

Supporting Information

Graphene Oxide Nanofiltration Membranes Stabilized by Cationic Porphyrin for High Salts Rejection

Xiao-Ling Xu,[†] Fu-Wen Lin,[†] Yong Du,[‡] Xi Zhang,[‡] Jian Wu,^{*,†} and Zhi-Kang Xu^{*,‡,§}

[†] Department of Chemistry, Zhejiang University, Hangzhou, 310027, China. E-mail:
jianwu@zju.edu.cn

[‡] MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, 310027, China. E-mail:
xuzk@zju.edu.cn

[§] Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM)

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1. Experimental

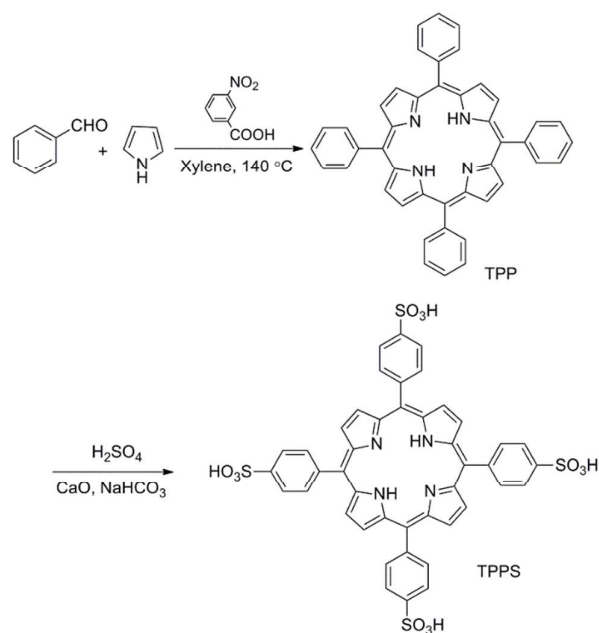
Materials: Graphite powder (150 μm) was purchased from Qingdao Shun Ming Graphite Co., Ltd, China. TMPyP was purchased from frontier scientific, USA. All other reagents were procured from Sinopharm Chemical Reagent Co., Ltd, China and used as received without further purification.

Characterization: UV-vis spectra were recorded on a Shimadzu UV 2450 spectrophotometer (Shimadzu, Japan). Fluorescence spectra were determined on a Shimadzu RF-5301 PC fluorescence spectrophotometer (Shimadzu, Japan). Standard quartz cuvettes with a 10 mm light path were used for all UV-vis spectra detection. NMR spectrum was recorded on a Bruker Avance III 400 MHz NMR spectrometer using DMSO as solvent and calibrated using tetramethylsilane ($\text{Si}(\text{CH}_3)_4$) as internal standard. Chemical shifts were quoted in ppm. AFM images were obtained on a Bruker Multimode 8 under tapping mode (Bruker, Germany). The samples were prepared by depositing one droplet of GO or TMPyP/GO suspension on mica substrate and dried in ambient temperature. Zeta potentials were measured by laser Doppler electrophoresis using a Zeta-Nanosizer (Nano ZS, Malvern Instruments Ltd., Worcestershire, UK). SEM images were obtained from Hitachi SU-8010 field-emission SEM system (Hitachi, Japan). XRD was carried out on Empyrean 200895 diffractometer equipped with Cu Ka radiation (PANalytical B.V., Holland). The samples in wet state were achieved by soaking GOLMs in water for 10 s. The concentration of salt solution was detected by an electrical conductivity meter (METTLER-TOLEDO, FE30, Switzerland).

Preparation of GO: Graphene oxide (GO) was typically synthesized by an improved method.^[S1] A 5:1 mixture of concentrated $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ (200:40 mL) was added into a mixture of graphite flakes (5.0 g) and KMnO_4 (25.0 g) in ice-water bath. The solution was heated to 40 $^\circ\text{C}$ and stirred constantly for 6 h. After cooling to room temperature, the reacted solution was poured into ice water (400 mL) with 30% H_2O_2 (25 mL). This mixture was then separated by a centrifuge (4000 rpm for 4 h), and the supernatant solution was decanted away. The rest of solids were washed in succession with 1 mol/L HCl for 8 times and deionized water for other 8 times; After each wash, mixture was separated by the centrifuge (15000 rpm for 2 h) and supernatant decanted away. The remaining material was coagulated by multiple-wash process with 200 mL of ether, and resulted suspension was filtered over a PTFE membrane with 0.45 μm pore size. The solid GO obtained on the filter was vacuum-dried over-night at room temperature.

Preparation of tetra-phenylporphyrin (TPP): A solution of benzaldehyde (8.48 g, 80 mmol), pyrrole (5.36 mL, 80 mmol), and xylene (70 mL) was dropwise added to the mixture of 3-nitrobenzoic acid (12.7 g, 76 mmol) and xylene (190 mL) under refluxing by 30 minutes, then refluxing for 2.5 h. Cold methanol (90 mL) was added to the reaction mixture when the solution was cooled to room temperature. Then the system was refrigerated overnight. Black solid was obtained by vacuum filtration. By washed with methanol 3 times, black solid changed to atropurpureus solid. The raw product was dried under air to give solid of 3.6 g.

Synthesis of TPPS (Scheme S1): A solution of TPP (2 g) in 40 mL of concentrated H_2SO_4 was stirred at 105 °C for 5 h, then at room temperature for 18 h. Ice-water (90 mL) was added to stop reaction. Green solid was obtained via vacuum filtration followed by washing with acetone. The dark red solid was obtained by neutralization with CaO and NaHCO_3 . Finally, the raw product was recrystallization using methanol/ethanol to gain red TPPS. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ (ppm): 8.88 (d, 8H, pyrrole β -H), 8.21 (d, 8H, *meta*-H phenyls bonded to sulfonate), 8.07 (d, 8H, *ortho*-H phenyls bonded to sulfonate), -2.94 (s, 2H, pyrrole NH) (Figure S1). UV-vis λ_{max} (H_2O): 413 nm.



Scheme S1. Synthetic route to TPPS.^[S2]

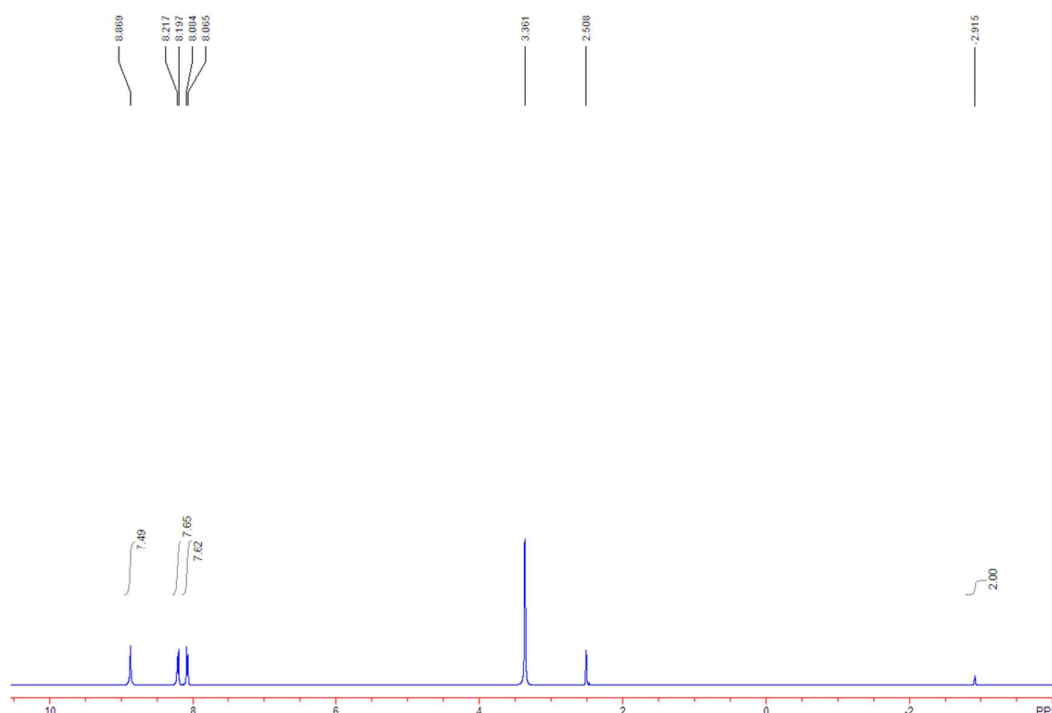


Figure S1. ^1H NMR spectrum of TPPS.

Preparation of the GO standard solution (GO-SS): The resulting GO aqueous dispersion (1 mg/ mL) was sonicated for 10 min followed by centrifugation at 15 000 rpm for 15 min. The supernatant was collected and diluted to 0.4 mg/mL with ultrapure water.

Preparation of the TMPyP standard solution (TMPyP-SS): TMPyP solid was dissolved in ultrapure water with a concentration of 0.1 mM.

Preparation of the TPPS standard solution (TPPS-SS): TPPS solid was dissolved in NaOH aqueous solution (pH = 9.0) with a concentration of 0.1 mM.

Titration of GO solution with the porphyrin standard solutions: Tracking by UV-vis or fluorescence spectra: 30 μL GO-SS (0.4 mg/mL) was diluted with ultrapure water into 3 mL in standard quartz cuvette, then titrated with TMPyP-SS (0.1 mM) or TPPS-SS (0.1 mM).

Tracking by zeta potential: 30 μL GO-SS (0.4 mg/mL) was diluted with ultrapure water into 2 mL, then titrated with TMPyP-SS (0.1 mM) or TPPS-SS (0.1 mM).

Solutions for Zeta potential measurement: A certain volume of TMPyP-SS was added in 1 mL ultrapure water with 15 μL GO-SS.

Fabrication of GOLMs: The assembled GO dispersions were prepared by adding a certain volume of the standard GO solution into ultrapure water (20 mL) followed by 5 min sonication. The $V_{\text{TMPyP-SS}}/V_{\text{GO-SS}}$ was controlled. In order to fabricate GOLMs with different thicknesses, GO standard solutions with different volumes were used ranged from 50 μL to 200 μL . Then the dilute GO dispersions (20 mL) were filtrated on microfiltration membranes such as polyether sulfone (PES) membranes or polycarbonate (PC) track-etched membranes (Whatman, 47 mm diameter, 0.2 μm pore size) under vacuum. The prepared membranes were dried in air for 2 d at room temperature before use. Samples for XRD characterization were prepared by filtrating solutions with 5000 μL standard GO solution or TMPyP/GO assemblies solution through PES membranes. All other measurements were carried out using GOLMs with PC track-etched substrate membranes.

Measurements of Permeation Flux and Rejection: Permeation flux and rejection measurements were performed on a laboratory scale cross-flow flat membrane module under 0.8 MPa. Effective area was 7.07 cm^2 for each sample. Samples were pre-compacted under 0.8 MPa for 2 h before performance evaluation. Various salt solutions of Na_2SO_4 , MgSO_4 , MgCl_2 , and NaCl at the concentration of 2000 mg/L were used as feed solutions with a fixed cross-flow rate of 25 L/h (cross-flow velocity: 0.1 m/s, Reynolds number: 596). Permeation flux (F_w , $\text{L}/\text{m}^2 \cdot \text{h}$) and rejection (R , %) were calculated by the following equations:

$$F_w = \frac{Q}{A \cdot t} \quad (1)$$

Q : the volume of permeated water; A : the effective membrane area; t : the permeation time.

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2)$$

C_p : the solute concentration in permeate; C_f : the solute concentration in feed.

All results presented were repeated at least three times.

2. Absorbance spectra: GO, TPPS, and TPPS/GO complex

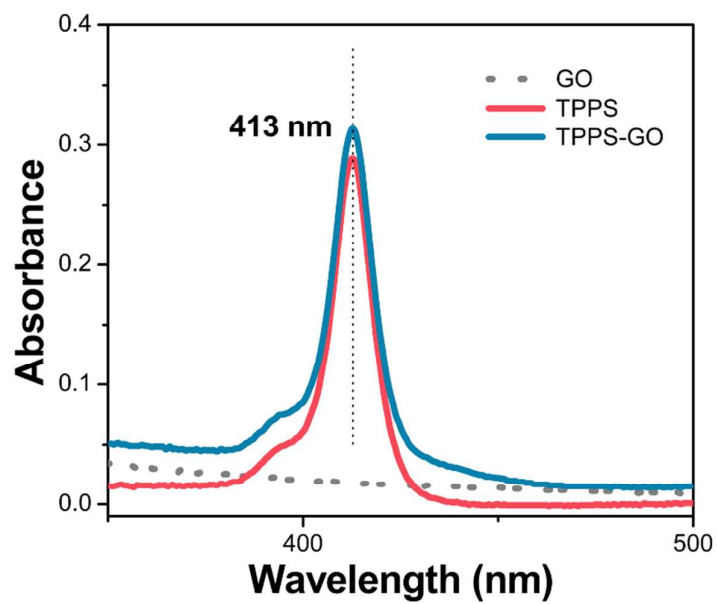


Figure S2. Absorbance spectra of GO, TPPS, and TPPS/GO complex. $V_{GO} = 30 \mu\text{L}$, $c_{GO-SS} = 0.4 \text{ mg/mL}$, $c_{TPPS-SS} = 0.1 \text{ mM}$.

3. Absorbance spectra versus the titration volume of TPPS-SS

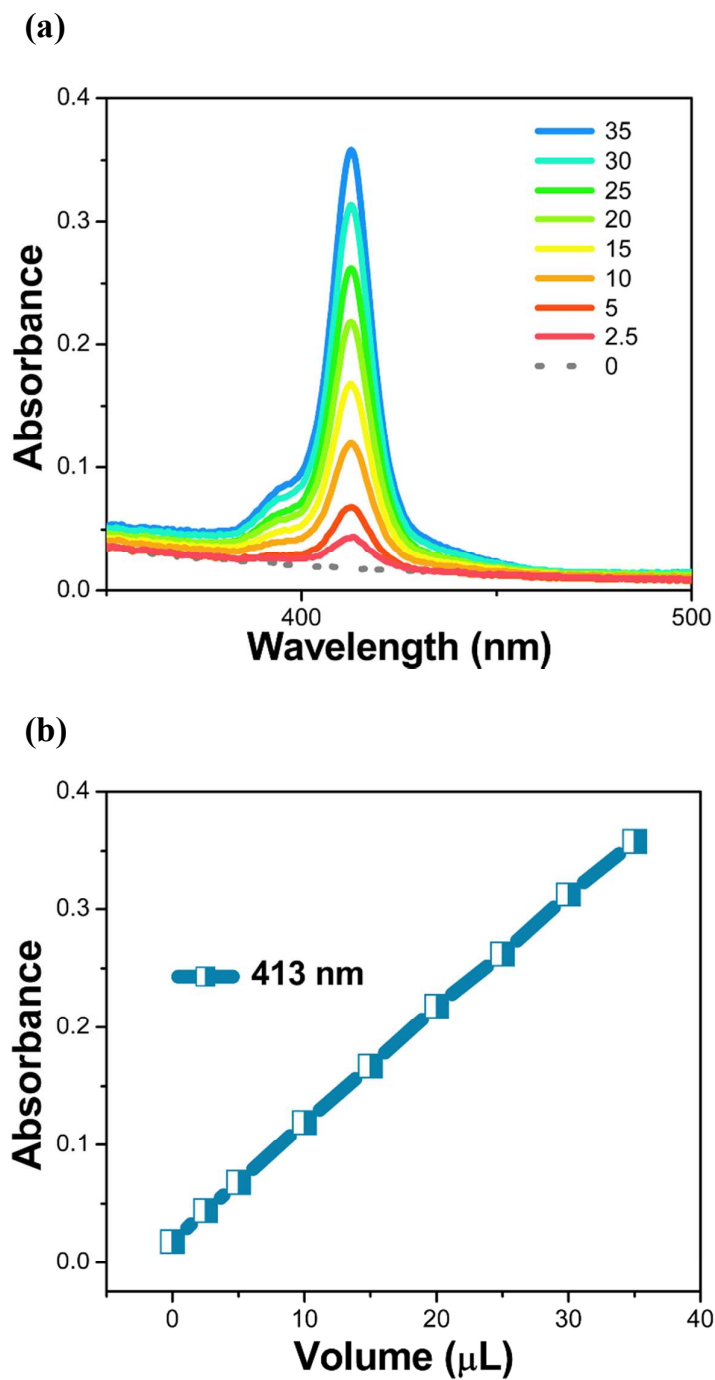
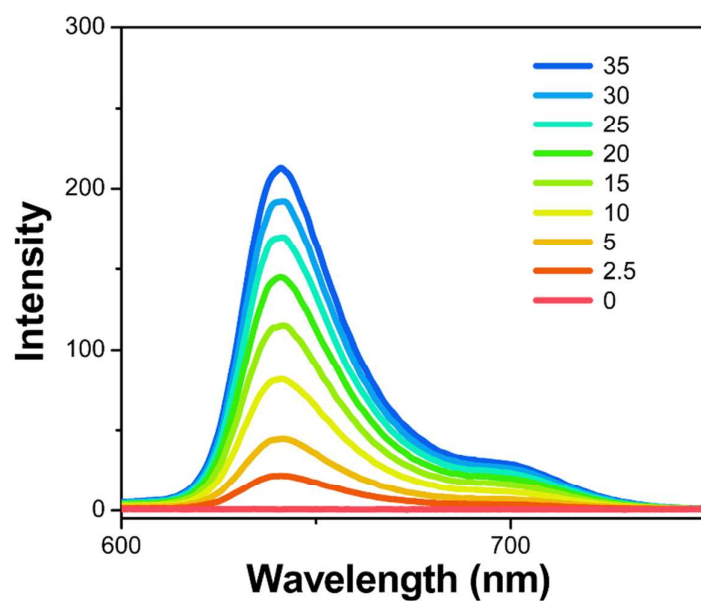


Figure S3. (a) Absorbance spectra and (b) absorbance at 413 nm the versus titration volume of TPPS-SS. $V_{GO} = 30 \mu\text{L}$, $c_{GO-SS} = 0.4 \text{ mg/mL}$, $c_{TPPS-SS} = 0.1 \text{ mM}$.

4. Fluorescence spectra versus the titration volume of TPPS-SS

(a)



(b)

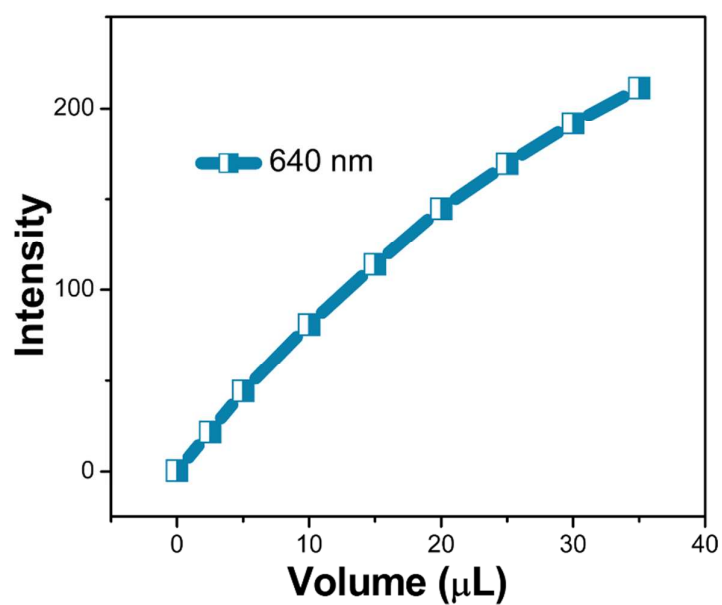


Figure S4. (a) Fluorescence spectra and (b) intensity at 640 nm versus the titration volume of TPPS-SS. $V_{\text{GO}} = 30 \mu\text{L}$, $c_{\text{GO-SS}} = 0.4 \text{ mg/mL}$, $c_{\text{TPPS-SS}} = 0.1 \text{ mM}$.

5. Digital photographs of the mixed solutions with different $V_{\text{TMPyP-SS}}/V_{\text{GO-SS}}$

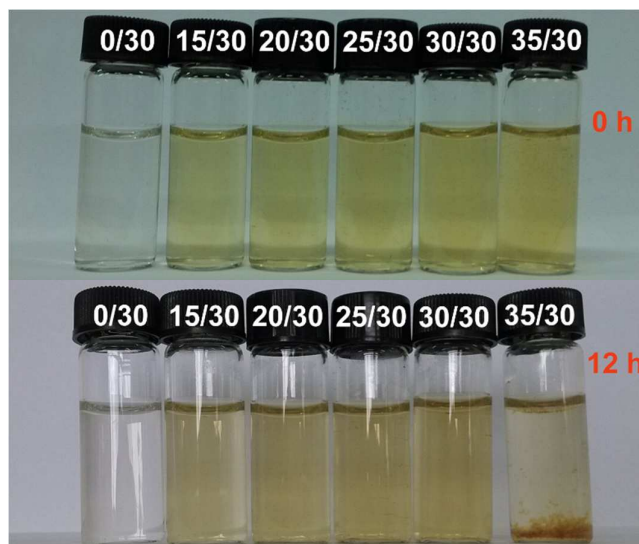


Figure S5. Digital photographs of the mixed solutions with different $V_{\text{TMPyP-SS}}/V_{\text{GO-SS}}$ standing for 0 h (up) and 12 h (down).

6. SEM images of GOLMs with different $V_{\text{TMPyP-SS}}/V_{\text{GO-SS}}$

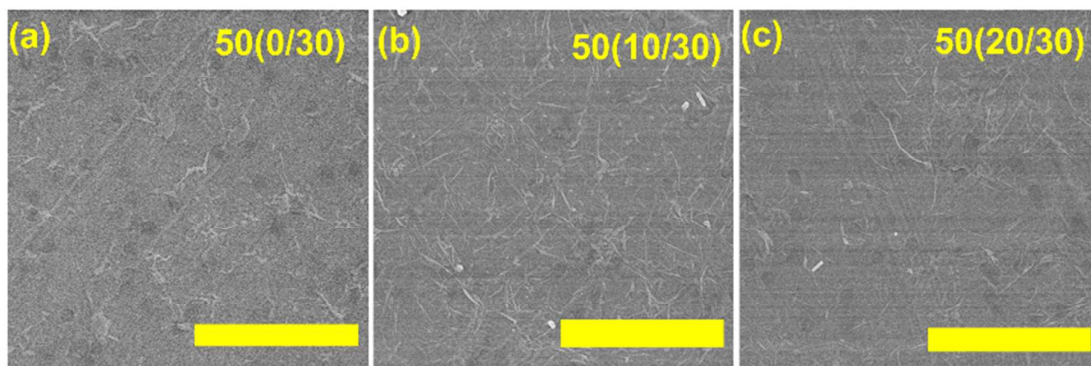
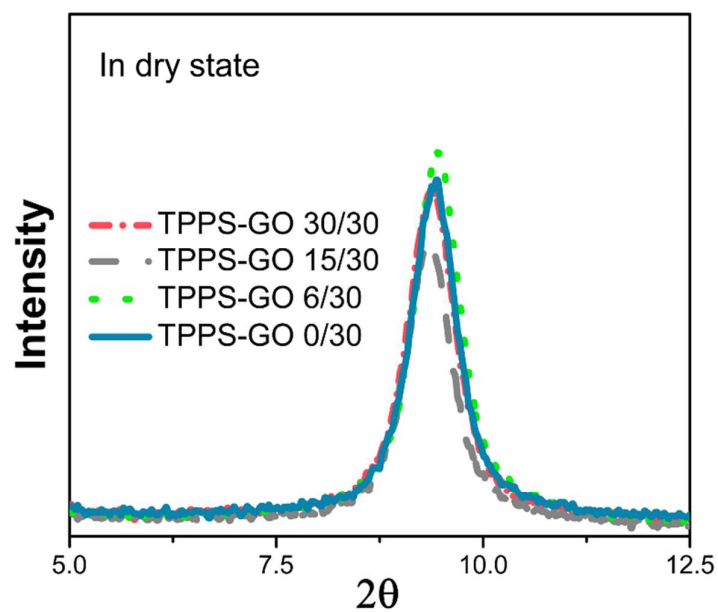


Figure S6. SEM images (top view) of (a) GOLM-50-0/30, (b) GOLM-50-10/30, (c) GOLM-50-20/30. Scale bar = 2 μm .

7. XRD patterns of GOLMs with different $V_{\text{TPPS-SS}}/V_{\text{GO-SS}}$

(a)



(b)

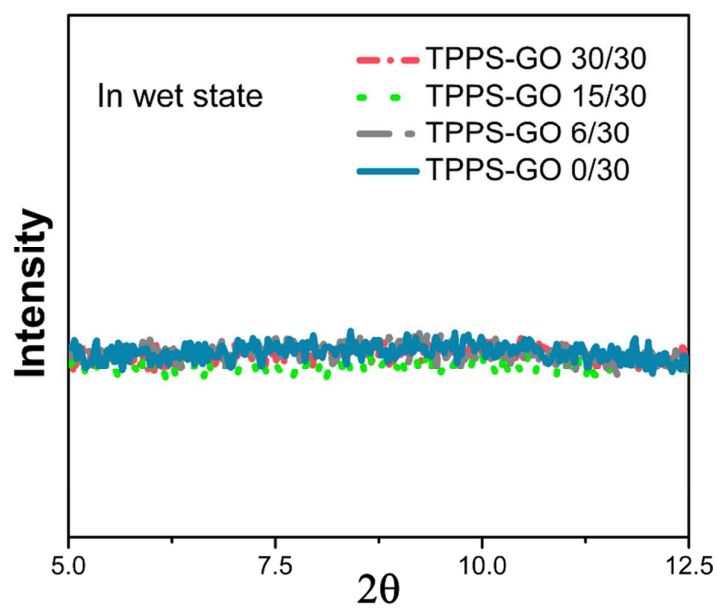


Figure S7. XRD patterns of GOLM-5000-0/30, GOLM-5000-6/30, GOLM-5000-15/30, and GOLM-5000-30/30 (a) in dry state and (b) in wet state.

8. Permeation flux and rejection of GOLMs with different $V_{\text{TPPS-SS}}/V_{\text{GO-SS}}$

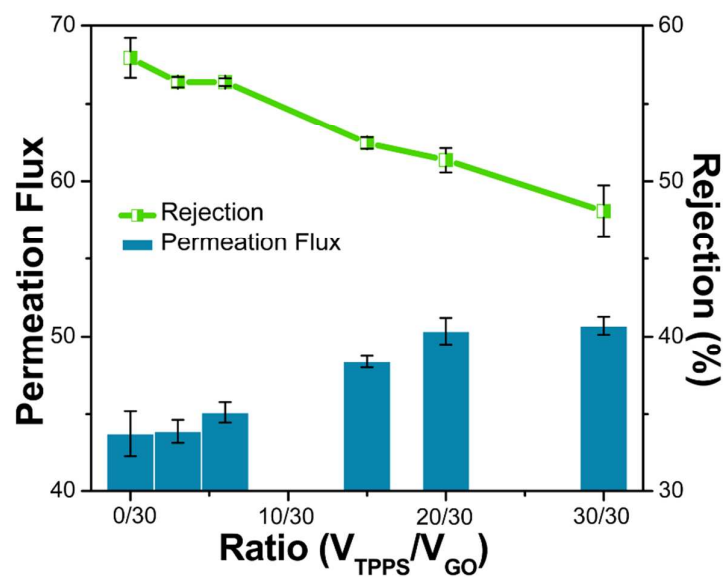


Figure S8. GOLM performance with different $V_{\text{TPPS-SS}}/V_{\text{GO-SS}}$ (GOLM-50). Test conditions: Na_2SO_4 , salt concentration = 2000 mg/L, 0.8 MPa, cross-flow rate = 25 L/h.

9. Permeation flux and rejection of GOLMs with different thicknesses

9.1 $V_{\text{TMPyP-SS}}/V_{\text{GO-SS}} = 1.5/30$

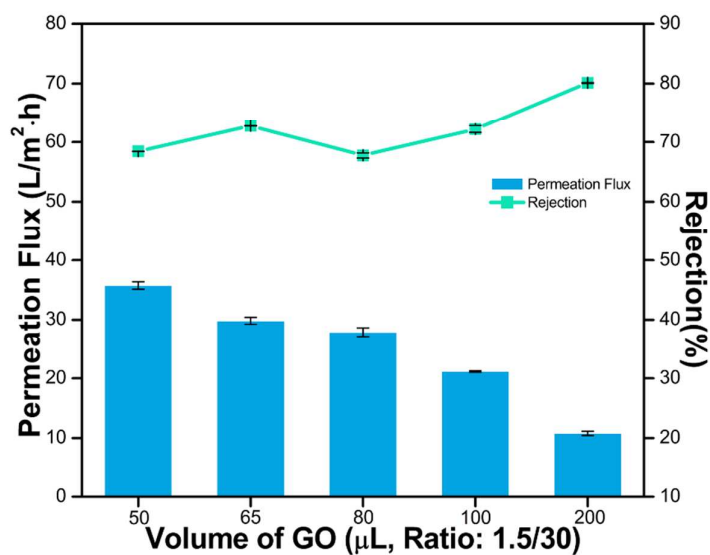


Figure S9. Effect of GOLMs thickness on the separation performance. $V_{\text{TMPyP-SS}}/V_{\text{GO-SS}} = 1.5/30$; Test conditions: Na_2SO_4 , salt concentration = 2000 mg/L, 0.8 MPa, cross-flow rate = 25 L/h.

9.2 $V_{\text{TMPyP-SS}}/V_{\text{GO-SS}} = 3.0/30$

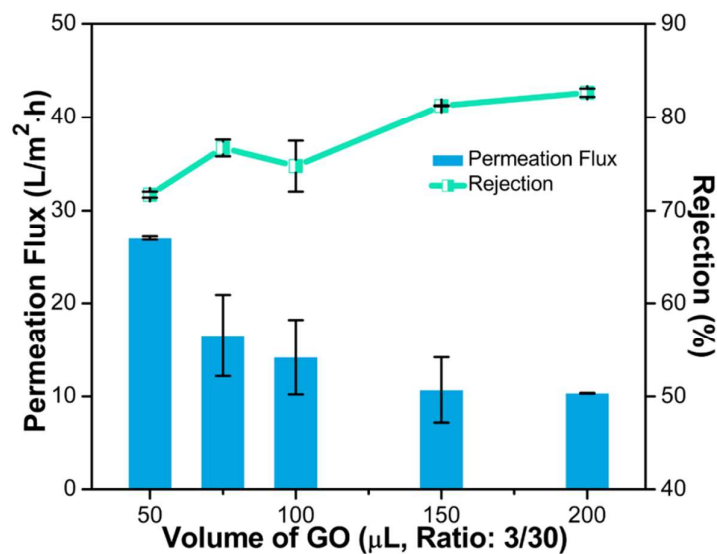


Figure S10. Effect of GOLMs thickness on the separation performance. $V_{\text{TMPyP-SS}}/V_{\text{GO-SS}} = 3.0/30$; Test conditions: Na_2SO_4 , salt concentration = 2000 mg/L, 0.8 MPa, cross-flow rate = 25 L/h.

Reference

- [S1] Marcano, D. C.; Kosynkin, D. V.; Berlin, J. M.; Sinitskii, A.; Sun, Z.; Slesarev, A.; Alemany, L. B.; Lu, W.; Tour, J. M. Improved Synthesis of Graphene Oxide. *ACS Nano* **2010**, *4*, 4806-4814.
- [S2] Dong, Z.; Scammells, P. J. New Methodology for the N-Demethylation of Opiate Alkaloids. *J Org. Chem.* **2007**, *72*, 9881-9885.