

## Supporting Information

### CO<sub>2</sub>-switchable-hydrophilicity membrane (CO<sub>2</sub>-SHM) triggered by electric potential: faster switching time along with efficient oil/water separation

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#### Experimental procedures

#### Materials

Stainless steel mesh with pore size of about 50 μm was purchased from a local market. Chloroform, dimethyl formamide (DMF), dioxane and hexane were supplied from Merck and used as solvents. All solvents were used as received without further purification. Methyl methacrylate (MMA) and N, N-diethylaminoethylmethacrylate (DEAEMA), as monomers, were obtained from Aldrich and distilled before use to remove inhibitor. The initiator, 2,2-azobisisobutyronitrile (AIBN), was purchased from Aldrich and was recrystallized in methanol twice before use.

#### Methods

#### Synthesis of PMMA-co-PDEAEMA copolymer

PMMA-co-PDEAEMA copolymer was synthesized by free radical solution polymerization according to the following procedure. DEAEMA (9.97 mmol, 1.84 g) and MMA (12.18 mmol, 1.22 g) were added to a round-bottom flask and then 6 mL dioxane was added to the mixture by stirring at room temperature to form a uniform solution. AIBN as the initiator (0.18 mmol, 30 mg) was added to the mixture and purged with nitrogen for 20 min before the start of polymerization. The flask was immersed in an oil bath with magnetic stirring. The polymerization was carried out at 70 °C for 24 h. The flask was cooled to room temperature. The crude product precipitated in excess hexane three times to remove the unreacted monomer. The precipitated PMMA-co-PDEAEMA was dried for 24 h in a vacuum oven. The polystyrene equivalent weight average molecular weight (MW) of the copolymer was 135000 Da. Fig. S1 shows the 1H NMR spectrum of the resulting polymer. The molar percent of PDEAEMA in the copolymer was calculated by following Eq. (S1):

$$\% \text{ PDEAEMA} = \frac{\frac{a}{2}}{\frac{b}{3} + \frac{a}{2}} * 100 \quad \text{S1}$$

Where a corresponds to the peak area of the methylene protons attached to oxygen in PDEAEMA and b is proportional to the area of the peak of methoxy protons of PMMA. According to the calculation based on Eq. S1, the copolymer was 45 mol% PDEAEMA.

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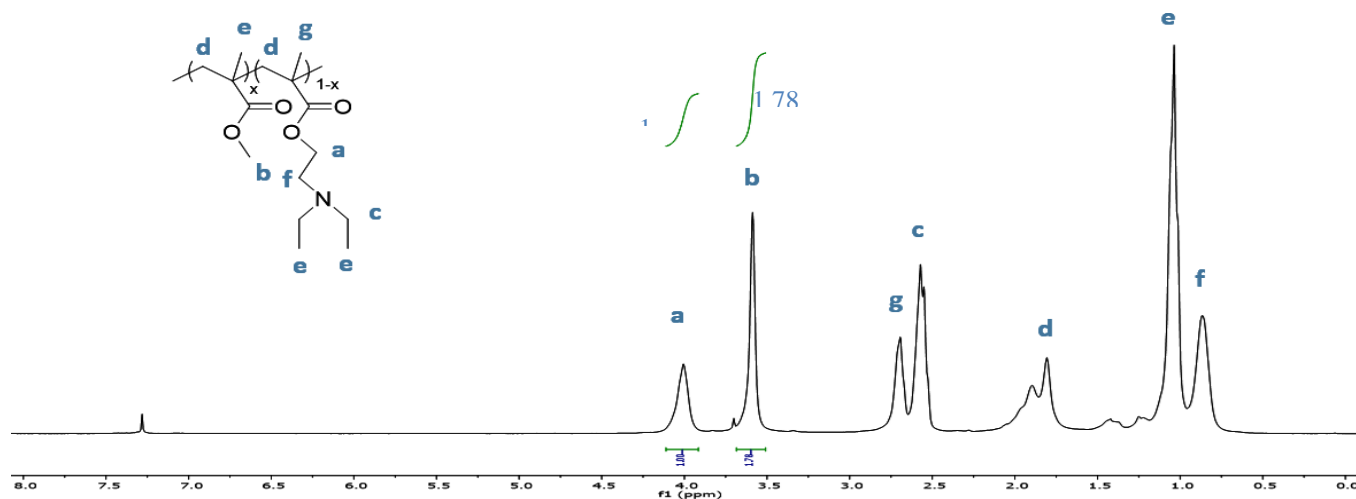


Fig. S1  $^1\text{H}$  NMR spectrum of PMMA-co-PDEAEMA in  $\text{CDCl}_3$  prepared by free radical solution polymerization.

## Electrospinning

The electrospinning machine (SISTANA ES LAB SBS) was provided from Nanoazma Company (Iran). Nanofibers were collected on a pre-cleaned round stainless steel mesh. To conduct the electrospinning process, copolymer solutions were prepared by dissolving different w/w ratios (15%, 20%, 25%) of PMMA-co-PDEAEMA in  $\text{CHCl}_3/\text{DMF}$  (2/1) solvent. Solutions were stirred for 5 h at room temperature to ensure uniform solutions. The syringe contained 5 mL solution of PMMA-co-PDEAEMA with a 22 G needle tip ( $L = 34$  mm and  $D = 0.4$  mm). The distance between needle tip to collector was fixed at 15 cm. The copolymer solution was pumped at a rate of 0.1 mL/h and the voltage set at a constant value of 7 kV. A take-up speed of 100 rpm was used to collect the electrospun nanofibers. The electrospinning process was carried out at room temperature ( $22 \pm 2$  °C) and room humidity ( $40 \pm 5\%$ ). The fibrous membrane was dried at 50 °C for 12 h to completely remove residual solvent.

## Characterization techniques

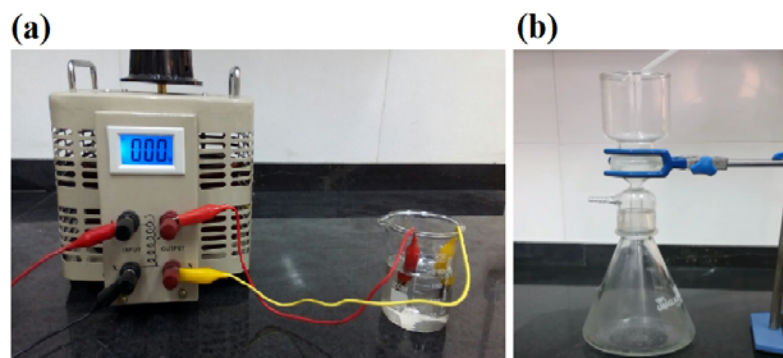
An Agilent 1100 GPC was used for evaluation of average molecular weight and distributions. THF (Merck, HPLC grade) was used as the eluent at a flow rate of  $1 \text{ mL min}^{-1}$  at 30 °C. Linear polystyrene standards (Sigma-Aldrich) were used to generate the calibration curve. Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra were recorded on a Bruker DRX-300 (300 MHz). The morphologies of the as-prepared membranes were obtained by a Mira3-XMU; Seron Technology, AIS2100; KYKY, EM3200 scanning electron microscope (SEM). The diameters of the nanofibers of all the prepared samples were measured from their SEM images by using the software Image J; the average diameter of each sample was calculated by the analysis of at least 50 fibers.

## Contact angle measurements

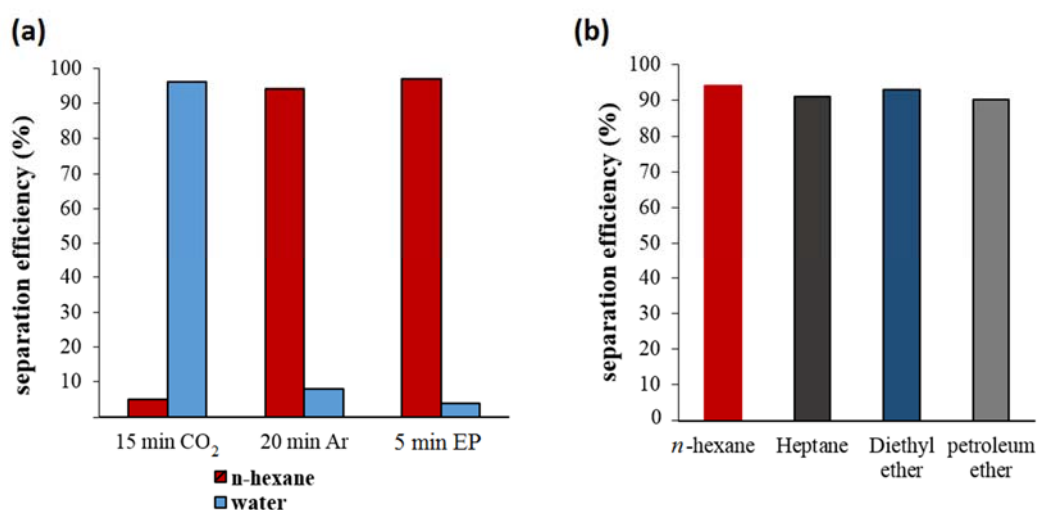
For the measurement of water contact angle, the nanofibrous membrane was attached to a quartz cuvette, and 2.0  $\mu\text{L}$  of a water droplet was dropped onto the surface of the sample in air. Each average value of the contact angle was calculated from three repeated measurements.

## Oli/water separation process

To apply electric potential (EP) a power supply was used (Fig. S2a). A beaker was filled with DI water. To increase the electrical conductivity,  $\text{KNO}_3$  (20 ppm) was dissolved in DI water. Then the as-prepared membrane which was already coated on stainless steel mesh was put inside of the beaker. Alligator clips were used to secure the stainless steel mesh coated membrane. After applying EP for a specified time, the SHM was removed from the beaker and was then fixed between two glass apparatus tubes to form a filter (Fig. S2b). A beaker was placed under the filter to collect the liquid which passes through the membrane. A layered mixture of deionized water (DI water) and oil (*n*-hexane) at 1/1 volume ratio (20 mL each) were mixed and directly poured into the upper glass apparatus. All the separation processes were driven solely by gravity and exhibited similar separation behaviors (the liquid passed through the membrane quickly because of the macroporous network structure of the fiber).



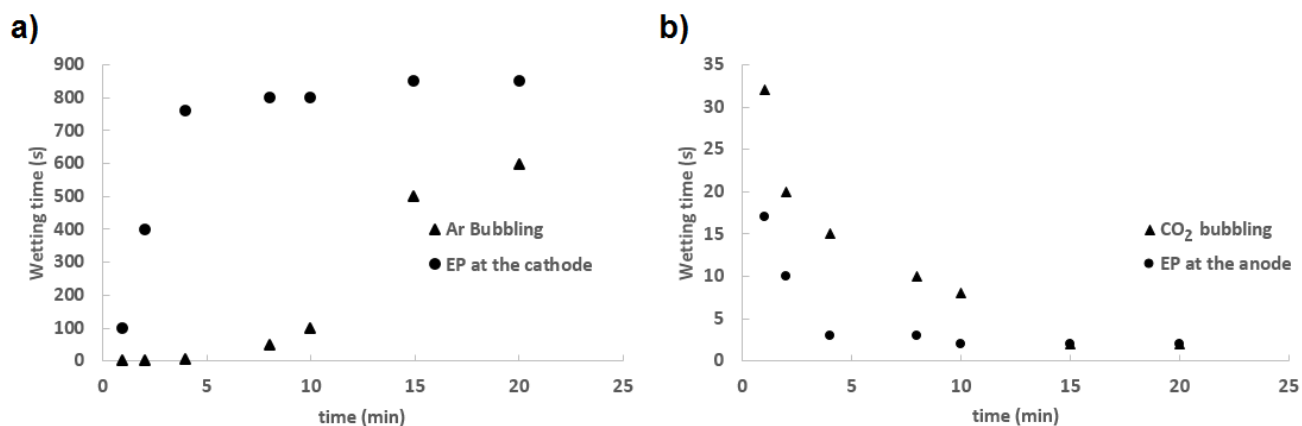
**Fig. S2** a) Power supply used for applying EP to switch between hydrophilic and hydrophobic state of the as prepared membrane; b) set up used for oil/water separation.



**Fig. S3** Separation efficiency for: a) sample which was switched to hydrophilic state by CO<sub>2</sub> (120 mL min<sup>-1</sup> for 15 min) and switched back to the hydrophobic state by argon gas and electric potential (EP) (15 v voltage for 5 min); and b) different oils which were switched back to the hydrophobic state by EP.

## Wetting time measurements

To confirm whether the rate of switching time between hydrophilic and hydrophobic states by EP is different from that by CO<sub>2</sub> or argon bubbling, wetting times at different time intervals were measured for both hydrophobic state triggers (Ar bubbling and EP at the cathode) and hydrophilic state triggers (CO<sub>2</sub> bubbling and EP at the anode). Wetting time is the time needed for a water drop to spread on the surface of the membrane. Fig. S4 shows the variations of wetting times for hydrophobic and hydrophilic triggers. The results show that EP is faster trigger for both switching to hydrophobic and hydrophilic states.



**Fig. S4** The wetting time measurements at different time intervals for hydrophobic state triggers: a) Ar bubbling and EP at the cathode (15 V); and hydrophilic state triggers: b) CO<sub>2</sub> bubbling and EP at the anode (15 V).

## pH measurements

To evaluate pH in the course of applying various triggers, typical SHM samples with the same size were prepared. Samples were put in different containers containing electrodes (Fig. 2) and KNO<sub>3</sub> (20 ppm) was dissolved in each container. The initial pH values for all samples before applying triggers were about 8.13, which means they were in the hydrophobic state. The samples were then exposed to different hydrophilic triggers including; 1) HCl (0.01 M), 2) CO<sub>2</sub> for 15 min, 3) EP (5 min, 15v), to achieve hydrophilic state membranes. All samples, after being exposed to the hydrophilic state triggers, were removed from the primary containers and washed with distilled water. Samples were then put into the new containers containing ~15 mL of distilled water with neutral pH around 7. After gently stirring, the pHs were measured. All samples showed pHs lower than the initial pH of 8.13 (Table S1) from it which can be concluded that the PDEAEMA in the SHM was (partially) protonated.

All samples were then successfully returned to their hydrophobic state by applying EP at the cathode (5 min, 15 v). In all cases the pHs were increased close to the original pH (~8.5). It is confirmed that EP as a new deprotonation trigger can effectively induce the hydrophobic state of the SHM. The measured pHs after applying different hydrophilic and hydrophobic state triggers have been summarized in Table S1.

It is noteworthy that, for all samples potassium nitrate (KNO<sub>3</sub>) was added to the system as an electrolyte to increase ionic strength and electrical conductivity of the solution. Lone electrons normally can not pass through the solution. Usually a chemical reaction occurs at the cathode, providing electrons to the electrolyte. Another reaction occurs at the anode, consuming electrons from the electrolyte. As a result, a negative charge cloud develops in the electrolyte around the cathode, and a positive charge develops around the anode. The ions in the electrolyte neutralize these charges, enabling the electrons to keep flowing and the reactions to continue. By introducing potassium (K<sup>+</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>) ions to the system, after applying EP, the positively charged potassium ions K<sup>+</sup> will migrate toward the cathode, neutralizing the negative charge of OH<sup>-</sup> there. In contrast, the negatively charged nitrate ions NO<sub>3</sub><sup>-</sup> will migrate toward the anode, neutralizing the positive charge of PDEAEMA<sup>+</sup> (Eq. S1) there to form stable salt (PDEAEMA<sup>+</sup>NO<sub>3</sub><sup>-</sup>) on the surface of the SHM. To make sure that the switch of the membrane to hydrophilic would not reverse once the application of voltage is terminated, the switched membrane was removed from electrolysis container (Fig. S2 a) before the EP was terminated and was transferred to the oil/water separation apparatus (Fig. S2 b).

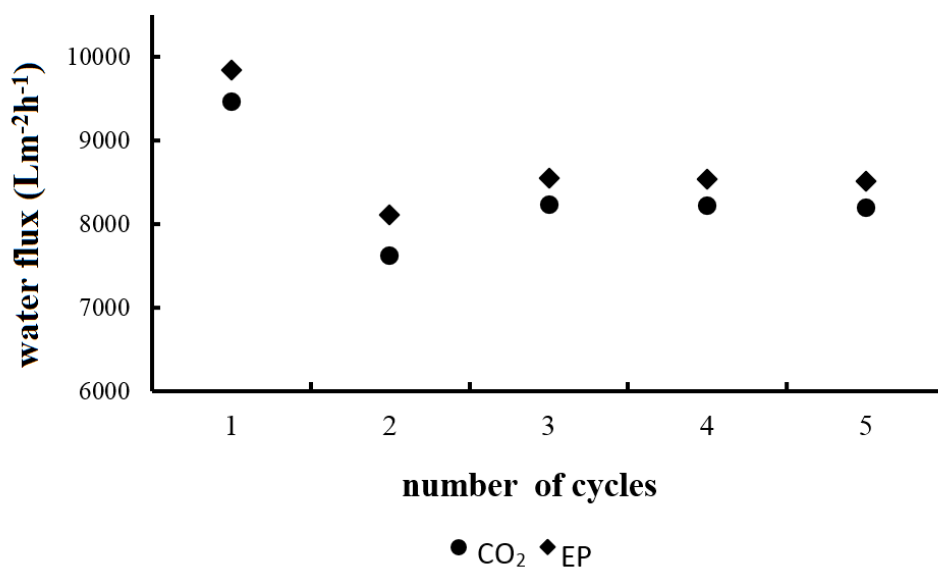


All the above mentioned experiments were done in the presence of KNO<sub>3</sub> as an electrolyte. To confirm the effect of KNO<sub>3</sub>, a similar sample was prepared and the electrolysis process was performed in the absence of KNO<sub>3</sub> (Table S1, entry 4). The results revealed that in the absence of KNO<sub>3</sub>, the decrease in pH was not as much (pH = 7.65) from which it can be deduced that the PDEAEMA in the SHM was not efficiently protonated. This observation might be attributed to a lack of a stable counter ion (such as NO<sub>3</sub><sup>-</sup>) for PDEAEMA<sup>+</sup> and also insufficient electrical conductivity.

**Table S1** pH data after, applying different triggers during hydrophilic/hydrophobic switching

entry	Hydrophilic state trigger, pH	Hydrophobic state trigger, pH
1	HCl (0.01 M), pH = 6.09	EP (5 min, 15v), pH = 8.20
2	CO <sub>2</sub> for 15 min, pH = 6.20	EP (5 min, 15v), pH = 8.61 Ar for 20 min, pH = 8.54
3	EP <sub>a</sub> (5 min, 15v), pH = 4.68	EP <sub>c</sub> (5 min, 15v), pH = 8.33
4 <sup>a</sup>	EP <sub>a</sub> (5 min, 15v), pH = 7.65	EP <sub>c</sub> (5 min, 15v), pH = 8.65

The initial pH, before applying any triggers was pH = 8.13.  
 EP<sub>a</sub>: electric potential where the SHM was applied as anode.  
 EP<sub>c</sub>: electric potential where the SHM was applied as cathode.  
<sup>a</sup> electrolysis process was done in the absence of KNO<sub>3</sub> (electrolyte).



**Fig. S5** Water flux of SHM switched to the hydrophilic state by CO<sub>2</sub> bubbling or applying EP in 5 cycles. EP at the cathode (15 volts for 5 minutes) was applied to switch the SHM back to the hydrophobic state.