

**Fabrication of a graphene oxide-embedded separation bilayer  
composite nanofiltration membrane using a combination of layer-by-  
layer self-assembly and interfacial polymerization**

Supporting Information

**Contents**

|   |   |
|---|---|
| Section S1. Characterization of graphene oxide.....                         | 2 |
| Section S2. PA NF membrane preparation method.....                          | 3 |
| Section S3. PFOA separation and HA fouling experiment operation steps ..... | 4 |
| S3.1. PFOA separation experiment .....                                      | 4 |
| S3.2. HA fouling experiment.....  | 5 |
| Section S4. Average roughness .....   | 5 |
| References .....  | 6 |

## Section S1. Characterization of graphene oxide

XRD was used to characterize graphite and GO. From Fig. S1a, it can be seen that graphite has a strong peak at  $2\theta = 26.56^\circ$ , and its lattice spacing is 0.34 nm, which coincides with the (002) crystal plane of graphite. GO appears as a diffraction peak at  $2\theta = 9.82^\circ$  (Fig. S1b). From this, the lattice spacing of GO is calculated to be 0.90nm. It can be found that the interlayer spacing of GO is more significant than that of graphite. This is because graphite introduces hydroxyl, carboxyl, epoxy, and other oxygen-containing functional groups and water molecules during the oxidation process, which causes the interlayer spacing to increase<sup>1</sup>. From the ATR-FTIR diagram of GO (Fig. S2), it can be seen that there are -OH, -C=O, C=C, and C-O-C at  $3188\text{ cm}^{-1}$ ,  $1727\text{ cm}^{-1}$ ,  $1617\text{ cm}^{-1}$ , and  $1045\text{ cm}^{-1}$ , respectively.

The stretching vibration peak indicates that GO has many oxygen-containing groups, which can significantly improve the hydrophilicity of GO. It can be seen from Fig. S3 that the single-layer graphene oxide is corrugated and has uneven thickness distribution under the SEM test. This is similar to the surface microstructure of single-layer graphene. This corrugated fold can increase the stability of graphene oxide<sup>2</sup>.

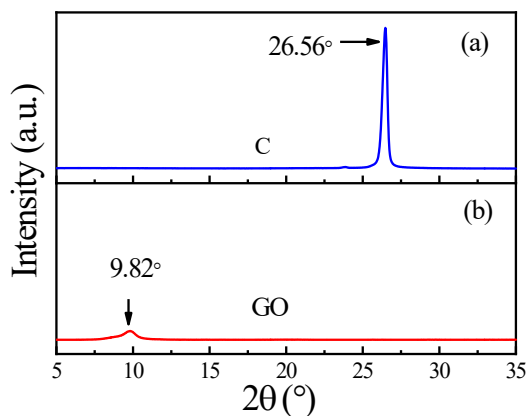


Fig S1. XRD spectra of graphite (a) and GO (b)

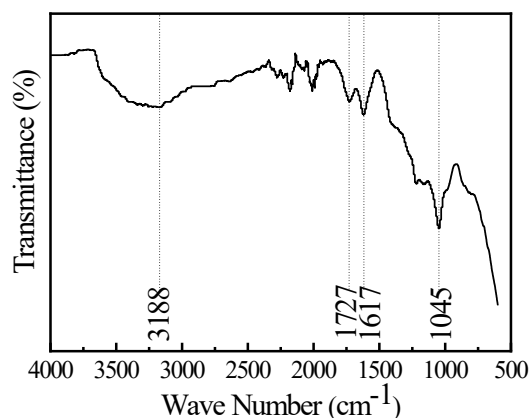


Fig S2. ATR spectra of GO

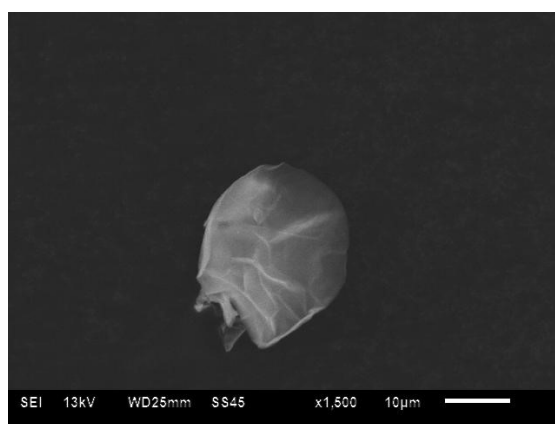


Fig S3. SEM image of GO

## Section S2. PA NF membrane preparation method

Asymmetric PAN ultrafiltration support membrane was prepared via phase inversion induced by immersion precipitation using a casting solution containing PAN and PVP in DMAc as solvent<sup>3</sup>. For preparing the homogeneous solution, all components were simultaneously blended with DMAc and mixed by a mechanical stirrer for 12 h at  $60^\circ\text{C}$ . Then, the solution was left in a vacuum oven at  $60^\circ\text{C}$  for 12 h to remove air bubbles. The resultant polymer solution was cast on smooth glass plate using a self-made casting knife with a gap of 0.1 mm. The plate was immediately

immersed in a water gelation bath at room temperature with a smooth motion. The solution layer gelled into a white microporous sheet immediately, and the top face was used as a support surface for the nanofiltration (NF) membrane. After primary phase separation and membrane formation, the membranes were washed thoroughly with deionized (DI) water and stored in DI water for at least 24 h until the solvent and water-soluble polymer was almost removed.

Polyacrylonitrile (PAN) NF membrane was fabricated in three steps. In the first step, a flat-sheet PAN ultrafiltration support membrane was prepared via phase inversion induced by the immersion precipitation method. In the second stage, after the PAN membrane was modified with  $1.5 \text{ mol}\cdot\text{L}^{-1}$  NaOH at  $45^\circ\text{C}$  for 90 minutes, the h-PAN membrane was obtained. The pure water flux of the h-PAN membrane was  $138 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ . In the third stage, the polyamide barrier layer on top of the h-PAN porous substrate was prepared by an *in situ* interfacial polymerization process between MPD in water and TMC in hexane, followed by curing and washing. Membrane samples were stored in fresh DI water (replaced regularly).

### **Section S3. PFOA separation and HA fouling experiment operation steps**

#### **S3.1. PFOA separation experiment**

First, the NF membrane was used to filter deionized water for more than 1.5 hours. After the flux was stable, the permeation flux  $J_{P0}$  of the NF membrane to the deionized

water was recorded. Then, the PFOA feed water was used to investigate the separation performance of NF membrane. To ensure a constant chemical composition of the stock solution, a recycled mode was adopted. After the PFOA solution was run for 24 hours, the membrane flux was recorded as  $J_{P1}$ . Permeate and feed samples were collected at 24h to evaluate PFOA retention of the NF membranes.

The PFOA concentration in the water samples were measured by an ultraperformance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS). The membrane normalized flux and rejection rate ( $R$ ) were calculated using equations (1) and (2):

$$\text{Normalized flux} = \frac{J_{P1}}{J_{P0}} \quad (1)$$

$$R = \left(1 - \frac{C_p}{C_0}\right) \times 100\% \quad (2)$$

Where  $C_p$  and  $C_0$  were the concentrations of PFOA in the permeation and feed solution, respectively ( $\mu\text{g}\cdot\text{L}^{-1}$ )

### **S3.2. HA fouling experiment**

First, the NF membrane was used to filter deionized water for more than 1.5 hours. After the flux was stable, the permeation flux  $J_{H0}$  of the NF membrane to the deionized water was recorded. Then, the HA feed solution was used to conduct a fouling experiment. To ensure a constant chemical composition of the stock solution, a recycled mode was adopted. After the HA solution was run for 24 hours, the membrane flux was

recorded as  $J_{H1}$ .

Next, the surface of the NF membrane was rinsed with deionized water for 30 minutes to remove accumulated foulants. Finally, the NF membrane was used to filter deionized water for more than 1.5 hours and the stable NF membrane flux  $J_{H2}$  was recorded.

The flux recovery ratio (*FRR*) and total decay ratio (*DR*) were calculated using equations (3) and (4):

$$DR = \left( \frac{J_{H0} - J_{H1}}{J_{H0}} \right) \times 100\% \quad (3)$$

$$FRR = \frac{J_{H2}}{J_{H0}} \times 100\% \quad (4)$$

#### Section S4. Average roughness

The average roughness of the  $PE_n$ -PA and  $(PE+GO)_n$ -PA NF membrane surfaces are summarized in Table S1.

Table S1. The  $R_a$  of  $PE_n$  and  $(PE+GO)_n$  membranes.

| LbL double layer number | $R_a$ /nm   |             |
|-------------------------|-------------|-------------|
|                         | $PE_n$      | $(PE+GO)_n$ |
| 0                       | 2.11 ± 0.23 | 2.11 ± 0.23 |
| 0.5                     | 2.30 ± 0.31 | 2.30 ± 0.31 |
| 1                       | 1.73 ± 0.20 | 2.15 ± 0.41 |
| 1.5                     | 2.57 ± 0.54 | 3.85 ± 0.19 |
| 2                       | 2.13 ± 0.12 | 2.91 ± 0.41 |
| 2.5                     | 3.48 ± 0.49 | 4.29 ± 0.13 |

## References

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