Supplementary Information

Nitrogenated graphene oxide decorated metal sulphides for better antifouling and dye removal

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S1. Experimental

S1.1. Graphene oxide synthesis by modified Hummers method (Ji Chen et al, Carbon 64 (2013) 225-229):

Briefly, graphite powder (3 g) was added to conc. H₂SO₄ (70 ml) in an ice bath under stirring. KMnO₄ (9 g) was added slowly under vigorous stirring to keep the temperature of the
suspension lower than 20 °C. Consecutively, the reaction mixture was transferred to an oil bath by maintaining the temperature of 40 °C and stirred vigorously for nearly 0.5 hr. Later, 150 ml distilled water was added subsequently by a very slow addition of 15 ml H₂O₂. The obtained mixture was filtered and washed with 1:10 HCl aqueous solution (250 ml) to remove metal ions. The resulting solid was dried in air and diluted to 600 ml, making a graphite oxide aqueous dispersion. Finally, it was purified by dialysis for one week using a dialysis membrane. The resultant graphite oxide aqueous dispersion was then diluted to 1.2 L, stirred overnight and sonicated for 30 min to exfoliate it to GO. The GO dispersion was then centrifuged at 3000 rpm for 40 min to remove the unexfoliated graphite. Obtained compound is used for further studies.

**S1.2. CuS-rGO synthesis**

CuS-rGO composite was synthesized using the reported literature [23]. Briefly, 0.2 g of GO and 1.7 g of CuCl₂.2H₂O were dispersed in 100 ml of 1, 2-propane diol in a round bottom flask. Then, the reaction mixture was stirred for 20 min at 120 °C. Later, 3.1 g of thiourea was slowly added to the above solution and the mixture was heated up to 170 °C with continuous stirring and maintained for 5 hrs. The obtained product was washed with ethanol and distilled water and dried in vacuum oven at 50 °C for 10 hrs.

**Table S1: Compositions of PSF membranes with different concentration of CuS-rGO nanoparticles**

| Membrane | Composition (wt %) |
|----------|--------------------|
|          | PSF | CuS-rGO | NMP |
| M0       | 17  | 0       | 83  |
| M1Cr     | 16.5| 0.5     | 83  |
### S2. Membrane Characterization

Before analysis, all the membrane samples were dried overnight at 60 ºC to remove moisture.

#### S2.1. FESEM Analysis
- Prior to scanning, membrane samples of appropriate size were dipped in liquid nitrogen for few seconds and were then fractured cryogenically in order to obtain sharp cross sections. The fractured samples were then coated with a very thin conductive layer of platinum and the images were captured.

#### S2.2. Contact angle measurements
- In brief, a water droplet of ~2 µL was dropped on membrane's surface at four random places and the images were captured in order to calculate the contact angle of PSF membranes and the average of four trials has been reported.

#### S2.3. Zeta Potential Measurements:
- Zeta potential analysis were done using Electro Kinetic Analyser (Anton Paar Surpass 3) and the zeta potential at the membrane surface was determined from the measurement of the streaming potential using adjustable gap cell. The conductivity of the Dip-in-cell was calibrated before use. The membrane sheets were cut into a required size and mounted on the measuring cell. Before measurement, the analyser was rinsed with KCl buffer (0.01M) solution and the results were analysed.

### S3. Membrane Performance studies

#### S3.1. Pure water flux measurements:
- The pure water flux of the prepared membranes was measured using self-constructed dead-end filtration unit. The unit was connected to nitrogen cylinder in order to facilitate the required pressure. The membrane of effective area 10.17 cm² was fixed into the cell and water was filled. Initially, the membrane was compacted by pressurizing at 4 bar for 30 min in order to reach the steady permeate state and then the pressure
was lowered to the working pressure of 2 bar wherein the permeate of PSF-based membranes was collected for every 10 min interval during 2 hrs. The pure water flux of the membranes was calculated using the formula given in (Eqn. (S1))-

\[ J_w = \frac{Q}{A \Delta t} \]  

(S1)

where, \( J_w \) is the pure water flux in terms of \( \text{L/m}^2\text{h} \); \( Q \) is the volume of water collected in litres (l); \( A \) is the effective area of membrane in \( \text{m}^2 \) and \( \Delta t \) is the permeation time in hours (hrs).

**S3.2. BSA Filtration:** Initially, the dead-end filtration unit was filled with 200 mgL\(^{-1}\) BSA solution as feed and it was stirred using magnetic stirrer at 300 rpm to minimize the effects of concentration polarization. Then the rejection studies were performed at 2 bar pressure for 2 hrs and the percentage rejection of BSA was calculated from the equation (Eqn. (S2)),

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

(S2)

where, \( C_p \) and \( C_f \) are the concentrations of BSA in the permeate and feed solutions respectively, which was determined using UV-Visible spectrophotometer (Shimadzu 1800 PC) at absorption wavelength of 280 nm.

**S3.3. Antifouling studies:** Antifouling properties of the prepared membranes were determined using dead-end filtration unit and BSA of 200 mgL\(^{-1}\) concentration was used as foulant. In the beginning, the pure water flux (\( J_1 \)) of the membranes was measured with a working pressure of 2 bar at room temperature. In the next step, the unit was filled with 200 mgL\(^{-1}\) BSA solution and permeate was collected for every 10 min interval during the period of 2 hrs. After BSA filtration, the membranes were thoroughly washed with distilled water for 45 min and finally the water flux (\( J_2 \)) was measured again. The antifouling property was usually measured in terms
of Flux Recovery Ratio (FRR), which can be calculated using the formula as given in (Eqn. (S3))[32, 33].

\[
\% \text{ FRR} = \left( \frac{J_2}{J_1} \right) \times 100
\]  

(S3)

**S3.4. Congo red dye removal study:** Initially, the dead-end filtration unit was filled with 50 ppm of congo red dye solution and the rejection study was performed at 4 bar pressure for 2 h. The concentrations of feed and permeate of congo red solution was measured using UV-Visible spectrophotometer at an absorption wavelength of 497 nm. The % rejection of dye solution was calculated using following equation (Eqn. (S2)), where, \( C_p \) and \( C_f \) are the concentrations of dye in the permeate and feed solutions respectively.

**S4. Results and Discussion**

**S4.1. XRD spectrum of CuS-rGO nanoparticles**

![XRD spectrum of CuS-rGO nanoparticles](image)

Figure S1. XRD spectrum of CuS-rGO nanoparticles
CuS/rGO nanocomposite displays a similar XRD patterns to pure CuS (JCPDS card no.06-0464), which indicates that the addition of GO does not change the crystal orientations of CuS in the composites.

S4.2. FESEM images of CuS-rGO nanoparticles

![FESEM images](image)

Figure S2: a) and b) FESEM images of CuS-rGO nanoparticles at different magnification c) Adsorption/Desorption isotherm of CuS-rGO nanoparticles

S4.3. TEM and EDX spectrum of CuS-rGO nanoparticles
Figure S3: TEM images of CuS-rGO nanoparticles

Figure S4: EDX spectrum of CuS-rGO nanoparticles

S4.4. XRD spectra of bare PSF and PSF CuS-rGO membrane
Figure S5: XRD spectra of M0 and M3Cr membranes

The diffraction peaks between 30° and 60° confirms the successful incorporation of CuS-rGO nanocomposites in PSF membrane matrix.

S4.5. Permeability studies of bare PSF and PSF CuS-rGO nanocomposite membranes

Table S2 showing permeability values of bare PSF and PSF CuS-rGO nanocomposite membranes

| Membranes | PWF (L/m²h) |
|-----------|-------------|
| M0        | 6 ± 2.91    |
| M1Cr      | 10 ± 3.16   |
| M2Cr      | 15 ± 2.70   |
| M3Cr      | 19 ± 1.89   |
Figure S6: Antifouling study of M3Cr membrane