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## COMMUNICATION

# Polydopamine layer as nucleation center of MOF deposition on “inert” polymer surfaces to fabricate hierarchically structured porous films

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Effective deposition of MOFs on “inert” solid surfaces is very challenging. In this work, we found that polydopamine, which can be facilely and tightly formed on any types as well as any forms of solid surfaces, could be used as effective nucleation center for MOFs deposition. Based on this finding, various MOFs were successfully deposited on nanofibrous polymer membranes, especially the commercially available “inert” ones, affording hierarchically structured porous films.

The ultrahigh surface areas, ordered crystalline structure with highly regularized pores, and enabling structures with tunable pore sizes and adjustable internal functionality of metal-organic frameworks (MOFs) endow the frameworks with an inherent flexibility producing a variety of applications in different fields, such as gas storage, separation, sensors, catalysis, and drug delivery.<sup>1</sup> However, microporous MOFs tend to lack sufficient transport pore for the molecular flux of analytes or substrates which hinders a wide range of its applications in catalysis, adsorption and separation fields, where the sufficient transport pore has a significant influence on the production rates.<sup>2</sup> Many attempts have been made to overcome this drawback by introducing proper mesoporous or macroporous structure into MOFs materials.<sup>3</sup> Among these, hierarchical porous films by deposition of MOFs on polymer fibrous supports could simplify handling, regeneration and deployment, and combine excellent transport properties of the macropores with the increased surface area and selectivity associated with micropores.<sup>4</sup>

To produce the integrated MOF-polymer fibrous composite membranes, the effective deposition of MOF materials and at the same time achieving enough binding strength between the MOF crystals and polymer fibers are two crucial factors, especially for the case of “inert” polymeric surfaces.<sup>5</sup> Thus to address these problems, the functionalization is usually required to increase the concentration of reactive groups. However, very few attempts to date have been made to modify the fiber surface to facilitate the

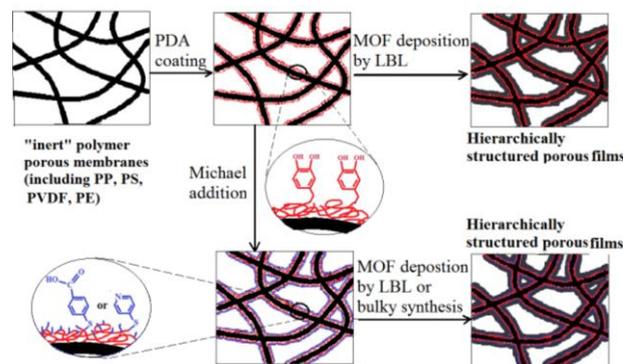
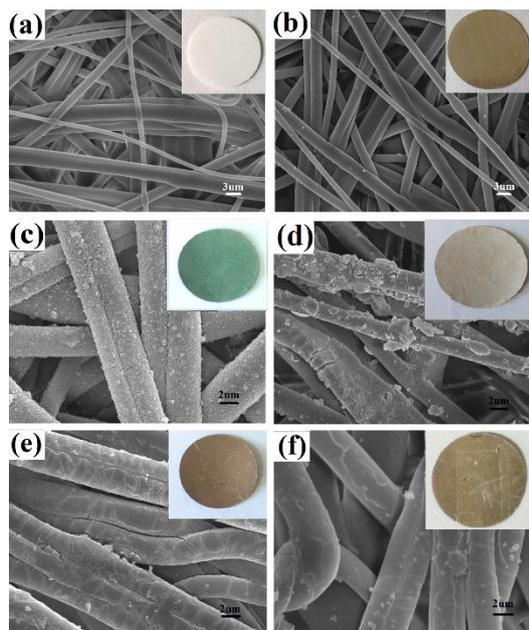


Fig. 1 Schematic illustration of the strategy of effective deposition MOF on the “inert” polymer fibrous membranes by using polydopamine layer as nucleation center to fabricate hierarchically structured porous films.

nucleation and growth of MOF crystals on them, except for the recent ones on growing HKUST-1 onto polyvinylamine coated polyester fibers and deprotonated carboxylic group coated silk yarn.<sup>4, 6</sup> Unfortunately, these methods reported generally led to either small MOF loading or only HKUST-1 deposited on them. Thus, development of new strategy for facilely and effectively deposition of MOF materials on polymer surfaces, specially the challenging “inert” polymer surfaces is highly desirable.

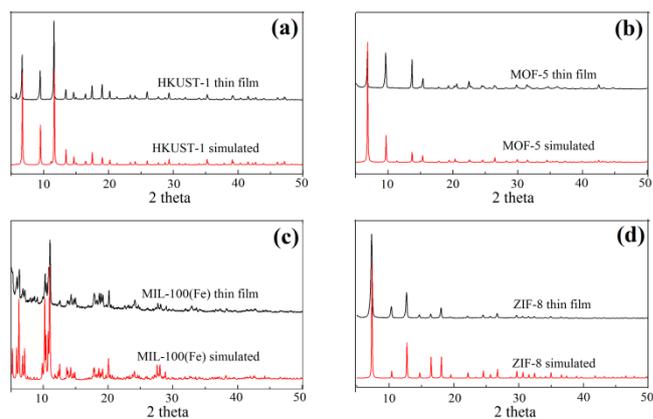
Recently, dopamine has received considerable attention due to its unique properties like self-polymerization, anchor capability, special recognition, and so on.<sup>7</sup> Remarkably, it can self-polymerize in weak alkaline aqueous solution (pH 8.5) without the use of any other reagent, creating a tightly adhesive polydopamine (PDA) coating on virtually any surface by directly dipping substrates into reaction media. This self-polymerization ability of dopamine can be employed as a facile and efficient method to modify versatile surface including “inert” polymer surfaces. Moreover, it is found that PDA exhibits a powerful adhesive ability to attach foreign objects, indicative of a favorable



**Fig. 2** SEM images of (a) original PP fibrous membrane and (b) PDA-coated PP membrane; SEM images of PDA-modified PP membrane followed by the deposition of HKUST-1 (c), MOF-5 (d), MIL-100(Fe) (e) and ZIF-8 (f). Insets are the optical photos of original PP, PDA, or MOF-modified PP membranes.

property for the formation of composites. Additionally, due to the presence of the residual catechol groups, the PDA coating holds active secondary reaction entities that could be further derivated with molecules containing primary amine or thiol groups through mild Michael addition or Schiff-base reaction. Inspired by the unique features of dopamine, in this work, we report on polydopamine layer as nucleation center for MOF deposition on commercially available “inert” polymeric membrane systems, which are hardly applicable for integration of MOFs. It is found that after the introduction of PDA coating the nucleation and growth of MOF materials on “inert” nanofibrous membranes became possible, affording hierarchically structured porous films with good mechanical property. The strategy described is generally applicable to all “inert” polymer membranes. In particular, when appropriate ligand (pyridine or benzoic acid) is further introduced into the coated PDA surface through Michael addition, various MOFs can be facily deposited on the used membranes by both layer-by-layer and bulky synthesis (Scheme 1).

As demonstration, in this work, four typical macroporous polymeric membranes including polypropylene (PP), polyethylene (PE), polystyrene (PS) and polyvinylidene fluoride (PVDF) were chosen as substrates for deposition of MOF materials. These nanofibrous polymer membranes have macroporous structure and exhibit very low surface energy and surface tension due to the lack of polar and reactive functional groups on polymer surface. The later characteristic makes the deposition of MOF materials onto these “inert” polymer membranes impossible. Fortunately, we found that polydopamine coating, which can be facily and tightly formed on any types as well as any forms of solid surfaces,<sup>7</sup> could be used as effective nucleation center for MOFs deposition and thus, employed as a general approach to solve the mentioned problems. In our case, the PDA-modified polymer membranes were prepared by simply immersing the

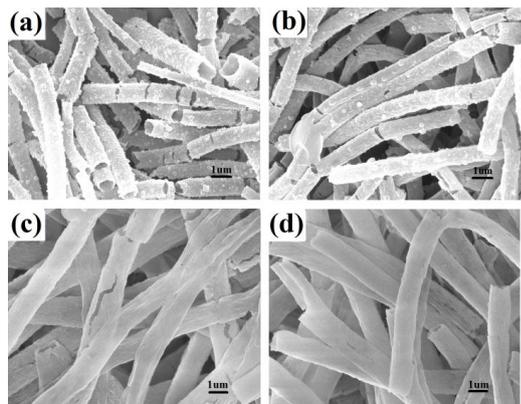


**Fig. 3** Comparison of PXRD patterns of simulated MOF crystals and deposited MOFs film after removal of support polymer nanofibers: (a) HKUST-1, (b) MOF-5, (c) MIL-100(Fe), and (d) ZIF-8.

original membranes into the aqueous solution of 2mg/mL dopamine · HCl at pH 8.5 (tris-HCl buffer) as the procedure reported in literature.<sup>7</sup> After 12 h treatment with dopamine, polymer membranes were thoroughly washed with water and dried in air. Figure 2a-b show the SEM images of the PP membrane before and after the treatment. Clearly, the morphology and integrity of the PP membrane were retained well, meanwhile the color of the membrane was changed from white to dark brown, which is similar to previous observation and indicates the formation of the PDA-layer. The similar results were observed for the cases of PS, PE, and PVDF membranes (Figure S1 in Supporting Information). ATR-FTIR analysis provides direct evidence for the successful modification of the membranes by the formation of PDA coating. Representatively, Figure S2a-b shows the reflective FTIR spectra of the PP membrane before and after dopamine treatment. It is clear to see that the characteristic peaks assigned to the bending vibration and stretching vibration of aromatic ring appear at 1596  $\text{cm}^{-1}$  and 1509  $\text{cm}^{-1}$  compared to the spectrum of original PP membrane. Additionally, the peak at 1288  $\text{cm}^{-1}$  and broad peak spanning at 3100-3600  $\text{cm}^{-1}$  are consistent with C-O-H and N-H/O-H stretching vibration in the polydopamine coating. Under TEM observation a thin and uniform polymer layer on PP fibers is also clearly detectable (Figure S3).

Layer-by-layer method (LBL) which based on sequential dipping a substrate in alternating bath of organic ligands solution and metal ions solution was used for the deposition of MOF materials on PDA-modified polymer membranes. Since catechol group has strong coordination capability with metal ions, it is expected that the rich catechol moieties on PDA coating can act as anchoring sites to combine with metal ions, which can initiate the first pulse of stepwise deposition. Subsequently the attached metal ions combine with organic ligands when soaking into the ligand solution, which is similar to the growth of MOF films on functionalized monolayers.<sup>8</sup>

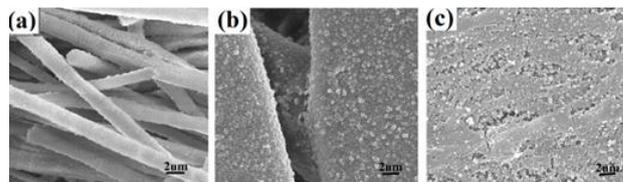
HKUST-1, prototypical MOF ( $\text{Cu}(\text{Ac})_2$  and tricarboxylbenzene), was first exemplified to deposit onto the modified PP membrane under optimized deposition conditions.<sup>9</sup> For direct comparison, the growth of HKUST-1 on the original PP membrane was also studied under the same conditions. As shown in Figure S4a, no HKUST-1 film could be deposited on the surface of the original PP fibers, even after



**Fig. 4** SEM images of the resulting MOF nanotubes after the removal of the underlying polymer fibers in THF solvent: (a) HKUST-1 nanotube, (b) MOF-5 nanotube, (c) MIL-100 (Fe) nanotube, and (d) ZIF-8 nanotube.

30 deposition cycles only sporadic MOF particles were detected probably due to the physical absorption of MOF materials. In contrast, the deposition of a uniform and continuous film without cracks or other defects on the individual PP fibers (Figure 2c) became possible after the modification with PDA coating. The crystal structure of the compact film deposited on PDA-modified PP membrane was investigated by powder X-ray diffraction (PXRD) measurements (Figure S5a). With the peak background of the PP membrane the diffraction peaks are consistent with those of the conventional HKUST-1 microcrystal, indicating that HKUST-1 coating was successfully formed on PP membranes.

To prove the general applicability of the suggested strategy, more prototypical MOFs including ZIF-8, MOF-5 and MIL-100 (Fe) were used to coat the PP membrane.<sup>10</sup> Like the case of HKUST-1 none of these MOF materials could be created on the “inert” PP surface, even after longer deposition time (Figure S6). However, the simple modification of PP fibers with PDA can substantially change the mentioned situation or problem. It is found that all of the chosen MOF materials could form on PP membranes. Compared to the smooth surface of the original or PDA-modified PP fibers (Figure 2a-b), continuous, homogeneous and ragged layers appeared after the deposition of MOF precursors using LBL approach as shown in Figure 2c-f. Figure S5 shows the comparison of PXRD patterns of the original PP membrane, the conventional MOF microcrystals, and the PP membrane with deposited layers. The X-ray diffraction analysis confirmed the deposition of metal-organic coordination complexes. However, it is obvious that compared to the corresponding MOF materials (ZIF8, MOF-5 or MIL-100) the PXRD data in Figure S5 show absences of some expected reflections, or major shifts in the 2θ values for some peaks. The main reason for this phenomenon is that the quality of the MOF crystals, which were deposited at room temperature, is not good enough. Indeed, when the deposited MOF materials are further aged at higher temperature (50 °C) in mother liquor for two days, the quality of the PXRD data was significantly improved. Especially, after the removal of support polymer fibers the obtained PXRD patterns are in consistent with the simulated ones (Figure 3). These results clearly indicate that the thin PDA could serve as a general applicable nucleation center to realize the deposition of various MOF materials on “inert” polymer membranes.



**Fig. 5** SEM images of the prepared HKUST-1/PS (a), HKUST-1/PVDF (b) and HKUST-1/PE (c) composite membranes after the modification of the polymer membranes with PDA.

The formed PP-MOF membranes exhibit good mechanical property. During the manipulation and storage of the prepared composites at lab conditions no exfiltration of the deposited MOF layers were observed. Additionally, due to the very low swelling and solubility of PP fibers in common organic solvents the PP-MOF composite membranes show good stability in organic solvents. This property prevents the removal of PP fibers to provide the direct evidence of the formation of MOF layers on polymer fibers. Thus, instead of PP membrane, in this work, PS nanofibrous membrane (see Figure S1a) was used as substrate to produce PS-MOF composite membranes. After 20 cycles deposition by LBL on the PDA-modified PS membrane followed by the removal of PS by immersing the PS-MOF composite in THF for 12 hours at ambient condition, large amounts of MOF (HKUST-1, ZIF-8, MOF-5 or MIL-100 (Fe) nanotubes were obtained respectively as shown in Figure 4a-d. The remnants show good nanotube morphologies, and PXRD analysis (Figure 3) confirmed the integration and homogeneity of the deposited MOFs. Probably due to the swelling of PS in THF, some cracks appeared in the wall of all of the four MOF tubes after dissolving the PS fibers.

As mentioned previously, dopamine can be self-polymerized in buffered aqueous solution at pH 8.5 to form strong adhesive PDA coating on virtually all types of surfaces. Thus, further two commercially available polymer membranes (PVDF and PE) were tested for producing polymer-MOF composites. As expected, in all cases a dense and continuous MOF coating could be successfully deposited onto different polymeric substrates. Representatively, Figure 5 shows the SEM images of the formed PS-HKUST-1, PVDF-HKUST-1 and PE-HKUST-1 composites. Remarkably, we found that even when highly hydrophobic and inert polymers such as PVDF were used, the resulting polymer-MOF composites still exhibit excellent mechanical stability. The MOF materials on the PDA coating remained stable after ultrasonication and were still firmly attached to the underlying polymer substrates. In fact, a number of recent reports demonstrated good interfacial stability of PDA under various conditions and strong adhesive ability of PDA to foreign objects.<sup>11</sup> More recently, PDA coating was also employed to improve the anchoring property of ZIF-8 to Al<sub>2</sub>O<sub>3</sub> or stainless-steel-nets supports.<sup>12</sup> Our results here, however, indicate that the introduction of PDA coating could not only serve as glue layer, but also make the deposition of MOFs on “inert” polymeric substrates possible. As a result, the two different material systems, which are completely incomparable, could be “perfectly” integrated together to form the hierarchically structured porous membranes with the combined properties of MOFs and

macroporous polymers.

A facile surface coating method based on the polydopamine significantly changes the surface properties of “inert” polymer fibers, and the surface-anchored catechol moieties in PDA can strongly bind to various metal ions to facilitate the formation of MOF crystals. In fact, the anchored PDA coating could act as a useful platform for further tailoring of surface functionality through secondary reaction like Michael addition or Schiff-base reaction.<sup>13</sup> Based on this property, the commonly used ligands such as pyridine and benzoic acid can be directly introduced to the PDA modified surface by immersing PDA-coated substrates into the solution of 4-mercaptopyridine or 4-mercaptobenzoic acid, as confirmed by ATR-FTIR analysis (see Figure S2). Importantly, we found that besides the LBL approach MOF materials could be conveniently deposited by simply immersing the ligand-modified porous polymers into MOF precursor solution.<sup>12a, 14</sup> As illustrated in Figure S6, the MOF coating with the same quality could be also achieved by using this approach, but with higher deposition efficiency compared to LBL method. This result together with the results described above clearly indicate that PDA coating is a facile way to introduce a wide variety of desired properties onto virtually any inert polymeric surface and provides a universal approach to realizing the integration of MOFs and polymers.

The application of the polymer films with coated MOF was demonstrated by using MIL-100(Fe)-PP membrane as absorption membrane. The aqueous solution of rhodamine B (0.01 mM) was used as contaminated water in our case. Remarkably, compared to the original PP membrane the MOF-modified PP shows excellent absorption capability and could efficiently remove the dye molecule from water. The adsorption results were shown in Figure S7. The UV spectra confirmed the high performance of MIL-100-PP membrane. This preliminary result indicates the promise applications of the MOF-modified polymers as efficient absorption membranes.

In summary, by using PDA coating platform we have successfully deposited for the first time the adhesive and integrated HKUST-1, MOF-5, MIL-100(Fe) and ZIF-8 film coatings on various membrane surfaces, which are chemically inert. The results demonstrated a simple and efficient synthesis strategy to fabricate hierarchically structured porous composite films combining the unique features of MOFs and macroporous polymers. We also demonstrated that the PDA-modified “inert” polymer could be further functionalized with common ligands, such as benzoic acid or pyridine, through Michael addition to promote anchoring of MOF materials in mother liquor of bulk synthesis. Our study clearly confirms the unique potential of the PDA as nucleation center for the controlled growth of desired MOF materials on various polymeric membranes, especially on the commercial “inert” polymeric membranes. We believe that by exploiting the unique properties of MOFs the strategy reported here could provide a practical way to significantly expand or enhance the applications of the commercially available porous polymer membranes in various fields.

## Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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