Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Highly Stable MIL-101(Cr) Doped Water Permeable Thin Film Nanocomposite Membranes for Water Treatment

Yuan Xu, [a, b] Xueli Gao, *, [a, b] Qun Wang, [a, b] Xinyan Wang, [c] Zhiyong Ji, [d,] and Congjie Gao, [a, b]

a. Key laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Qingdao 266100, China

b. College of Chemistry & Chemical Engineering, Ocean University of China, Qingdao 266100, China

c. Shandong Zhaojin Motian Co. Ltd., Zhaoyuan 265400, China

d. School of Marine Science and Engineering, Hebei University of Technology, Tianjin 300130, China
Email: tcwdxy@163.com, gxl_ouc@126.com

Experimental Section

Materials: Chromium(III) nitrate nonahydrate (Sinopharm Chemical Reagent Co. Ltd.), terephthalic acid (Sinopharm Chemical Reagent Co. Ltd.), and methanol (Sinopharm Chemical Reagent Co. Ltd.) were used to synthesize MIL-101(Cr) nanoparticles. Trimesoyl chloride (TMC; TCI Co. Ltd.), m-phenylenediamine (MPD; Sigma-Aldrich), sodium dodecyl sulfate (SDS; Sigma-Aldrich), and n-hexane (Sinopharm Chemical Reagent Co. Ltd.), were used to prepare the PA layer on the polyether sulfone support. Polyether sulfone substrate was purchased from the Hangzhou Water Treatment Center (Hangzhou, China). All chemicals were of analytical grade and used without further purification.

Synthesis of MIL-101(Cr): $Cr(NO_3)_3.9H_2O$ (2.0 g, 5 mmol), terephthalic acid (0.83 g, 5mmol), and deionized water (20 mL) were blended and briefly sonicated resulting in a dark blue-colored suspension. The suspension was placed in a Teflon-lined autoclave and kept in an oven at 218 °C for 16 h without stirring. After the synthesis and equilibration at room temperature, the MOFs solids were separated from water using a centrifuge (7,000r/min, 5 min) and washed with methanol. The resulting solids were separated by centrifugation, dried at 75 °C overnight, and then under vacuum at ambient temperature for 2 days.

Characterization methods: The ATR-FTIR spectroscopy was performed using Tensor 27 spectrometer (Bruker, Germany) at room temperature. The XRD of the MIL-101(Cr) sample was recorded on a Bruker D8 ADVANCE instrument equipped with a Cu Kα radiation within the range of 2θ = 5° to 16° at the rate of 1°/min. The nitrogen sorption isotherm was collected by a Micromeritics ASAP 2420 analyzer at 77 K. A multiple-point BET method was used to calculate the specific surface area of MIL-101(Cr). The SEM (Hitachi S-4800, Japan) was utilized to investigate the cross section and surface area of the membranes and the morphology of the MIL-101(Cr) nanoparticles. Samples were deposited on sample holders with adhesive carbon foil and were sputtered with gold before measurement. The cross–section was obtained by freezing and fracturing the membrane in liquid nitrogen. The XPS measurement was performed on ESCALAB 250 spectrophotometer (Thermo Fisher SCIENTIFIC, USA) to determine the elemental compositions of the membranes. Atomic force microscopy

(AFM) images were recorded using Multimode-V microscope (Veeco, USA) in contact mode. Contact angle measurements were performed with a DSA100 contact angle analyzer (Kruss, Germany) using a sessile drop technique. The Membrane Performance Evaluation Instrument (Fig. S8) (Hangzhou Water Treatment Center) was used to evaluate water flux and rejection of membranes via cross-flow filtration at room temperature. Prior to filtration, the membranes were wetted by pressurization at 10 bar for 0.5 h. The effective membrane area is 11.3cm^2 and operating pressure is 10 bar Water flux (F) and solute rejection (R) are defined as follows:

$$F = \frac{Q}{At}$$

$$R\% = 1 - \frac{C_p}{C_f} \times 100$$

Where Q (L) is the volume of water passing through the membrane of surface area A (m^2) during a certain time t (h). C_p and C_f (ppm) are the concentrations of permeate and feed solutions, respectively.

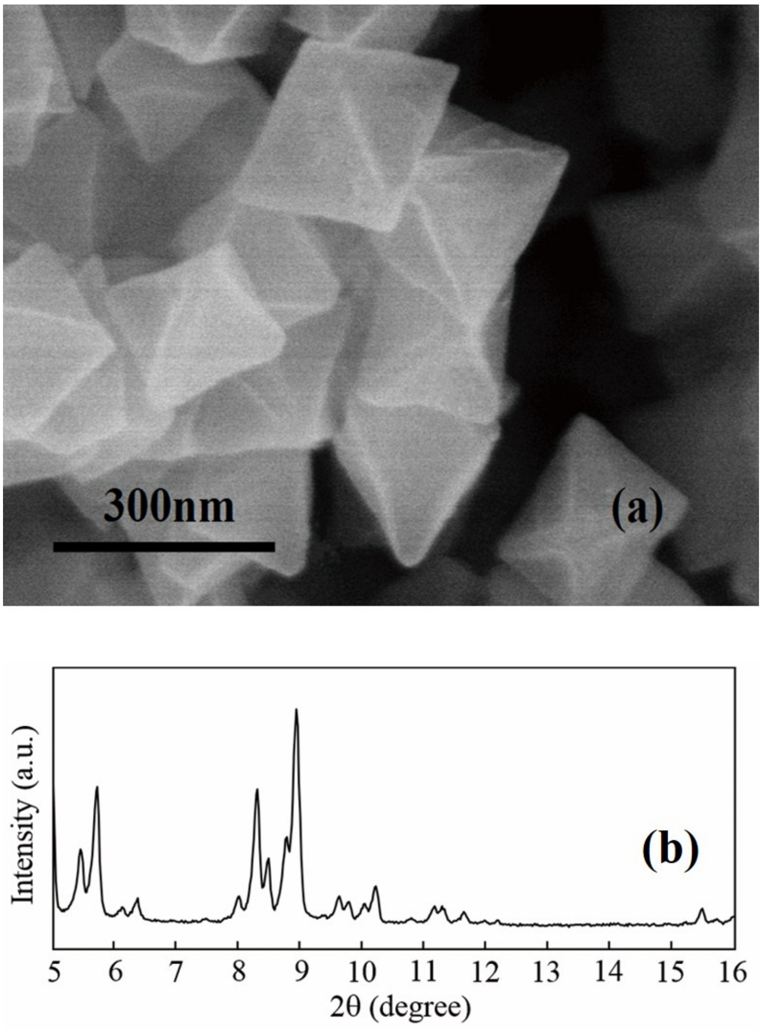
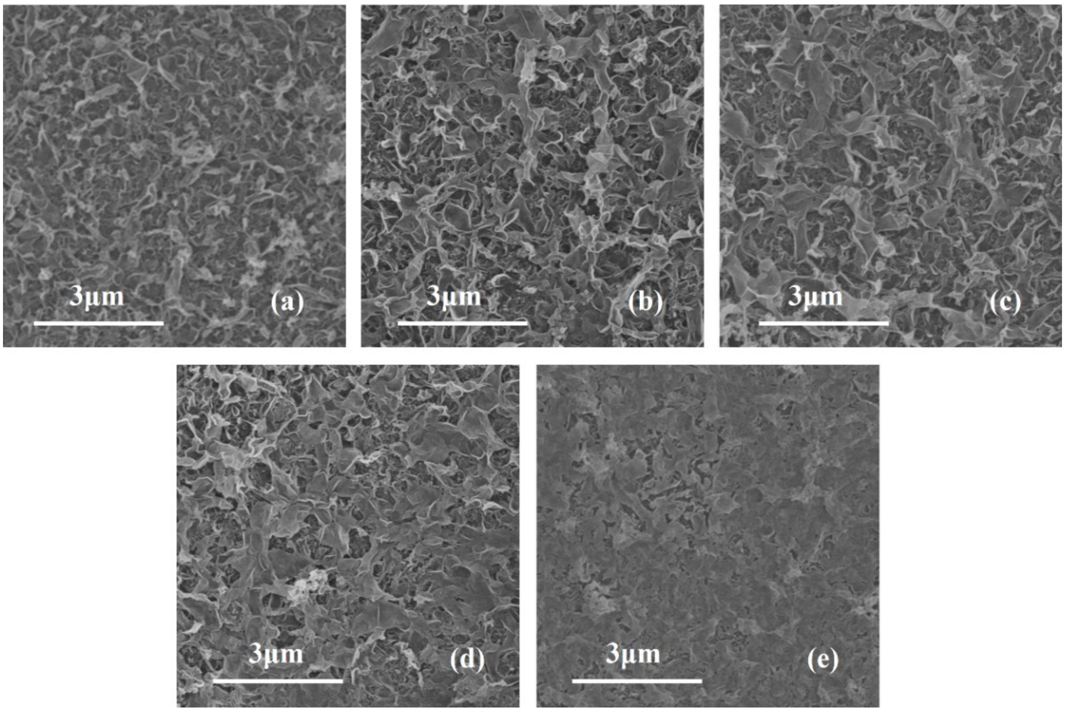


Fig. S1 (a) SEM image of MIL-101 nanoparticles, (b) XRD pattern of MIL-101 nanoparticles.



Fig, S2 (a) SEM image of the TFMN (A) (0.025 w/v%) membrane. (b) SEM image of the TFMN (A) (0.05 w/v%) membrane. (c) SEM image of the TFMN (A) (0.1 w/v%) membrane. (d) SEM image of the TFMN (A) (0.2 w/v%) membrane. (e) SEM image of the TFMN (A) (0.4 w/v%) membrane.

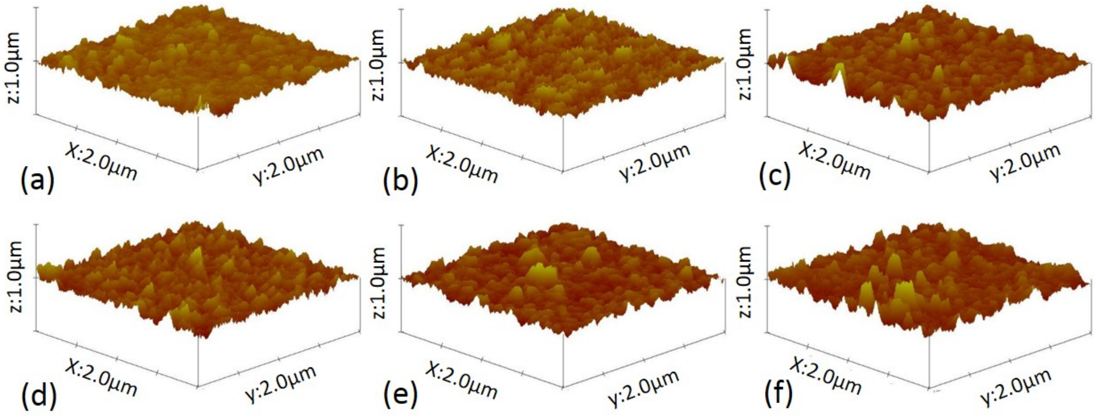


Fig. S3 (a) AFM image of the TFC membrane. (b) AFM image of the TFMN (O) (0.025 w/v%) membrane. (c) AFM image of the TFMN (O) (0.05 w/v%) membrane. (d) AFM image of the TFMN (O) (0.1 w/v%) membrane. (e) AFM image of the TFMN (O) (0.2 w/v%) membrane. (f) AFM image of the TFMN (O) (0.4 w/v%) membrane.

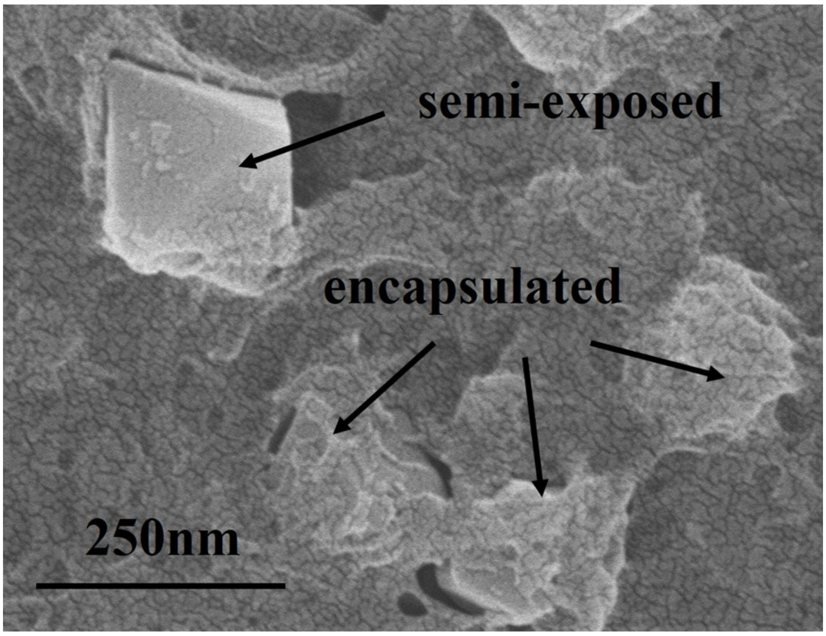


Fig. S4 SEM image of MIL-101(Cr) nanoparticles in the PA layer.

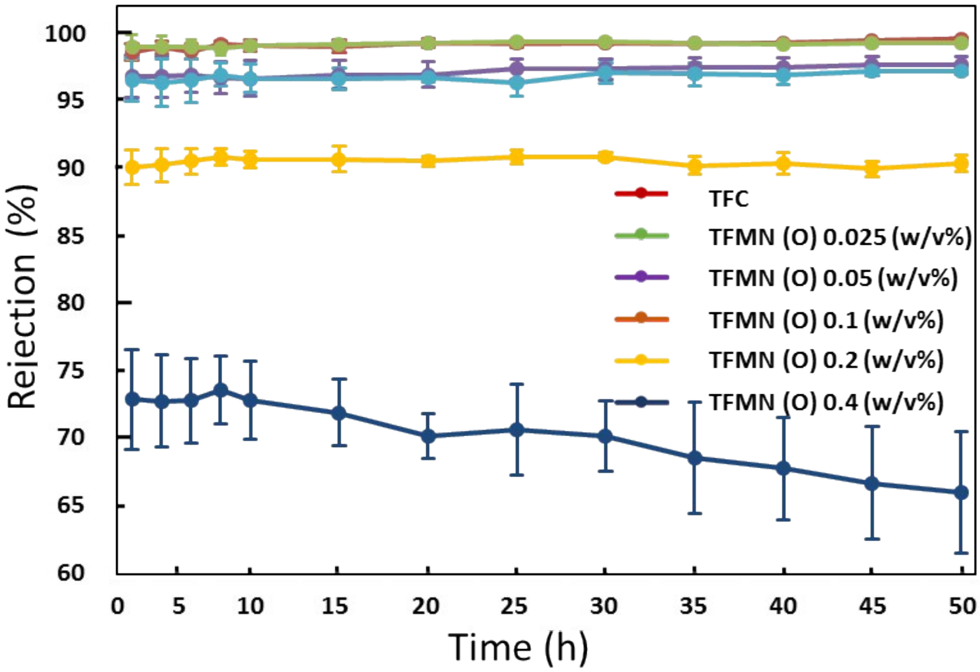


Fig. S5 Na_2SO_4 rejections of TFMN (O) membranes during 50 h stability test with 2000 ppm Na_2SO_4 aqueous solution at 10 bar and 25 °C.

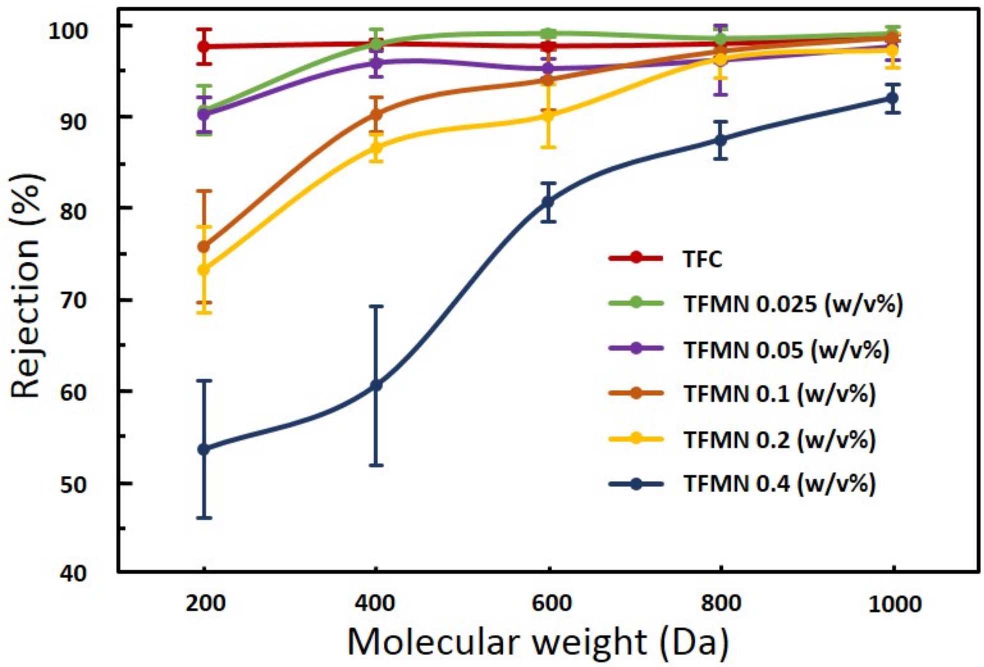


Fig. S6 Molecular weight test by PEG.

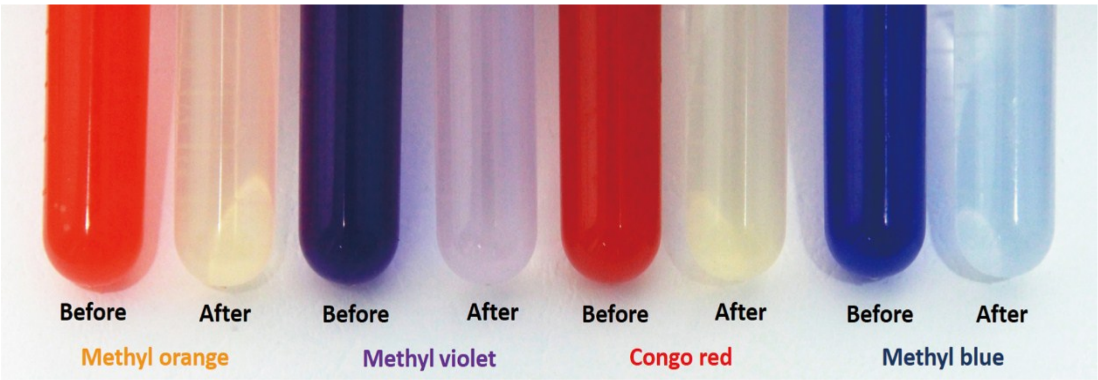


Fig. S7 The before and after photos of dye removal test.

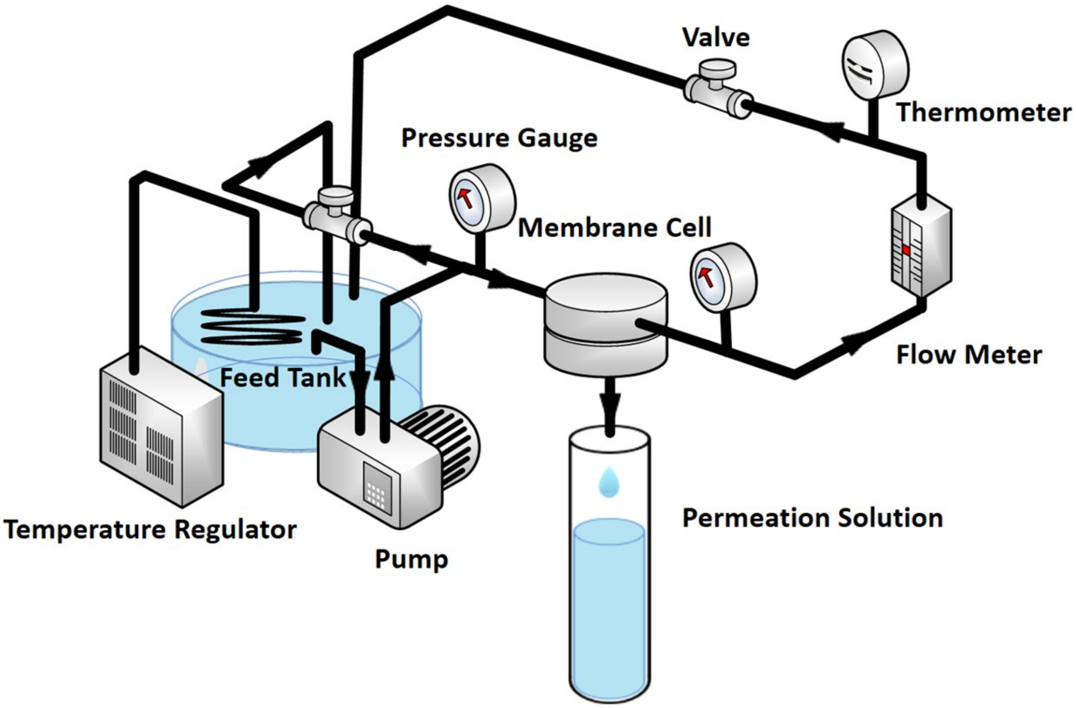


Fig. S8 Schematic representation for the membrane performance evaluation instrument.