Polydopamine as a promoter layer of MOF deposition on “inert” polymer surfaces to fabricate hierarchically structured porous films

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Experimental

Chemicals and Materials

Polystyrene (PS, Mw=29 000), dopamine hydrochloride, Tris(Hydroxymethyl)aminomethane (99%), 4,4'-Bipyridine (98%), 1,3,5-Benzenetricarboxylic acid (H_3BTC)(98%), 2-Methylimidazole (97%), triethylamine (99%) and terephthalic acid (H_2BDC) (98+%) were purchased from Alfa Aesar. Copper(Ⅱ) acetate monohydrate($Cu(CH_3COO)_2 \cdot H_2O$), Iron(Ⅲ) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) and Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd. 4-mercaptopyridine was obtained from J&K Scientific Ltd. 4-mercaptobenzoic acid was purchased from TCI (Shanghai) Development Co., Ltd. Tetrahydrofuran (THF), N, N-dimethylformamide (DMF), absolute ethanol and other reagents were purchased from Beijing Chemical Reagents Company and used without any purification. PP, PE, PVDF membranes were commercially available. PS porous membrane was prepared by electrospinning as follows. Spinning solution (20 % w/w) was prepared by adding polystyrene in DMF and THF mixture (3:1 W/W) under vigorous stirring. This mixture solution was further stirred for 5 h at room temperature. Thus, a homogeneous solution can be obtained. Then the feeding solution was contained in a 10 mL plastic syringe with a stainless steel gauge needle connected to a high-voltage generator as anode. The cathode covered with aluminum foil was used as the fibers collector. A voltage of 18 kV, with the tip-to-collector distance was 20 cm, was applied to the solution. The solution was pumped out from syringe by a trace syringe pump at a constant flow rate of 0.8mL/h. A dense web of fibers was collected on the surface of the aluminum foil. The obtained fiber mats were initially annealed at 80 ℃ for 0.5 h to enhance their mechanical strength. Finally, the fibrous mats were cut into square shapes for further usage.

Preparation of PDA-coated polymer membranes

Commercial PP fibrous membrane was treated with oxygen plasma before the PDA coating process and then immersed into 2 mg/mL dopamine hydrochloride solution prepared by dissolving dopamine hydrochloride in an 10 mM Tris-HCl (pH 8.5) buffer for about 12 h for self-polymerization. After coating, the membrane was rinsed with deionized water and ethanol, and then dried in a vacuum oven for 24 h at room temperature. PDA-coated electrospun PS, commercial PVDF and PE fibrous membranes were prepared in the same way.

Growth of HKUST-1 on the surface of PDA-coated polymer membranes by LBL method

The PDA-coated commercial PP fibrous membrane (or PS electrospun nanofibrous membrane, commercial PVDF or PE fibrous membrane) were dipped alternately in an ethanolic solution of $Cu(CH_3COO)_2 \cdot 2H_2O$ (10 mM) for 15 min and then in an ethanolic solution of H_3BTC (10mM) for 30min at room temperature in a static reaction vessel. Between each growth step, the films were rinsed with ethanol for 10 min to remove excess reagent and dried in a nitrogen stream for 5 min. This process was repeated 10-30 cycles that can observe HKUST-1 films with different thickness. After the deposition of HKUST-1 materials at room temperature they are further aged at higher temperature (50℃) in mother liquor for two days. For surface comparison experiments, unmodified fibers were carried out in the same way.

Growth of MOF-5/ *MIL-100(Fe)/ZIF-8 film* on the surface of PDA-coated polymer membranes by LBL method

MOF-5: PDA-coated commercial PP fibrous membranes (or PS electrospun nanofibrous membrane, commercial PVDF or PE fibrous membrane) were dipped alternately in an ethanolic solution of $Zn(NO_3)_2 \cdot 6H_2O$ (5 mM) for 15 min and then in an mix ethanolic solution of H_2BDC (5mM) and triethylamine for 30min at room temperature in a static reaction vessel. Between each growth step, the films were rinsed with ethanol for 10 min to remove excess reagent and dried in a nitrogen stream for 5 min. After 30-cycle growth, the resultant films were dried and kept at room temperature. After the deposition of MOF-5 materials at room temperature they are further aged at higher temperature (50℃) in mother liquor for two days.

MIL-100(Fe): PDA-coated commercial PP fibrous membranes (or PS electrospun nanofibrous membrane, commercial PVDF or PE fibrous membrane) were dipped alternately in an ethanolic solution of $FeCl_3 \cdot 6H_2O$ (10mM) for 15 min and then in an ethanolic solution of H_3BTC (10mM) for 30min at room temperature in a static reaction vessel. Between each growth step, the films were rinsed with ethanol for 10 min to remove excess reagent and dried in a nitrogen stream for 5 min. After 30-cycle growth, the resultant films were dried and kept at room temperature. After the deposition of MIL-100 materials at room temperature they are further aged at higher temperature (50℃) in mother liquor for two days.

ZIF-8: PDA-coated commercial PP fibrous membranes (or PS electrospun nanofibrous membrane, commercial PVDF or PE fibrous membrane) were dipped alternately in a methanolic solution of $Zn(NO_3)_2 \cdot 6H_2O$ (10 mM) for 15 min and then in a methanolic solution of 2-methylimidazole (10 mM) for 30min at room temperature in a static reaction vessel. Between each growth step, the films were rinsed with ethanol for 10 min between to remove excess reagent and dried in a nitrogen stream for 5 min. After 30-cycle growth, the resultant films were dried and kept at room temperature. After the deposition of ZIF-8 materials at room temperature they are further aged at higher temperature (50℃) in mother liquor for two days.

Grafting of pyridine or benzoic acid on PDA coating

PDA-coated commercial PP membrane was dipped into 10 mM ethanolic solution of thiol-containing compounds which was prepared by dissolving a certain amount of 4-mercaptopyridine or 4-mercaptobenzoic acid in 20 mL absolute ethanol. After reaction for 5 hours at room temperature, the membrane was taken out and rinsed with ethanol for several times to remove the unreacted molecules. Then the membrane was dried in vacuum oven at 40℃ for 12 hours.

Growth of HKUST-1 and ZIF-8 on commercial PP membrane by bulky synthesis

Growth of HKUST-1: 10 mL aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.31 M) was added with 10 mL ethanol solution of H_3BTC (0.17 M). The mixed synthesis solution was transferred into a Teflon-lined steel autoclave and heated in an air oven at 75℃ for 8 days. After cooling in an ice-water bath, the solid products were filtered. The filtrated clear solution was used as mother solution for growth of HKUST-1. The benzoic acid modified PP membrane was placed upright into the HKUST-1crystallization solution at ambient temperature. PDA-coated PP membrane was also immersed in the solution under same condition as reference. Both samples were taken out of the solution after 2 days and washed with ethanol several times and dried in vacuum oven at 40℃ for 12 hours.

Growth of ZIF-8: A solid mixture of 0.538 g zinc chloride, 0.648 g 2-methylimidazole and 0.268 g sodium formate was dissolved in 50 ml methanol completely. Pyridine grafted PP membrane was immersed upright into the synthesis solution which had been transferred into a Teflon-lined steel autoclave and heated at 85 °C in air oven. After solvothermal reaction for 8 hours and cooling to room temperature, the MOF-PP composite membranes were washed with methanol repeatedly to remove the loose powder, and then dried in vacuum oven at 40℃ overnight. As reference, PDA-modified PP-membrane without pyridine modification was treated under the same condition.

Adsorption performance of MIL-100(Fe)-PP membrane

Rhodamine b solution (0.01 mM) was prepared by dissolving rhodamine b in water at room temperature. The filtration experiments were performed using a two-chamber cylindrical membrane filtration holder made of polypropylene. The PP and MIL-100(Fe)-PP membrane was used directly to remove rhodamine b. The rhodamine b solution was forced to circulate through the membrane filtration holder by using a peristaltic pump (BT100-1J, Longer Pump, China). The circulation time was set to 180 min. The residue solution was measured on an UV spectrophotometer.

Characterization:

PXRD measurements were performed on Bruker D8 Advance X-Ray powder diffractometer. The morphologies of the fabricated membranes were observed using a field emission scanning electron microscopy (FESEM) on a JEOL JSM-5400 system. The surface chemical structures of the coated polymer fibers were characterized by Attenuated total reflection-Fourier transform infrared spectra (ATR-FTIR) (Perkin Elmer Spectrum GX). UV-Vis spectra were collected on PerkinElmer Lambda35 spectrometer.

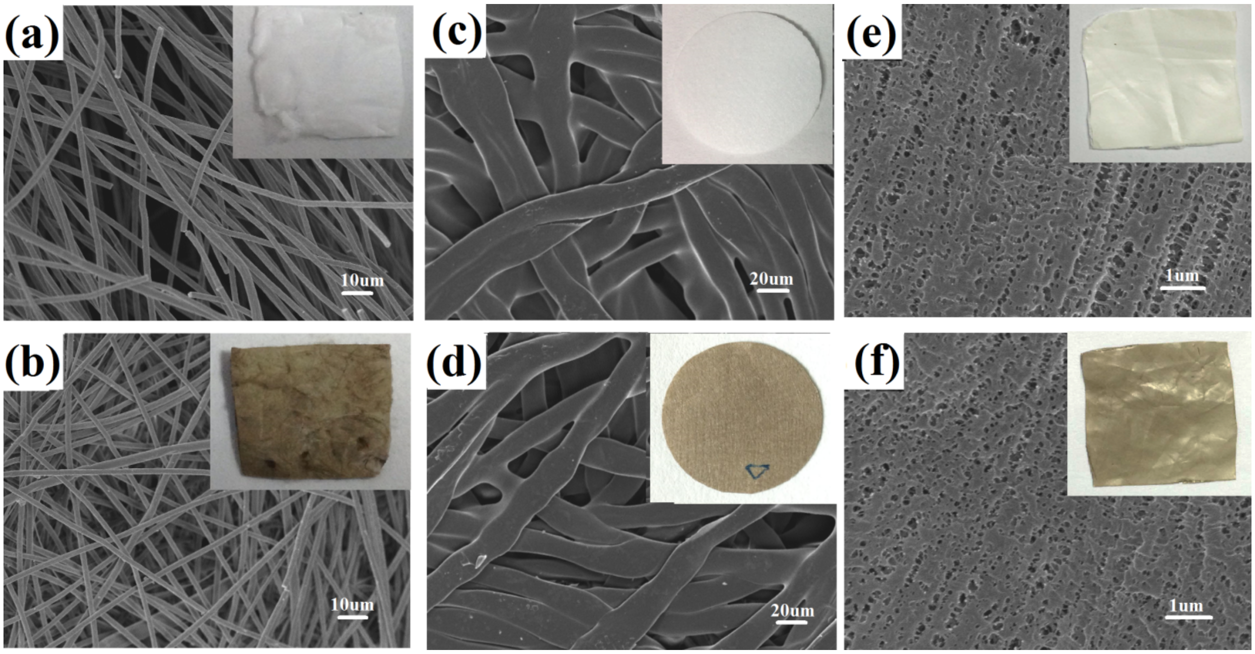

Fig. S1 SEM images of PS electrospun fibrous membrane (a) without and (b) with PDA coating; commercial PVDF fibrous membrane (c) without and (d) with PDA coating; commercial PE porous membrane (e) without and (f) with PDA coating; insets are the corresponding optical photos.

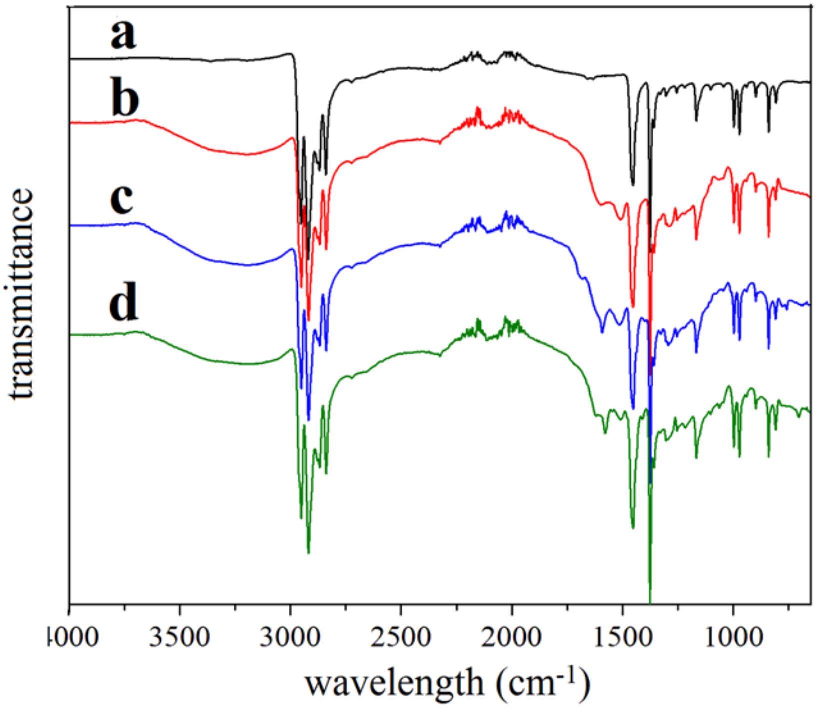

Fig. S2 ATR-FTIR spectra of commercial PP fibrous membrane (a) without and (b) with PDA coating; ATR-FTIR spectra of commercial PP fibrous membrane after grafting (c) pyridine and (d) benzoic acid on PDA coating.

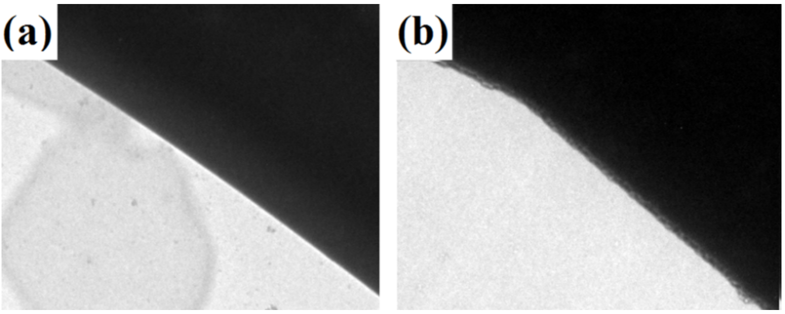

Fig. S3 TEM images of the edge of the commercial PP fibre (a) without and (b) with PDA coating.

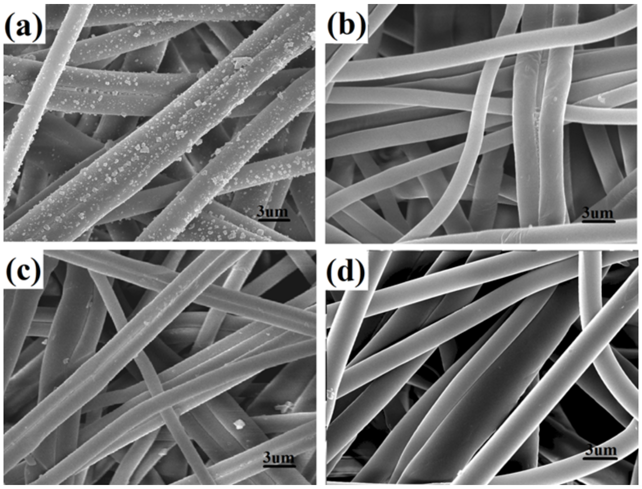

Fig. S4 SEM images of unmodified coummercial PP fibres after 30 cycles (a)HKUST-1; (b)MOF-5; (c)MIL-100(Fe); (d)ZIF-8 deposition.

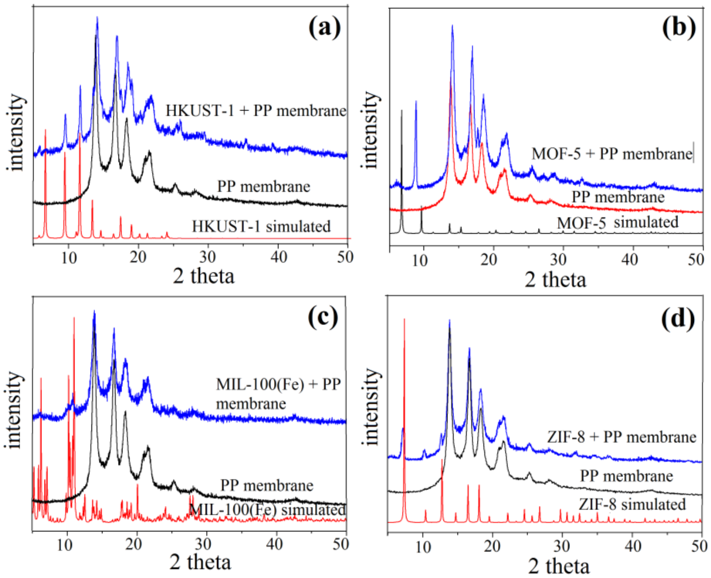

Fig. S5 Comparison of PXRD patterns of original PP membrane, simulated MOF, and PP membrane with deposited MOF: (a) HKUST-1, (b) MOF-5, (c) MIL-100(Fe), and (d) ZIF-8.

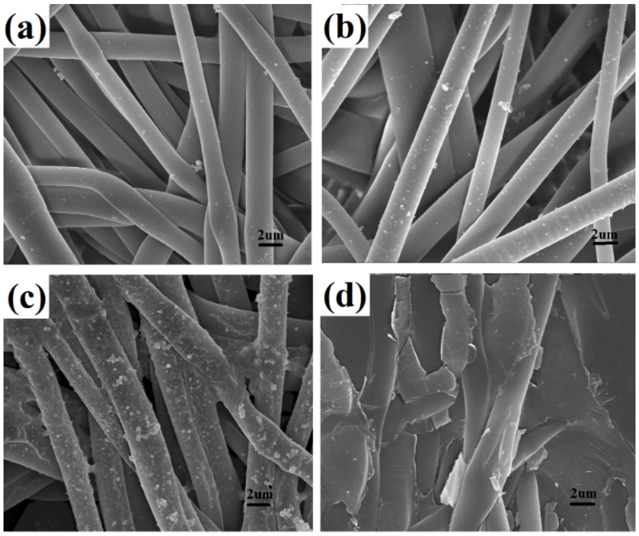

Fig. S6 SEM images of PDA-coated PP fibrous membrane after deposition of (a) HKUST-1 and (b) ZIF-8; (c) benzoic acid grafted PP fibrous membrane after deposition of HKUST-1 and (d) pyridine grafted PP fibrous membrane after deposition ZIF-8.

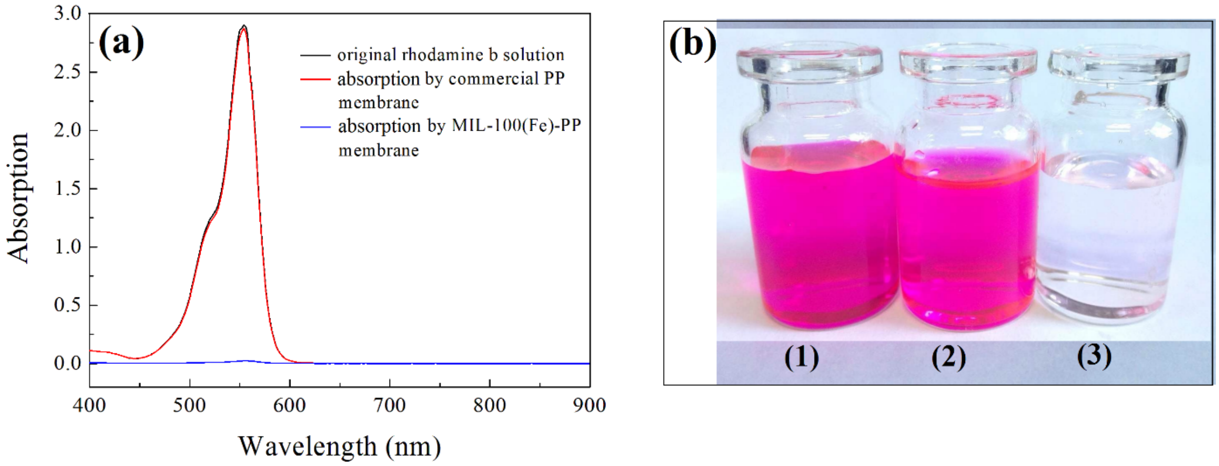

Fig. S7 (a) UV-Vis spectra of the original rhodamine B solution and the rhodamine B solution after adsorption by PP membrane and MIL-100(Fe)-PP membrane for 180 min at 40 ℃, respectively; (b) Photographs of (1) original rhodamine B solution and rhodamine B solution after absorption by (2) commercial PP membrane (3) MIL-100(Fe)-PP membrane, respectively.