CO_2-responsive Polymer Membranes with Gas-tunable Pore Size

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1. Synthesis and Characterization

1.1 Materials

2-(Diethylamino)ethyl methacrylate (Reagent plus, 99 % Aldrich)was passed through an activated basic alumina column to remove the inhibitory substances. 2,2'-Azobis(2-methylpropionitrile) (AIBN) (Sigma-Aldrich, 98%) was recrystallized from methanol before use. The chain transfer agent of DMTA was synthesized according to a previous report.[1]Dopaminehydrochloride (DA, Aldrich, 98%) and tris(hydroxymethyl)-aminomethane (Tris base, Aldrich, 98%) was used as received. Polyvinylidene fluoride microfiltration membranes (α-PVDF, mean pore size 0.22μm, diameter 47 mm) were purchased from Shanghai Xingya Purification Material. Other chemical reagents were all commercially available and of analytical grade.

1.2 Instrumentations

^{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 (ABB Bomem, MB Series) 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 to10.0 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).

1.3 Preparation of PDEAEMA-PDA@PVDF membrane

PDA@PVDF membrane. PVDF membrane was dipped into a solution of dopamine hydrochloride (2 mg/mL) dissolved in 15 mM Tris-buffer (pH 8.5, ultrapure water). The reaction vessel was shaken and the membranes were coated for 4h at room temperature. The membranes were rinsed thoroughly with ultrapure water and then dried at 60 °C under reduced pressure before use.

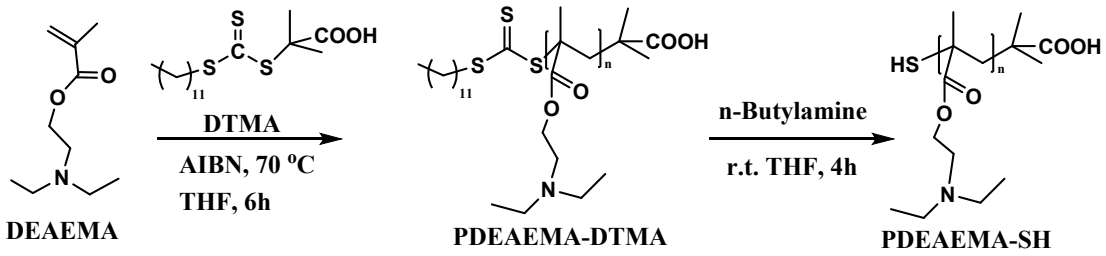
Synthesis of PDEAEMA *via* RAFT. 2-(Diethylamino) ethyl methacrylate (3.33 g), AIBN (3.94 mg), CTA (36.43 mg), and THF (3 mL) were added into a Schlenk tube

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 maintained at 70 °C for a certain time, respectively. Subsequently, the purified polymer was isolated by hexane precipitation after dissolving in THF. Finally, the obtained material was dried under vacuum.

Preparation of PDEAEMA-SH. PDEAEMA-CTA was dissolved in THF and then treated with *n*-butylamine to obtain thiol terminated PDEAEMA-SH[2]. The reaction was accomplished at room temperature for4 h, with acolor change from dark yellow to colorless. After the reaction, the product PDEAEMA-SH was also precipitated in cold *n*-hexane, centrifuged and vacuum-dried at room temperature for 24h before further characterization and reactions.

PDEAEMA-PDA@PVDF membrane. PDA@PVDF membrane was dipped into 50 mL ethanol for 30min, and then a certain amount of ethanol solution of PDEAEMA-SH (0.3g/mL) was added and stirred for 24 h at room temperature. After cooling down to room temperature, the membrane was under stirring for additional 16 h. Subsequently, the membrane was rinsedthree times with ethanol and ultrapure water and dried at 60 °C before characterization.

Synthesis of triammonium citrate-capped gold nanoparticles. Triammonium citrate-capped gold nanoparticles (AuNPs) were prepared by using triammonium citrate as the reducing agent, following a procedure similar to that reported in the literature.[3] An aqueous solution of $HAuCl_4 \cdot 3H_2O$ (300 mL, 0.25 mM) was heated up to the boiling point with vigorous stirring (900 rpm), then the aqueous solution of triammonium citrate (1 mL, 243 mM) was introduced rapidly using a syringe. The solution was boiled for additional 30 min in an oil bath. Afterwards, the solution was cooled down to room temperature slowly. The final red solution of AuNPs was kept at room temperature.



Scheme 1 Synthetic route for PDEAEMA-SH

Table S1 Properties of the obtained PDEAEMA[a]

Sample	*Mn (g/mol)*	*Mw (g/mol)*	*Đ*
P1	15700	25600	1.6
P2	16900	27600	1.6
P3	20000	32000	1.6

[a]The apparently broad molecular weight distribution of the PDEAEMA samples ($Đ$=1.6) is likely to be caused by the interaction of the amine-containing polymer with the SEC column.

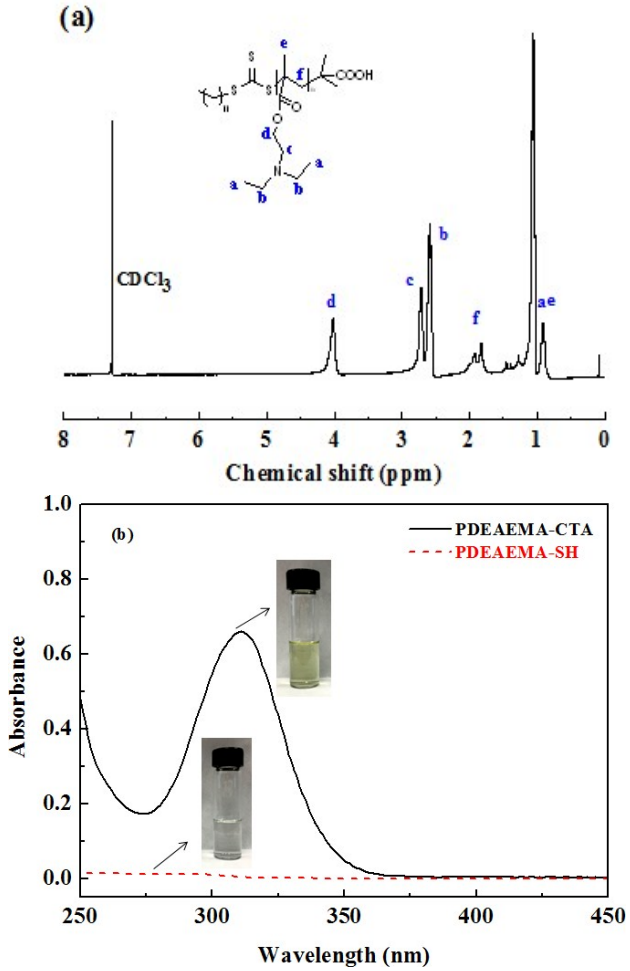


Figure S1[1]H NMR spectra of (a) PDEAEMA-CTA in $CDCl_3$ and (b)UV-vis spectra of PDEAEMA-CTA(solid) and PDEAEMA-SH(dashed).

1-4 Characterization of the membranes

The structure of the PDEAMEA-CTA was confirmed by[1] HNMR spectroscopy, as shown in Fig. S1(a).The peaks (a, b, c, d, e and f) corresponding to the protons of PDEAEMA are clearly visible, indicating the polymerization of DMAEMA monomers initiated by the CTA. The outcome of the aminolysis of PDEAMEA was also measured by UV-vis spectroscopy using the characteristic absorption centred at 310 nm of the trithiocarbonate group. As seen in Fig. S1 (b),the original PDEAEMA displays a strong

310 nm absorption, while no absorption appears in this spectral region for PDEAEMA-SH, indicating the complete aminolysis of trithiocarbonate groups.

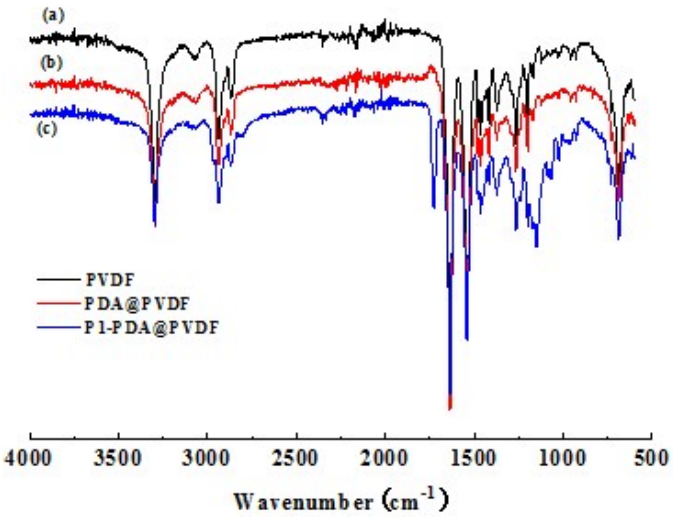


Figure S2 ATR-FTIR spectra of (a) PVDF membrane, (b) PDA@PVDF membrane, and (c) PDEAEMA-PDA@PVDF membrane.

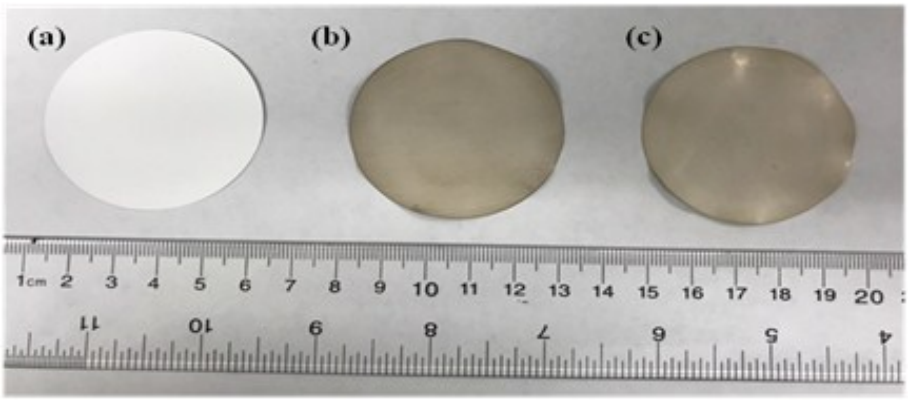


Figure S3 Photographs of (a) PVDF membrane, (b) PDA coated PVDF membrane, and (c) PDEAEMA-PDA@PVDF membrane.

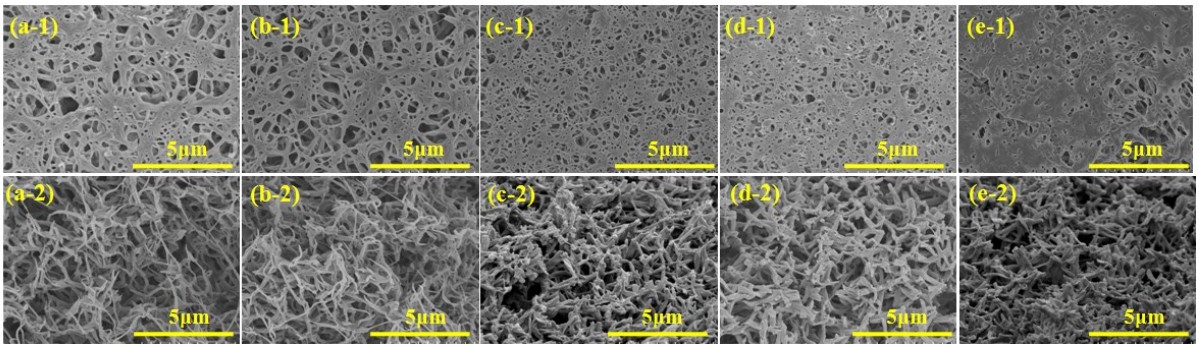


Figure S4 SEM images for (a-1and a-2) the PVDF membrane, (b-1and b-2) the PDA@PVDF

membrane, (c-1and c-2) the P1-PDA@PVDF membrane, (d-1 and d-2) the P2-PDA@PVDF membrane, and (e-1 and e-2) the P3-PDA@PVDF membrane. Top: surface view, and bottom: cross-section view.

The SEM analysis was used to investigate the morphology of membranes. As shown in Fig. S4, the pure PVDF membrane has an asymmetric structure with high pore density in the surface and spongy structure in the cross-section. There are no significant changes in morphology after modification, but the pore sizes of the membranes are reduced slightly after incorporation of functional polymers, which can be noticed in Fig. S4(c)-(e). In addition, the similar morphology for all membranes suggests that incorporation of PDEAEMA chains did not destroy the asymmetric morphology of the pristine membrane.

2. Grafting Density and Degree of PDEAEMA

The grafting density of functional polymers on the modified membrane surface was described as the weight of polymer brushes per unit area of membrane, and the grafting degree was calculated according to the weight difference of membrane before and after Michael-Addition reaction, showed as the following equation:

$$Y = \frac{W_1 - W_2}{A} \quad (1)$$

$$GD = \frac{W_1 - W_2}{W_2} \times 100\% \quad (2)$$

where Y is grafting density of the PDEAEMA grafted onto the PDA@PVDF membrane (mg/cm^2),and W_1 and W_2 are the weight of PDA@PVDF membrane and PDEAEMA-PDA@PVDF (g), respectively, and A is the area of the membrane (cm^2).

The obtained grafting density and grafting degree of modified membranes are shown in Fig. S5. It can be seen that the grafting density and degree of M1 membrane are higher than the other two membranes. This may be due to the fact that higher molecular weights (in M2 and M3) have longer polymer chains, which can bound to the surface and hinder the further attachment of chains in a localized area on the surface due to steric crowding.[4]

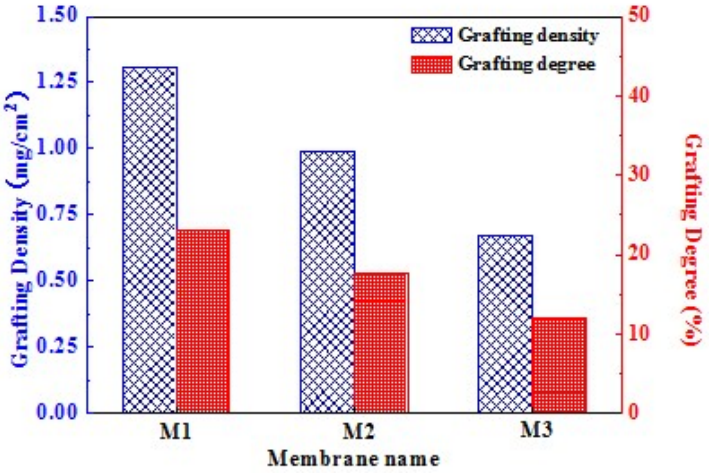


Figure S5 Grafting data of PDEAEMA-PDA@PVDF membranes (M1: P1-PDA@PDA membrane; M2: P2-PDA@PDA membrane and M3: P3-PDA@PDA membrane)

3. Water Uptake Measurements

Water uptake measurement was used to evaluate the adsorption of water of PDEAEMA-PDA@PVDF membranes. Prepared membranes were rinsed with deionized water and then dried at 60 °C under vacuum for 24 h, and its weight (W_d) was taken. After that, the dried membranes were immersed in deionized water with bubbling CO_2 time of 5, 10, 15, 20, 25 and 30 min, and the weight of the wet membrane (W_s) was obtained. The water content of microfiltration membrane was calculated by the following relationship:

$$Water\ uptake\ (\%) = \frac{W_s - W_d}{W_d} \times 100\% \quad (3)$$

The water uptake (%) of each membrane was obtained by weight fraction of the membrane. In Fig. S6, the water uptake (%) of the PDA@PVDF and PDEAEA-PDA@PVDF membranes are higher than those of the pristine one. For all PDEAEMA-PDA@PVDF membranes, the water uptake (%) increased with bubbling CO_2 time. This is because bubbling CO_2 can make the PDEAMEA chains protonated, enhancing the hydrophilicity of the membrane, and leading to more water absorption in the numerous pores in the membranes.

It should be noted that if the membrane is a polymer that becomes more hydrophilic upon CO_2 bubbling, the increased water uptake can favor water flux. However, in the present study, the openness of the pores inside the PVDF membrane determines the water flux. When the PDEAEMA layer becomes protonated upon CO_2 bubbling, although the water uptake of the whole membrane increases, the pores are blocked by the soluble PDEAEMA chains of extended conformation, which leads to decrease in water flux (permeability).

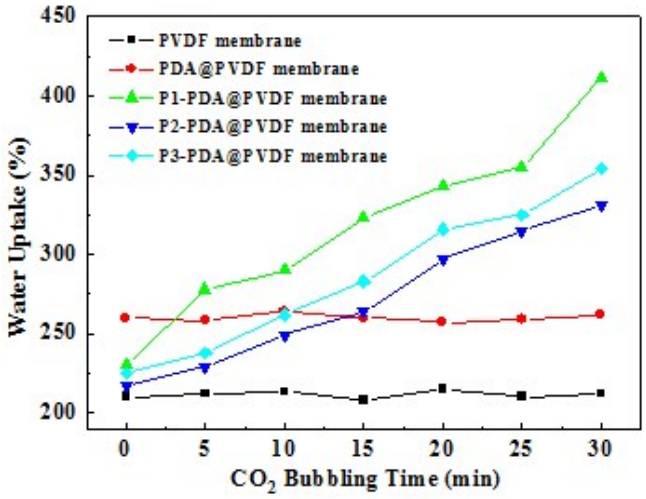


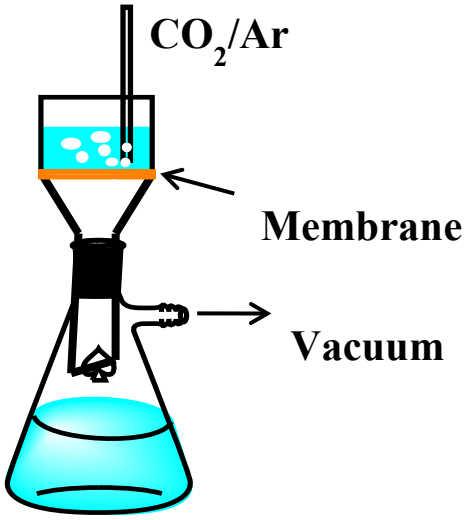
Figure S6 Water uptake (%) of PDEAEMA-PDA@PVDF membranes vs.CO_2bubbling time.

4. Water Flux under CO_2/Ar Stimulation

To verify the effective gas-responsive gating function of PDEAEMA-PDA@PVDF membranes, water filtration was performed at 25 °C under CO_2/Ar stimulation. As shown in Fig.S7, dead-end filtration cell with effective membrane area of 13.1 $cm^2$was used. The trans-membrane pressure was kept at 1 bar produced by vacuum. For CO_2 induced switching studies, the membrane was filtered with DI water first for a period of time to ensure a steady state. Then firstly bubbling CO_2 into solution for 30 min, next bubbling Ar for 20 min. Water flux samples were taken every 5min. 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:

$$J_W = \frac{V}{A \cdot t \cdot \Delta P} \qquad (4)$$

where V is the volume of DI water (L), t is the permeation time (h), A is the membrane area and Δp is the trans-membrane pressure.



FigureS7 Experimental setup used for gas-responsive water flux measurements.

5. Repeated Cycles of AuNP Separation

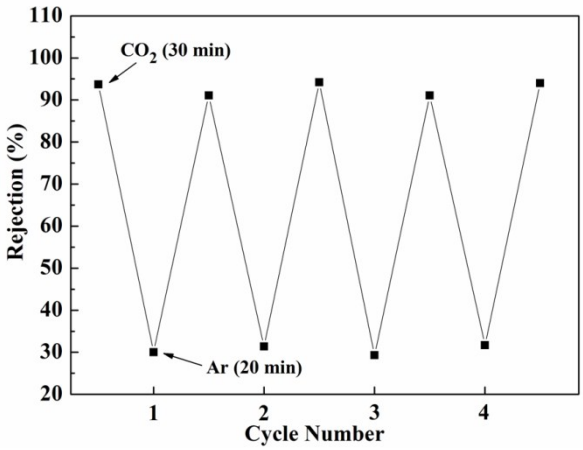


Figure S8 Cyclic change in rejection rate for AuNPs (50 nm) using the P1-PDA@PVDF membrane exposed alternately to 30 min CO_2 and 20 min Ar bubbling.

References

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