

Quaternized polysulfone and graphene oxide nanosheets derived low fouling novel positively charged hybrid ultrafiltration membranes for protein separation

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Experimental section

S1. Determination of degree of chloromethylation for polysulfone

The degree of chloromethylation (DCM) for polysulfone was determined from the change in molecular weight of PSf before and after chloromethylation.³⁵ For this purpose, the molecular weight of chloromethylated polysulfone (PSf-CH₂Cl) was first calculated as $MW = 442 m/m_0$, where 442 is the molecular weight of PSf repeat unit. The m and m_0 are the mass of PSf-CH₂Cl and PSf, respectively (the care was taken to avoid the loss/change in mass during handling and synthesis of PSf-CH₂Cl). DCM was then calculated using eqn (1):³⁵

$$DCM = \frac{(MW - 440)}{49.5} \quad (1)$$

where 440 is the molecular weight of PSf repeat unit and 49.5 is the molecular weight of chloromethyl group (-CH₂Cl).

S2. Synthesis of graphene oxidenanosheets

Graphene oxide (GO) nanosheets were synthesized from expandable graphite flakes by a modified Hummers method.^{27,28,36} Initially, 2 g of graphite flakes were heated in a 700 W microwave oven for 15 s to obtain expanded graphite (EG) flakes as precursor for synthesis of GO nanosheets. In a typical synthesis of GO, 2 g of EG flakes were added to a round bottom flask containing 250 ml H₂SO₄ (98%) and the resulting mixture was stirred for 1 h at 25°C. Then, 10 g KMnO₄ was added gradually to the mixture under stirring condition and a viscous dark-green mixture was obtained. The dark-green colour mixture was continuously stirred for 24 h at 25°C. Thereafter, the resulting mixture along with round bottom flask was transferred into an ice bath and a mixture containing 100 ml H₂O₂ (30 %) and 500 ml DI water was slowly added. The colour of the mixture solution changed to golden yellow after addition of H₂O₂ and DI water mixture. The resulting mixture solution was further stirred for 2 h and the obtained suspension was centrifuged at 10000 rpm to remove acid and salts impurities. The oxidized EG particles were treated with 10% HCl and centrifuged three times with 10% HCl solution. Subsequently, the oxidized EG particles were washed several times and centrifuged with DI water until a solution *pH* was reached to ≥ 5 . The gray colour paste was freeze-dried and stored in dry condition for future characterization and use.

S3. Determination of membrane water uptake and porosity

The membranes were initially kept in DI water at room temperature (RT) for 24 h. The membranes were then carefully removed from the water, the excess surface water was removed using a tissue paper and the mass of membranes in wet state was immediately measured on an analytical balance. The wet membranes were dried in a vacuum oven at 60°C for 8 h and the masses of the dried membranes were recorded. The water uptake measurement was conducted three times to ensure the reproducibility of reported data. The water uptake (φ , in %), and the porosity (ε , in %) of membranes were calculated using eqn (2) and (3):^{9,18,29}

$$\varphi(\%) = \frac{(W_w - W_d)}{W_d} \times 100 \quad (1)$$

and

$$\varepsilon(\%) = \frac{(W_w - W_d)}{A \times L \times \rho} \times 100 \quad (2)$$

where W_w and W_d are the weight of membrane (g) in wet and dry state, A is the membrane area (cm^2), L is the membrane thickness (cm) and ρ is the density of pure water (1 g cm^{-3}).

S4. Determination of ion-exchange capacity and fixed ion concentration

The ion-exchange capacity (*IEC*) of membranes was determined by an acid-base back titration method.^{25,34} The dried membrane samples ($2 \text{ cm} \times 2 \text{ cm}$) were submerged overnight in 0.1 M NaOH solution to convert the membranes into OH^- form and membranes were then cleaned with DI water to remove traces of NaOH. The cleaned membranes were soaked in 50 ml of 0.1 M standardized HCl solution for 24 h at RT to ensure the neutralization of OH^- in the membranes and membrane samples were taken out. *IEC* values were then determined by a back titration of excess HCl with 0.01 M NaOH solution using a phenolphthalein indicator. The wet membrane samples were dried in a vacuum oven at 60°C for 6 h to obtain constant weights. The weights of membranes were measured on an analytical balance. *IEC* measurements were performed in three replicates for each membrane to ensure the reproducibility of reported data. The *IEC* (meqiv.g^{-1}) of membranes was calculated using eqn (4):^{25,34}

$$IEC(\text{meqiv.g}^{-1}) = \frac{V_{0,\text{NaOH}}C_{\text{NaOH}} - V_{x,\text{NaOH}}C_{\text{NaOH}}}{W_d} \times 1000 \quad (4)$$

where $V_{0,\text{NaOH}}$ and $V_{x,\text{NaOH}}$ are the consumed volume of NaOH (ml) in titration without and with membrane, C_{NaOH} is the concentration of NaOH solution (mol ml^{-1}), and W_d is again the dry membrane weight (g). Calculated values of *IEC* were further used to calculate the fixed

ion concentration of the membranes. The fixed ion concentration (A_f ; mequiv.g⁻¹ H₂O) of the membranes was calculated as the ratio of IEC to the water content using eqn (5):^{9,37}

$$A_f = \left(\frac{IEC}{\phi} \right) \quad (5)$$

S5. Determination of states of water (free and bound water) for membranes

Differential scanning calorimetry (DSC) studies were conducted to analyze the states of water for membranes in wet condition. The membrane samples were kept in DI water for 24 h at RT to convert them to the fully swollen state. Thereafter, the membrane samples were taken out from DI water and ~ 10 mg of wet membrane sample was placed inside the airtight aluminium pan. DSC experiments were then performed using a Q200 series differential scanning calorimeter (TA instrument, USA) in the temperature range -20 to + 20°C under N₂ atmosphere with a flow rate of 50 ml min⁻¹ and a heating rate of 10°C min⁻¹. The obtained data for membranes with varied fraction of GO nanosheets (%) is presented in **Fig. S4** (*cf.* below).

S6. Procedure to determine tensile strength of membranes

Uniaxial tensile tests were conducted on a Zwick Z005 displacement controlled tensile testing machine to determine the tensile strength and the percentage elongation values at break point of membranes. The dried membrane samples were cut out in a dog-bone shape (78 mm × 12 mm) and the fixed grips were mounted onto the tensile testing machine. Abrasive paper was then placed between the membrane sample and the grip surface to prevent slippage of membrane samples during experiments. The stress and strain values for membranes were recorded at a crosshead speed of 2 mm min⁻¹. Three samples of each membrane were tested to ensure the reproducibility of reported data. Furthermore, the percentage elongation values at break point of the membranes were calculated from the initial slope of stress vs strain curve using instrument handling software (*cf.* **Fig. S5**).

Table S1. The composition of casting solutions for fabrication of positively charged hybrid membranes.

Membrane	PSf (wt%)	QPSf (wt%)	GO (wt%) ^a	NMP (wt%)
AG-0	8	8	-	84.0
AG-1	8	8	1	83.84
AG-2	8	8	2	83.68
AG-5	8	8	5	83.2

^aThe percentage of GO is based on the total fraction of PSf and QPSf in the membrane casting solutions.

Results

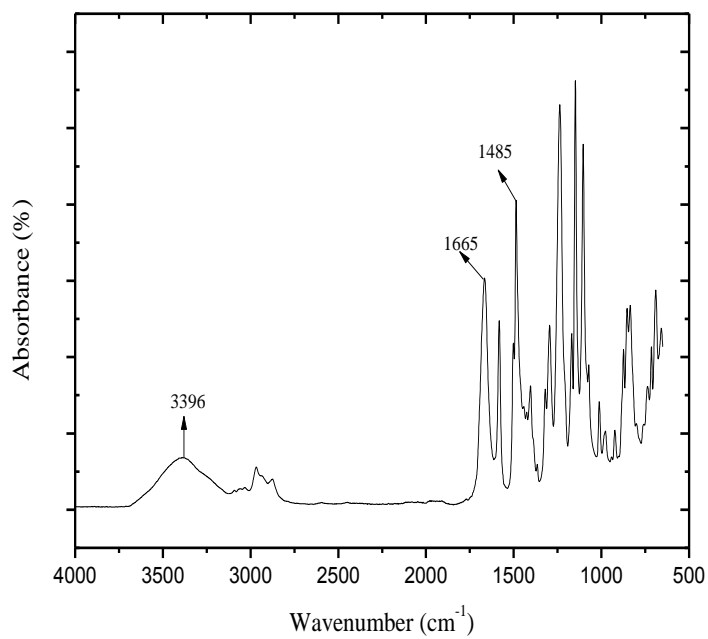


Fig. S1. FTIR spectrum for quaternized polysulfone.

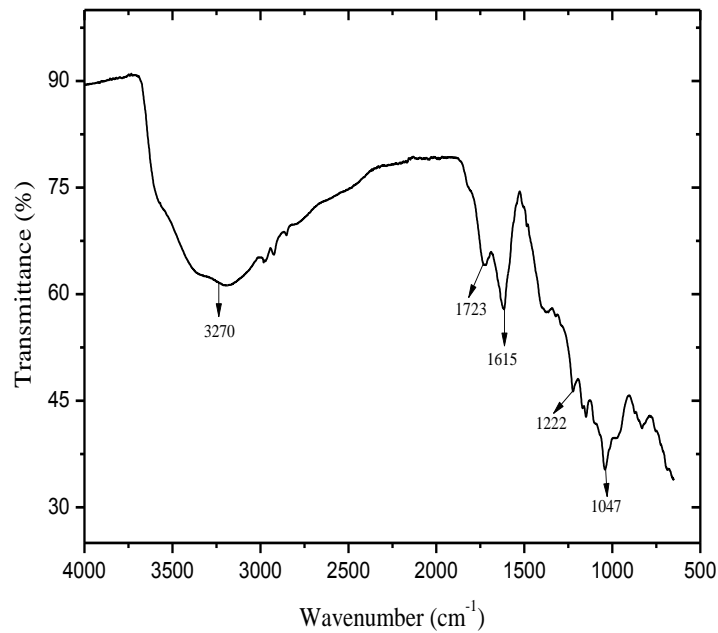


Fig. S2. FTIR spectrum for Graphene oxide nanosheets.

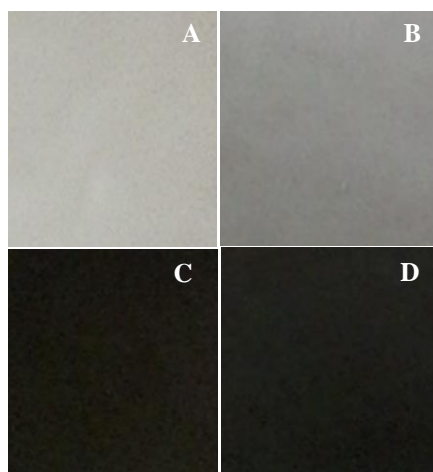


Fig. S3. Photographic images for positively charged hybrid membranes with varied fraction of GO nanosheets (%) (*cf.* **Table S1**): (A) AG-0; (B) AG-1; (C) AG-2 and (D) AG-5.

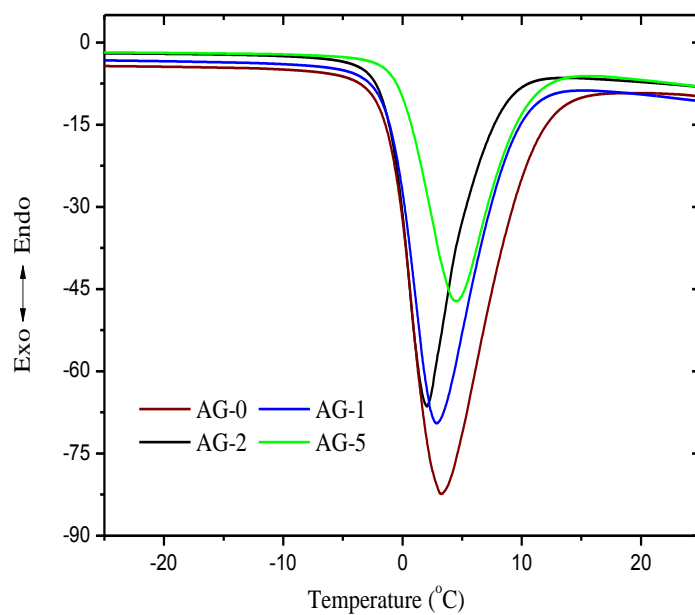


Fig. S4. DSC thermograms for positively charged hybrid membranes in swollen state with varied fraction of GO nanosheets (%).

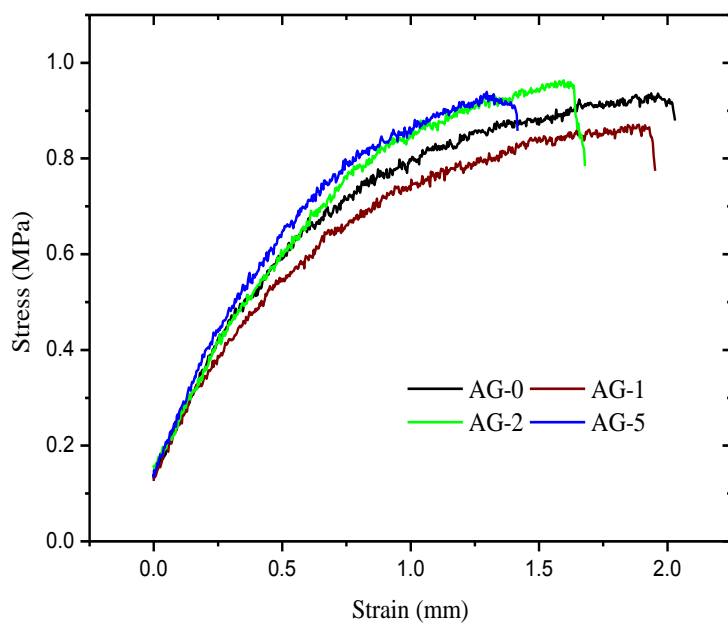


Fig. S5. Strain-stress curves for positively charged hybrid membranes with varied fraction of GO nanosheets (%).

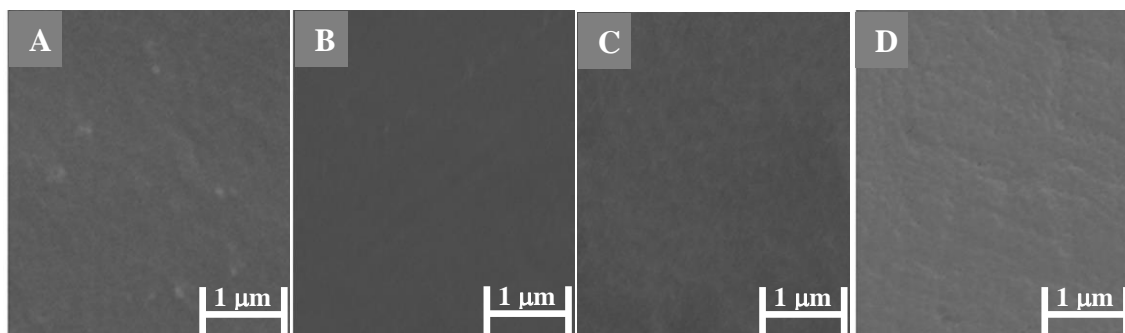


Fig. S6. Surface SEM images for positively charged hybrid membranes with varied fraction of GO nanosheets (*cf.* **Table S1**): (A) AG-0; (B) AG-1; (C) AG-2 and (D) AG-5.