nevertheless, solution phase chemical modification for the preparation of polymer-supported ZIF membranes can cause uneven swelling and adversely affect the polymeric membrane morphology and separation performance.[15] Also, the contaminants in chemical modifier solution increase with substrate modification cycle and need to be treated before reuse. Furthermore, the substrates after modification need to be rinsed and dried before growing ZIF.

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At a lab scale, fresh modifiers can be used and the substrate can be left at room temperature until completely dry; but at larger scale, these steps need to be improved on the basis of production cost and time.

Here we report a novel scalable strategy of using vapour phase ethylenediamine (EDA) to chemically modify the polymer support for ZIF membrane fabrication. An asymmetric bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) ultrafiltration membrane was fabricated by non-solvent induced phase separation (see Electronic Supporting Information† for method), and used as the support for growing a thin ZIF-8 layer via a rapid in situ route after chemical vapour modification (Fig. S1, ESI†). BPPO is a common polymer with a high glass transition temperature, high mechanical strength and excellent hydrolytic stability.[16] It attains superior membrane formation and functionalizable characteristics due to the abundant highly reactive -CH$_2$Br groups. EDA-vapour modification of BPPO results in the reduction of pore size of support and also provides a large number of nucleation sites. When combined with the rapid, in situ growth of ZIF, a submicron-thin and defect-free ZIF-8 membrane with high gas separation performance can be attained.
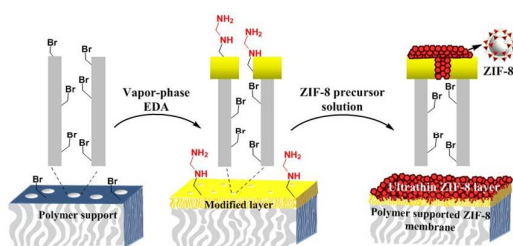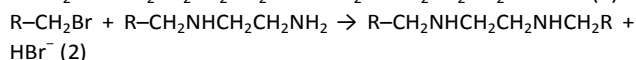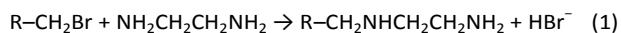

Fig. 1 Schematic diagram of the preparation of BPPO polymer-supported ZIF-8 membrane.

The method developed in this work involves two steps, as shown in Fig. 1. First, the physicochemical properties of the top layer of BPPO support were modified by using EDA-vapour. Then, ZIF-8 was grown inside the pores and on the surface of the support via a rapid, in-situ seeding method.[17] The modified BPPO is denoted as MBPPO-X (X: modification reaction time). EDA-vapour modification is surface-limiting with minimal swelling effect to the polymer support, and this process can be carried out at room temperature.[15] Unlike liquid phase modification, EDA is directly reusable in the vapour modification. Therefore, amine functional groups for the coordination with Zn^{2+} ions can be covalently attached on the top layer of BPPO support without affecting the sublayer structure. For formation of ZIF-8 layer, the vapour-phase-EDA-modified BPPO support was immersed vertically in the solution of zinc acetate dehydrate (0.22 g) in 9.6 g methanol and sonicated for 3 min. A solution of Hmim (0.164 g) in 9.6 g methanol was added to the above solution, followed by dropwise addition of ammonia hydroxide solution (0.12 g) and the mixture was then ultrasonically treated for another 3 min. The final precursor solution had a Zn: Hmim: NH$_3$: CH$_3$OH molar composition of 1: 2: 2: 300 and was kept constant in our

study. After crystallization at room temperature, the ZIF-8/BPPO composite membranes were washed with methanol and dried (see Electronic Supporting Information for detailed procedure). The following simultaneous amination and crosslinking reactions may take place during the surface modification.[18]

$$R–CH_2Br + NH_2CH_2CH_2NH_2 \rightarrow R–CH_2NHCH_2CH_2NH_2 + HBr^- \quad (1)$$
$$R–CH_2Br + R–CH_2NHCH_2CH_2NH_2 \rightarrow R–CH_2NHCH_2CH_2NHCH_2R + HBr^- \quad (2)$$

Reactions (1) and (2) are typical amination and crosslinking reactions. Reaction (1) takes place where one end of a diamine molecule reacts with bromine groups (−CH$_2$Br). Reaction (2) occurs where EDA reacts at both ends of the diamine molecule to form either interchain or intrachain crosslinks.

The chemical reaction between the BPPO support and EDA vapour during the modification was determined using the FTIR-ATR technique and the results are shown in Fig. 2. The pristine BPPO has IR bands at around 586 cm^{-1} and 633 cm^{-1}, which are attributed to the benzyl bromide (−CH$_2$Br) groups (C−Br stretching). After EDA-vapour modification, these bands almost disappear and a new broad band in the range of ~3100-3600 cm^{-1} emerges, which is ascribed to the N−H stretching and confirms the amination of BPPO. The ZIF-8 characteristic band at 421 cm^{-1} (Zn−N stretching) is observed in the BPPO-supported ZIF-8 membrane (ZIF-8-MBPPO-16). Furthermore, TGA results (Fig. S2 ESI†) suggest higher degradation temperature for main chains of BPPO after EDA vapour-phase modification, which could be attributed to the presence of partial crosslinking in the modified BPPO substrate. This was further verified by reduced water flux and increased rejection of the support after the modification, since the crosslinking causes tightening of the polymer network which increases the membrane dimensional stability and reduces the pore size of BPPO substrate (Fig. S3, ESI†). This reduces the flexibility of the polymeric substrate, which is favourable for reducing ZIF layer cracking.[4]
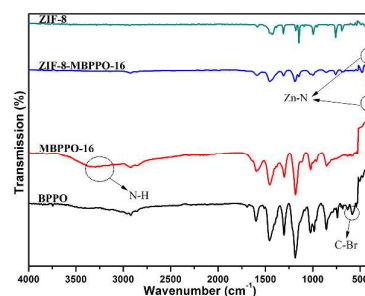

Fig. 2 FTIR ATR spectra of untreated BPPO support, BPPO modified with EDA-vapour for 16 h (MBPPO-16), MBPPO-16 supported ZIF-8 layer (ZIF-8-MBPPO-16), and synthesized ZIF-8 powder.

After the substrate modification, an ultrathin ZIF-8 membrane of about 200 nm is formed on top of the polymer support (Fig. 3). From the membrane cross section (Fig. 3a), it can also be observed that a fraction of ZIF-8 crystals formed inside the porous polymer support. This can be due to the diffusion of the EDA vapour into the polymer sublayer which creates

additional active sites for ZIF-8 nucleation. Energy-dispersive X-ray spectroscopy (EDS) line-scan analysis confirmed the existence of ZIF-8 within the support sublayer as zinc was detected up to ~150 nm underneath the membrane surface (Fig. S4, ESI†). Growth of the crystals partially inside the support could improve the membrane structural integrity. The top-view image (Fig. 3b) shows that the support surface was covered entirely with a continuous and compact ZIF-8 layer without any visible defects such as pinholes or cracks. This very thin, dense and defect-free ZIF-8 membrane on the support with large pore size is desirable for high-performance gas separation. By contrast, separate ZIF-8 crystals and crystal islands formed if the support surface was not modified with EDA before ZIF-8 crystallization (Fig. S5(c), ESI†). This difference in the morphology between ZIF-8-MBPPO and ZIF-8-BPPO provides strong evidence of the important role of EDA modification in growing a thin and compact ZIF-8 layer. The intensity of the XRD (Fig. 4) peaks of ZIF-8 in ZIF-8-MBPPO is much higher than those in ZIF-8-BPPO, indicating that the ZIF-8 layer has higher crystallinity and better surface coverage. Benzyl bromine groups ($-CH_2Br$) in the BPPO are readily transformed to primary amine groups ($-NH_2$) in the modification process. The obtained primary amine groups can subsequently react with Zn^{2+}, as reported by Liu et al.,[19] where stable zinc complexes are formed from Zn^{2+} coordinated with monoamine. The FTIR results also show that primary amine groups generated by the EDA treatment have been consumed in the reaction with Zn^{2+} during ZIF-8 nucleation step where the broad band ascribed to the N−H stretching disappeared (Fig. 2).
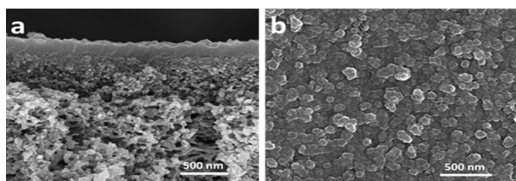

Fig. 3 SEM images of (a) cross-section and (b) surface of the ZIF-8-MBPPO-16.

On the basis of experimental results described above, it is clear that EDA can act as a covalent link between the ZIF-8 crystals and support, providing a large number of nucleation sites for the growth of the ZIF-8 layer. The existence of a strong interaction between ZIF-8 and MBPPO support was also confirmed by TGA results (Fig. S2, ESI†) in which a considerable shift from 310°C to 358°C is observed between the degradation peaks of MBPPO and ZIF-8-MBPPO; whereas the BPPO and its counterpart ZIF-8-BPPO membrane show only a slight difference in their degradation peaks. To gain an insight into the effect of EDA on the growth of ZIF-8 on the BPPO support, ZIF-8-MBPPO-4 and ZIF-8-MBPPO-10 were prepared and their SEM images (Fig. S5, ESI†) were compared to that of ZIF-8-MBPPO-16. These images reveal that the shorter EDA exposure resulted in ZIF-8 membranes with larger defects and pinholes. This can be explained by considering the multiple roles of EDA. By increasing the EDA exposure time, the

reaction extent increases, as confirmed by FTIR (Fig. S6, ESI†), resulting in aforementioned a higher number of nucleation sites (amine groups). In addition, ethylenediamination induces a change in the membrane microstructure. The effect of pore size of porous support on the formation of ZIF membranes was previously reported.[20] Increasing the EDA modification time leads to increased crosslinking and reduced substrate pore size, which is essential for the formation of a thin and defect-free ZIF-8 membrane. The corresponding pore size of MBPPO-16 is 11.4 nm.

To further evaluate the quality of the ZIF-8 membranes, single gas (H_2, N_2 and CO_2) permeation experiments were carried out, and the results are summarized in Table S1 (ESI†). ZIF-8-BPPO without modification showed no gas separation property because no continuous ZIF-8 film was formed. The result also confirms the formation of a continuous and compact ZIF-8 film on the modified BPPO substrate when it is sufficiently aminated. Lower amination time led to a low-quality ZIF-8 layer on the BPPO substrate (ZIF-8-MBPPO-4 and ZIF-8-MBPPO-10). ZIF-8-MBPPO composite membranes prepared with longer amination times show excellent gas selectivities. ZIF-8-MBPPO-16 exhibited H_2/CO_2 and H_2/N_2 ideal selectivities of 12.8 and 9.7 (Fig. 5), respectively; it also had H_2 permeance as high as 2.05×10^{-6} mol.m^{-2}.s^{-1}.Pa^{-1} (Fig. 5). This membrane is amongst the best ZIF-8 membranes reported previously (Table S2, ESI†). For instance, at a similar H_2/N_2 selectivity, the ZIF-8 membrane prepared in this study had two orders of magnitude higher H_2 gas permeance than those prepared by the epitaxy method.[10, 21]
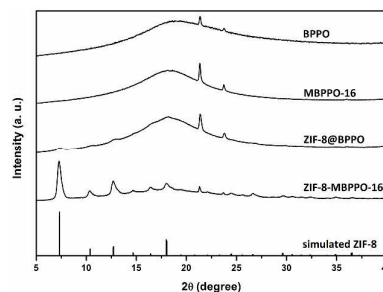

Fig. 4 XRD patterns of the membranes and simulated ZIF-8 powder.

Furthermore, all H_2 permeances and ideal selectivities of H_2/CO_2 and H_2/N_2 are similar for the membranes obtained from different synthesis batches (Table S3, ESI†), indicating the good reproducibility of the reported synthesis strategy.

It is worth mentioning that the N_2 permeance is higher than CO_2 permeance despite CO_2 having a smaller kinetic diameter than N_2. This behaviour can be attributed to the peculiar structure of ZIF-8 and to the combined linear structure and permanent dipole moment of CO_2.[22] The small CO_2 permeance may also be related to partially coordinated organic ligand (Hmim) molecules present in the ZIF-8 crystals as it was previously shown that this molecule is able to strongly coordinate with CO_2 gas.[22a] The similar behaviour was also observed in other ZIF materials.[23]
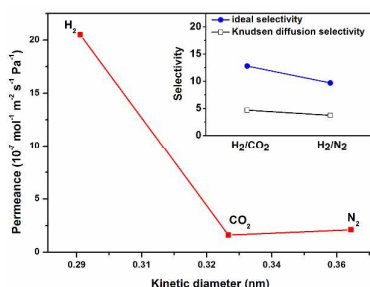
Fig. 5 Single gas permeances of ZIF-8-MBPPO-16 as a function of kinetic diameter of gas molecule.

The high permeance for hydrogen as well as high hydrogen selectivity in this study is due to the ultrathin ZIF layer ($\sim$ 200 nm) and the absence of pinholes or defects, which are attributed to vapour phase amination of asymmetrically porous BPPO support. Another possible reason for the high permeance may be the highly porous and asymmetric structure of the support, which minimises the overall hydraulic resistance of the permeate flow through the membrane structure. The formation of a thin and compact ZIF-8 layer in this study is essentially attributed to the enriched heterogeneous nucleation density and the reduction of the support pore size via EDA-vapour crosslinking. Thus, this work demonstrates a new strategy that can be applied to the formation of polymer-supported ZIF membranes through rational design and chemical modification of the thin polymer supports.

In summary, we have successfully prepared a compact, ultra-thin ZIF-8 layer on an asymmetric polymeric substrate by chemical vapour modification of the surface chemistry and pore structure. The thickness of the membrane fabricated by simultaneous modification of surface chemistry and pore structure is one of the thinnest ever reported. In addition, we have also demonstrated the influence of the surface microstructure and chemical composition of the polymer substrate on the formation of a continuous ZIF-8 layer. Vapour-phase EDA has been used to simultaneously tailor the chemical nature and pore size of the surface of BPPO for the successful growth of ZIF-8 membrane. The EDA treatment produced a large number of nucleation sites and modified the BPPO pore structure, promoting the formation of a thin ZIF-8 layer. The ZIF-8 membrane exhibits ideal selectivities (H_2/CO_2: 12.8; H_2/N_2: 9.8) and permeance (2.05×10^{-6} $mol.m^{-2}.s^{-1}.Pa^{-1}$) which is among the highest reported so far. The proposed chemical vapour modification followed by fast in situ synthesis provides a rapid, convenient and effective route for preparing thin yet continuous and defect free ZIF membranes on the surface of polymeric substrates.

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