Metal–Organic Frameworks Hot Paper

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Photoinduced Postsynthetic Polymerization of a Metal–Organic Framework toward a Flexible Stand-Alone Membrane**

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Abstract: *Metal–organic frameworks (MOFs) are a promising class of nanoporous polymeric materials. However, the processing of such fragile crystalline powders into desired shapes for further applications is often difficult. A photoinduced postsynthetic polymerization (PSP) strategy was now employed to covalently link MOF crystals by flexible polymer chains, thus endowing the MOF powders with processability and flexibility. Nanosized UiO-66-NH_2 was first functionalized with polymerizable functional groups, and its subsequent copolymerization with monomers was easily induced by UV light under solvent-free and mild conditions. Because of the improved interaction between MOF particles and polymer chains, the resulting stand-alone and elastic MOF-based PSP-derived membranes possess crack-free and uniform structures and outstanding separation capabilities for Cr^{VI} ions from water.*

Metal–organic frameworks (MOFs) are nanoporous polymeric materials constructed from metal ions or clusters that are covalently linked by organic ligands and thus possess the characteristics of both organic and inorganic materials.[1] Because of their high porosity, well-defined open channels, structural diversity, and rich functionalities, MOFs play significant roles in applications such as gas storage and separation,[2] catalysis,[3] the preparation of membranes or films,[4] and sensing.[5] Macroscopically, MOFs resemble inorganic crystalline materials, and the fragile frameworks are not soluble and cannot melt without their structures being destroyed. Therefore, despite the advantages of MOFs, improving their flexibility or processability for further industrial applications and device fabrications without changing their underlying topologies remains challenging.

Crystalline MOF powders need to be formed into shaped bodies by pressing or extrusion processes for industrial applications such as gas separation and catalysis.[6] Specifically, MOF powders can be processed by applying mechanical pressure, followed by crushing and sieving.[7] Another practical way is the mixing of MOF particles with suitable binders and additives to give a paste. The just dried paste is then transformed to a hard "cake", which is subsequently crushed and sieved. Alternatively, the paste can also be extruded into cylindrical shapes before drying and crushing.[8] A number of two-dimensional MOF shapes, that is MOF-based membranes, have been reported, mostly MOF thin films and mixed-matrix membranes. MOF thin films can be prepared by growing MOF layers on certain substrates through direct solvothermal synthesis, secondary growth, electrochemical methods, assembly of preformed MOF nanocrystals, liquid-phase epitaxy, and Langmuir–Blodgett layer-by-layer deposition.[4a–d,f,9] The incorporation of MOFs into polymer matrices endows the mixed-matrix membrane with the characteristics of polymers and MOFs.[4e–i,10] In order to achieve the desired properties and performance, challenges such as poor compatibility and particle aggregation must be overcome.[11] Despite the progress that was made in recent years, most of these MOF-based membranes lack homogeneity at the molecular level. It is noteworthy that supported membranes have been widely used in industrial processes, and the concept can be applied to combine MOF crystals with various substrates to give supported MOF membranes. Specifically, some pioneering studies have been conducted toward such MOF-based membranes for various applications, including gas separation, chemical sensing, and catalysis. To further understand the fundamental science and the role of MOF crystals, we focused on developing stand-alone MOF membranes.

In order to alter the chemical and physical properties of MOFs through further functionalization, Cohen and others proposed a postsynthetic modification (PSM) approach.[12] Many MOFs are furnished with novel and sophisticated properties by chemical modification after their synthesis. Other strategies, including cation exchange, linker exchange, and postsynthetic metalation, are also employed to tailor the properties of MOFs.[13] Inspired by these ideas, we investigated a fast and facile way to covalently link MOF crystals by flexible polymer chains in an ordered fashion, namely, postsynthetic polymerization (PSP). In this way, MOFs that bear polymerizable functional groups can copolymerize with organic monomers to achieve elasticity and processability (Scheme 1).

The copolymerization of MOFs and monomers is a promising method to endow MOF powders with flexibility.[14] However, conventional polymerization methods may inevitably destroy the structures of some MOFs under the harsh polymerization conditions or entrap undesirable solvent

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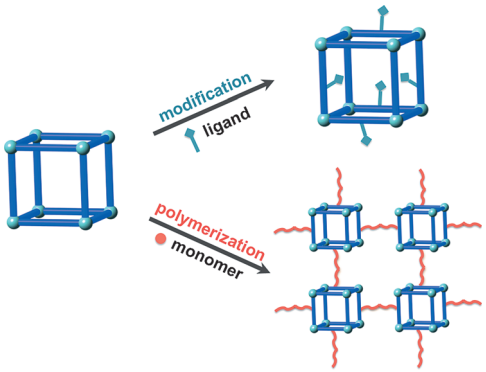

Scheme 1. Postsynthetic modification and polymerization of MOFs.

molecules during the process. These may further lead to undesired side reactions and tedious purification procedures. An alternative approach is the photopolymerization, which features advantages such as rapid curing, solvent-free process, and mild conditions.[15] By exposing suitable MOF crystals and added organic monomers to UV light, the polymerization can proceed instantly, leading to materials with predesigned shapes. Furthermore, the shape remains unchanged during the polymerization because in most cases no evaporation process is involved.[16] Compared with common shaping techniques, such as tableting or extrusion, photopolymerization is a "softer" and easier method.

In this work, a stand-alone and homogenous membrane with good separation capacity for Cr^{VI} ions in solution was successfully prepared by copolymerization of MOFs and acrylate monomers. Modified UiO-66-NH_2 nanoparticles[17] were copolymerized with acrylate monomers under UV light, thus fabricating membranes of predetermined shapes. The preparation process is schematically depicted in Figures 1 and 2. First, the PSM strategy was employed to functionalize UiO-66-NH_2 with methacrylamide groups. Second, the thus modified UiO-66-NH-Met was mixed with butyl methacrylate (BMA) in the presence of the photoinitiator phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide, and the suspension was dripped into a Teflon mould and subsequently irradiated with UV light for several minutes. The resulting square-shaped membrane could be easily peeled off to give an elastic stand-alone membrane. The application of this PSP strategy to the preparation of a MOF/polymer hybrid membrane (noted as PSP-derived membrane) avoids problems such as the aggregation of MOF crystals and poor compatibility between MOFs and polymers.

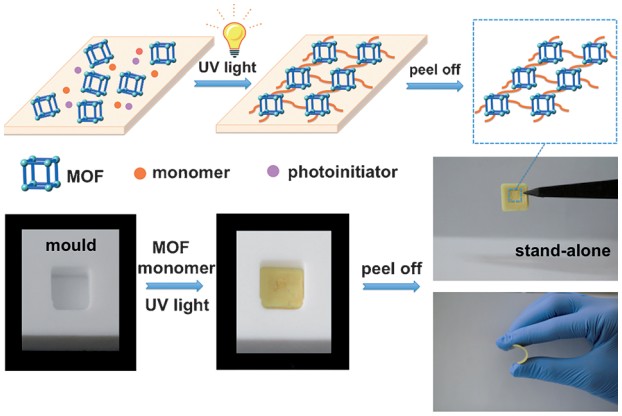

Figure 1. Preparation of a PSP-derived membrane by photoinduced postsynthetic polymerization.

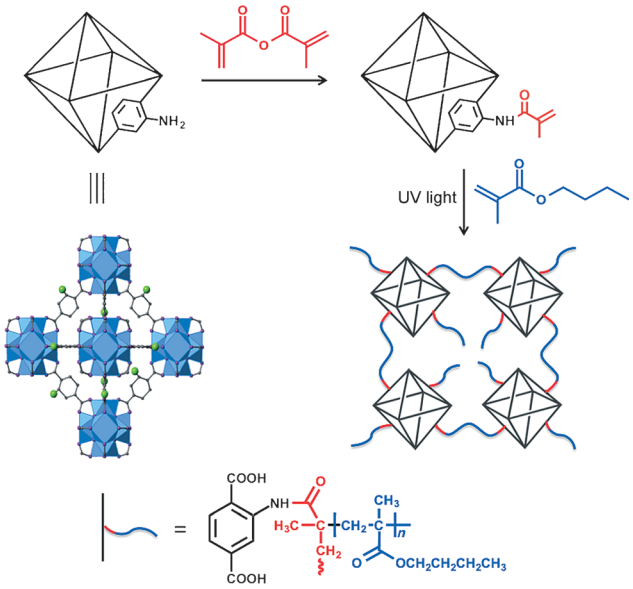

Figure 2. Postsynthetic modification of UiO-66-NH_2 with methacrylic anhydride and subsequent polymerization with butyl methacrylate (BMA) by irradiation with UV light.

The powder X-ray diffraction (PXRD) patterns of UiO-66-NH-Met and the PSP-derived membrane (Figure 3a) are consistent with that of the pristine UiO-66-NH_2, thus indicating that they maintain their crystallinity and underlying topology after modification and photopolymerization. Given the brittle nature of MOF crystals, the shaping process should be conducted with caution. Photopolymerization is a mild and largely noninvasive method compared with traditional polymerizations.

The CO_2 adsorption properties of the pure polymer, UiO-66-NH-Met, and the PSP-derived membrane were also measured (Figure 3b). The membrane of the self-polymerized BMA polymer (PBMA) showed low CO_2 uptake. Upon incorporation of MOF particles, the membrane exhibited an improved adsorption capacity, thus indicating that the pores of UiO-66-NH-Met are not blocked by PBMA polymer.

The modification of UiO-66-NH_2 was confirmed by ^{1}H NMR spectroscopy and ESI-MS. Modified samples that were degraded in a solution of HF in [D_6]DMSO featured new resonances at 2.0, 5.6, 5.9, 7.7, 8.1, and 9.2 ppm in the ^{1}H NMR spectra, which are consistent with the anticipated modified molecular ligand counterpart (Figure 3c). The degree of conversion from amine to amide calculated from the ^{1}H NMR spectrum is 67%, which is in good agreement with the results of the elemental analysis (Table S1). Mass spectra showed a corresponding peak at m/z 248 (Figure S2). N_2 adsorption isotherms measured at 77 K showed that after modification, the samples remained porous, although the BET surface area decreased from 854 to 675 $m^2 g^{-1}$ (Figure S3).

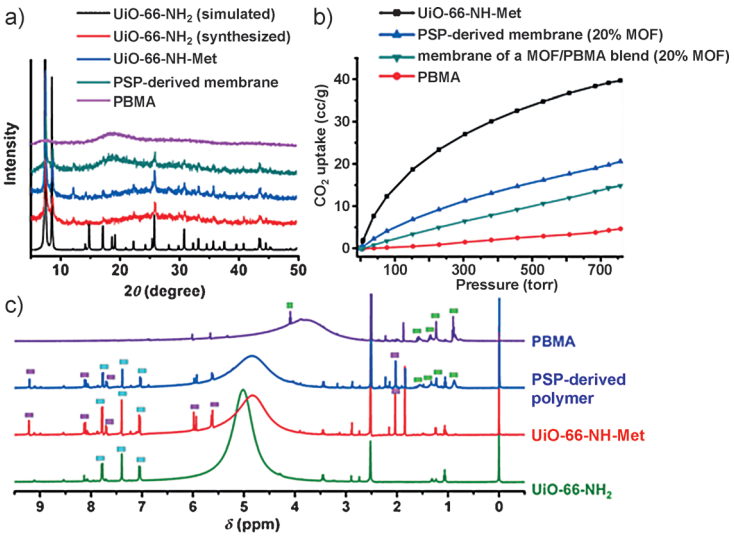

Figure 3. a) PXRD patterns of UiO-66-NH_2, UiO-66-NH-Met, a UiO-66-NH-Met/BMA PSP-derived membrane (20 wt% MOF loading), and PBMA, and simulated PRXD pattern of UiO-66-NH_2. b) CO_2 adsorption properties of UiO-66-NH-Met, a PSP-derived membrane (20 wt% MOF loading), a membrane of a UiO-66-NH_2/PBMA blend, and PBMA measured at 0 °C. c) ^{1}H NMR spectra of degraded UiO-66-NH_2, UiO-66-NH-Met, PSP-derived polymer, and PBMA. Note: The PSP-derived membrane was washed with an excess of CH_2Cl_2 to completely remove the self-polymerization product of BMA (PBMA), and the copolymer of UiO-66-NH-Met and BMA (PSP-derived polymer) are remained for ^{1}H NMR measurement.

The polymerization of UiO-66-NH-Met with BMA monomers was confirmed by ^{1}H NMR spectroscopy and dynamic light scattering (DLS) measurements. The PSP-derived membrane was first washed with an excess of CH_2Cl_2 to remove the self-polymerization product PBMA, while the copolymer of UiO-66-NH-Met and BMA (noted as PSP-derived polymer) was left for characterization. Compared with the postsynthetically modified samples, the presence of new resonances at around 0.9, 1.23, 1.3, and 1.6 ppm, which are consistent with the spectrum of PBMA, confirm the success of the polymerization (Figure 3c). We also observed an increase in particle size in the DLS measurements, which can be explained by the wrapping of the covalently bound polymer chains to the outside of the MOF particles (Figure S4, Supporting Information).

The scanning electron microscopy (SEM) image of the surface of the PSP-derived membrane (Figure 4a) shows that the UiO-66-NH-Met particles are uniformly dispersed within the membranes with no voids at the interfaces, which demonstrates that the introduced polymerizable functional groups have improved the chemical and physical interface interactions between MOFs and polymers. Nonmodified UiO-66-NH_2 particles, in contrast, aggregate into MOF conglomerates on the polymer membrane (Figure 4b). Such poor polymer–particle compatibility and the formation of nonselective voids could greatly influence the separation performance of membranes.

The photoinduced-PSP strategy was also adopted to the preparation of UiO-66-NH-Met/methyl methacrylate (MMA) PSP-derived membranes. The PXRD patterns and SEM image (Figure S5 and Figure S6) indicate that MOF particles are well dispersed within the polymer matrix, while they maintain their crystallinity and topology. The membrane also showed comparable CO_2 adsorption properties compared to a membrane of pure poly(methyl methacrylate) (PMMA) (Figure S7).

We also studied the separation capacity of the PSP-derived membrane for the removal of heavy-metal contaminants (Cr^{VI} ions) from water. The filtration setup is schematically shown in Figure 5. The first-cycle retention rate of the PSP-derived membrane with a MOF loading of 60% reaches 80% and the maximum separation capacity is 8 mg g^{-1}. The separation performance of the MOF/BMA copolymer membrane is better than that of a PBMA membrane, a membrane of a MOF/PBMA blend (replacing UiO-66-NH-Met with equal amounts of UiO-66, which bears no polymerizable functional groups), and a membrane of an activated carbon/PBMA blend (replacing UiO-66-NH-Met with equal amounts of activated carbon), which were fabricated using similar method. The pure polymer membrane shows no filtration and a separation capacity below 800 ppb based on the results of elemental analysis. The retention rate and separation capacity of a membrane of a MOF/PBMA blend are lower, which may be caused by poor polymer–particle compatibility and the formation of nonselective voids. The membrane of an activated carbon/PBMA blend gives a retention rate of 37% and a separation capacity of 4.3 mg g^{-1}. Despite the porosity of activated carbon, its pores without proper binding sites are not suitable for the filtration of metal ions. In contrast, the

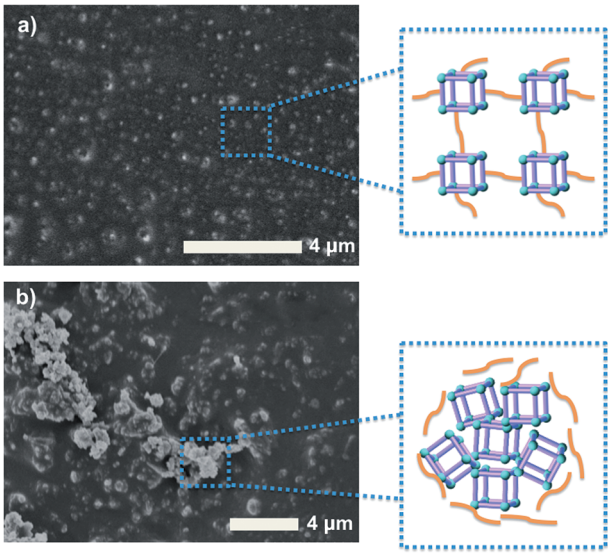

Figure 4. SEM images of the surfaces of a) a PSP-derived membrane with 20 wt% MOF loading and b) a membrane of a UiO-66-NH_2/PBMA blend with 20 wt% MOF loading.

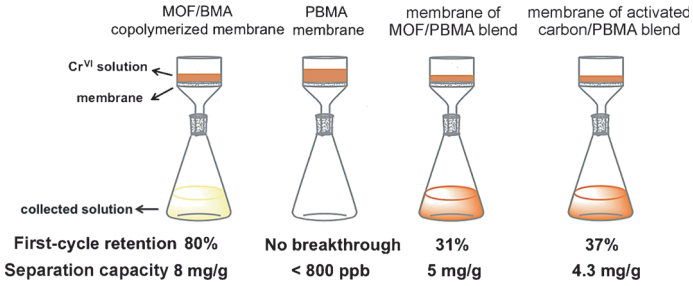

Figure 5. Separation capacity for Cr^{VI} ions of a MOF/BMA copolymer membrane, a PBMA membrane, a membrane of a MOF/PBMA blend, and a membrane of an activated carbon/PBMA blend (unadjusted pH value, initial concentration and volume of $K_2Cr_2O_7$ solution: 10 mg L^{-1} × 10 mL, performed in triplicate).

PSP-derived membrane overcomes all drawbacks of the aforementioned membranes. First, the incorporation of MOFs into the polymer brings in porosity and channels with a polarized surface, while the flexibility and processability of the polymer are maintained. Second, nanosized MOF particles with polymerizable functional groups are well dispersed and covalently anchored in the polymer without particle aggregation, and the formation of nonselective voids within and/or between the aggregates is thus avoided. Third, the copolymerization of MOFs and monomers contributes to the close interaction between particles and polymers, thus achieving homogeneity at the molecular level.

In summary, we have developed a facile postsynthetic polymerization strategy to orderly assemble MOF crystals with polymer chains. Photopolymerization was adopted to copolymerize MOF nanoparticles and acrylate monomers. Such PSP-derived membranes possess uniform structures and show outstanding separation capabilities for removing Cr^{VI} ions from water. The advantages of the photoinduced postsynthetic polymerization approach include its universality and ease of fabrication, which may lead to the development of new MOF membranes and shaped bodies for various applications.

Keywords: membranes · metal–organic frameworks · photochemistry · polymerization · separation capacity

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