Supporting Information

**CO$_2$-responsive Graphene Oxide/Polymer Composite Nanofiltration Membrane for Water Purification**

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1. Synthesis

*Materials:* GO (produced by The Sixth Element Materials Technology Co., Ltd, China) was kindly provided by Prof. Hesheng Xia (Sichuan University). 1-Pyrenemethanol, $N,N'$-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) were purchased from Aldrich and used without further purification. 2-(Diethylamino) ethyl methacrylate (DEAEMA, from Aldrich) was passed through an activated basic alumina column to remove the inhibitory substances. 2,2’-Azobis(2-methylpropionitrile) (AIBN) was recrystallized from methanol before use. The chain transfer agent of Py-DDMAT (2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid) was synthesized according to a literature report.$^{44}$ Polyvinylidene fluoride microfiltration membranes ($\alpha$-PVDF, mean pore size 220 nm, diameter 47 mm) were purchased from Shanghai Xingya Purification Material. Other chemical reagents were all commercially available and of analytical grade.

*Synthesis of Py-PDEAEMA:* The synthetic route is shown in Scheme S1. DEAEMA (3.33 g), AIBN (3.94 mg), Py-DMTA (36.43 mg) and THF (3 mL) were added into a Schlenk tube with a magnetic stir bar, and air was eliminated by a nitrogen flow for 20 min. Next, the solution was degassed by three freeze/vacuum/nitrogen cycles and then put into an oil bath at 70 °C for 6h, 12h and 24h, respectively. Subsequently, the mixture was diluted with THF and
precipitated in cold hexane for three times. Finally, the obtained material was dried under vacuum overnight.

![Scheme S1. Synthesis route of Py-PDEAEMA](attachment:image.png)

**Scheme S1.** Synthesis route of Py-PDEAEMA

### 2. Fabrication of Py-PDEAEMA/GO NFMs

The GO aqueous dispersion (0.1 mg/mL) was prepared by adding a certain amount of GO into water followed by 2h ultrasonication. Then, 15 mg of Py-PDEAEMA was firstly added into 15 mL of deionized water, followed by bubbling CO₂ until Py-PDEAEMA was completely dissolved in deionized water to form transparent Py-PDEAEMA aqueous solution (1 mg/mL). To fabricate Py-PDEAEMA/GO NFMs, 4 ml of GO aqueous solution (0.1 mg/mL) were initially mixed with an calculated amount of Py-PDEAEMA aqueous solution (1 mg/mL) for a desired mass ratio of Py-PDEAEMA to GO ($R_{P/G}$). The mixed solution was then diluted by water to a total volume of 20 mL and filtered on PVDF microfiltration membranes via vacuum filtration. After filtration, the samples were air-dried before use.

### 3. Characterizations

$^1$H NMR spectra were recorded on a Bruker 300 MHz using deuterated chloroform as the solvent and tetramethylsilane as the internal standard. Size exclusion chromatograph (SEC) measurements were performed on a Waters system equipped with a photodiode array detector (PDA 996) and a refractive index detector (RI 410). THF was used as the eluent at an elution rate of 1 mL/min, while polystyrene (PS) standards were used for calibration. Infrared spectra of the membranes were recorded on a FTIR between 800 and 4000 cm$^{-1}$ at a resolution of 4
cm⁻¹. The morphology of membranes was examined using a Hitachi S-4700 field-emission-gun scanning electron microscope (SEM) operating at 1.0 kV to 10.0 kV. For SEM observation, a fine platinum coating layer (a few nm) was deposited on sample surface by using a K550 sputter coater for 1 or 2 min. UV-visible spectra were obtained using an UV-vis-NIR spectrophotometer (Agilent Cary 50 Bio). Fluorescence emission spectra were recorded on a SPEX 1680 double-monochromator spectrometer. Atomic force microscopy (AFM) images were recorded on a Dimension Icon AFM instrument equipped with a NanoScope V controller (Veeco/Digital Instruments, Santa Barbara, CA). AFM topographical images were obtained under ScanAsyst mode at room temperature using a silicon nitride cantilever tip (force constant 0.4 N/m). The ζ-potential was measured using a Malvern Zetasizer Nano ZS ZEN3600 system with a helium-neon laser (λ = 633 nm). XRD was performed on a D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 0.15418 nm, Bruker, Germany). The average d-spacing within the GO layers was calculated by using the Bragg equation: \( \lambda = 2d \sin \theta \), where \( \lambda \) is the wavelength of the X-ray beam, \( d \) is the spacing between adjacent GO layers, and \( \theta \) is the diffraction angle.

4. Measurements of Pure Water Flux and Retention under CO₂/Ar Stimulation

Water filtration was performed at 25 °C under CO₂/Ar stimulation. A dead-end filtration cell with effective membrane area of 13.1 cm² was used. The trans-membrane pressure was kept at 1 bar produced by vacuum. For CO₂ induced switching studies, the membrane was first filtered with DI water for a period of time to ensure a steady state, then treated with CO₂ bubbling into solution for 30 min, and subsequently with Ar bubbling for 40 min. Water flux samples were taken every 5 min. The flux was calculated from the volume of solution permeated per unit time and per unit area of the membrane surface. Water flux \( (J_w) \) was calculated as follow:

\[
J_w = \frac{V}{A \cdot t \cdot \Delta P}
\]  

(S1)

where \( V \) is the volume of water (L), \( t \) is the permeation time (h), \( A \) is the membrane area and \( \Delta P \) is the trans-membrane pressure. The rejection rate of organic dye molecules and salt in aqueous solution can be calculated using the following equation:

\[
R = \left(1 - \frac{C_p}{C_f}\right) \times 100\%
\]  

(S2)
where $C_f$ is the dye or salt concentration in the feed solution (10 mg/L for dye concentration), and $C_p$ is the dye or salt concentration in the permeate solution. UV-vis-NIR spectrophotometer (Agilent Cary 50 Bio) was employed to measure the absorption spectra of dyes within the wavelength range of 200-700 nm using the standard absorbance vs. concentration calibration curve (linear correlation coefficient was 0.9999). The volume of feed solution for salt was 250 mL (2 mg/mL) and the salt concentration in solution was determined by conductivity meter (Cole-Parmer, 1481-90) based on the standard calibration curve (linear correlation coefficient was 0.9998).

5. Characterization Results

Table S1. Properties of the obtained Py-PDEAEMA

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w$ (g/mol)</th>
<th>$D$</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>6600</td>
<td>9500</td>
<td>1.4</td>
<td>75</td>
</tr>
<tr>
<td>P2</td>
<td>9600</td>
<td>15000</td>
<td>1.5</td>
<td>80</td>
</tr>
<tr>
<td>P3</td>
<td>13500</td>
<td>22300</td>
<td>1.6</td>
<td>85</td>
</tr>
</tbody>
</table>

The apparently broad molecular weight distribution of the Py-PDEAEMA samples is likely to be caused by the interaction of the amine-containing polymer with the SEC column.

Figure S1. $^1$H NMR of Py-PDEAEMA in CDCl$_3$
Figure S2. UV-vis absorption spectra of 1-pyrenemethanol and PDEAEMA with and without pyrene group. In this case, the molecular weight of Py-PDEAEMA is 13500 g/mol.

Figure S3. Fluorescence spectra (excited at 344 nm) of Py-PDEAEMA dispersion in water (under CO₂) and the mixture of Py-PDEAEMA/GO with \( R_{PEG} = 6 \) in water. The sharp decrease of fluorescence intensity after mixing Py-PDEAEMA with GO is attributed to the complexation due to electrostatic interaction between positively charged PDEAEMA and negatively charged GO as well as π-π interaction between pyrene and GO. In this case, the molecular weight of Py-PDEAEMA is 13500 g/mol.

Figure S4. Photos of mixtures of Py-DEAEMA (\( M_n \): 13,500 g/mol)/GO with different \( R_{PEG} \).
Figure S5. Cross-sectional SEM image of neat GO NFMs. In this case the used GO suspension (0.1 mg/mL) is 4 mL.

Figure S6. AFM image and corresponding height profile of pure GO. The thickness of GO sheets is about 0.8 nm, implying excellent exfoliation of GO sheets.

Figure S7. FTIR spectra of PVDF, Py-PDEAEMA, GO/PVDF and Py-PDEAEMA/GO/PVDF. In this case, the molecular weight of Py-PDEAEMA is 13500 g/mol and $R_{PVG}=6$. 
Figure S8. Variation of pure water permeability of GO membrane with different as GO loading under the pressure of 1 bar. When the GO aqueous solution is 8 mL, the water permeability is reduced to none.

Figure S9. XRD patterns of GO-based membranes: (a) membrane-3 with $R_{PG}=3$, (b) membrane-3 with $R_{PG}=4$, (c) membrane-3 with $R_{PG}=5$, (d) membrane-1 with $R_{PG}=6$ and (e) membrane-2 with $R_{PG}=6$, and (f) membrane-3 with $R_{PG}=6$. (g) Pure GO membrane for comparison.
Fig. S10 shows the XRD patterns of membrane-3 with $R_{PG}=6$ at the different states. The membrane was first pre-immersed in deionized water for 1 h before collecting XRD data from the wet state. Then this membrane was treated with CO$_2$ bubbling into solution for 30 min, and subsequently with Ar bubbling for 40 min for collecting XRD patterns from these two states. According to the Bragg equation, the $d$-spacing of the membrane at the different states was calculated and reported in Table S2. The interlayer spacings of membrane-3 increased from 0.98 nm at the dry state to 1.07 nm at the wet state, which is due to swelling of GO sheets in water. After 30 min of CO$_2$ bubbling, the interlayer spacing increased to 1.17 nm. This is because passing CO$_2$ through the solution makes the tertiary amine groups in Py-PDEAEMA protonated, which renders the polymer soluble in water. Consequently, the polymer chains of extended conformation increase the interlayer spacings of GO sheets. The subsequent passing of Ar through the solution removes CO$_2$ and brings Py-PDEAEMA chains back to the insoluble state with collapsed chain conformation, which makes the interlayer spacing return to its original value at the wet state.

Table S2. The $d$-spacing for the membrane-3 with $R_{PG}=6$ at the different states.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Dry state</th>
<th>Wet state</th>
<th>CO$_2$ (30 min)</th>
<th>Ar (40 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>membrane-3 with $R_{PG}=6$</td>
<td>0.98 nm</td>
<td>1.07 nm</td>
<td>1.17 nm</td>
<td>1.08 nm</td>
</tr>
</tbody>
</table>
Figure S11. Rejection measured for pure GO membrane for four different salt solutions with different ion valences. In this case, the used GO suspension (0.1 mg/mL) is 4 mL.

Figure S12. Zeta potential values for Py-PDEAEMA/GO mixtures. Note that $R_{PG} = 0$ and $\infty$ represent neat GO and Py-PDEAEMA, respectively. The molecular weight of Py-PDEAEMA is 13500 g/mol. The pH values for Py-PDEAEMA/GO mixtures are 3.7 (neat GO), 5.5 (Py-PDEAEMA), 5.0 ($R_{PG} = 3$), 5.4 ($R_{PG} = 4$), 5.3 ($R_{PG} = 5$) and 5.3 ($R_{PG} = 6$).
Figure S13. Comparison of pure water permeability and NaCl rejection of membrane-3 with commercial NFM (NF270)\(^1\) and recently reported GO-based NFMs: GO&EDA and GO&DEA_HPEI 60K,\(^2\) GO@PAN,\(^3\) TA-GO&PEI,\(^4\) GO&TMC,\(^5\) \(\mu\)GNMs,\(^6\) GO-OCMC/psf,\(^7\) GOLM-100-6/30,\(^8\) G-CNTm\(^9\) and (PDDA/GO)\(_{4.0}\)/PAN membrane.\(^{10}\)

Figure S14. Stability test of gas-switchable permeability of membrane-3 with \(R_{\text{PG}} = 6\).
Reference: