Supplementary data

High-Performance Ultrafiltration Membranes Based on Polyethersulfone/Graphene Oxide Composites

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1. Experimental

Preparation of PES/GO composite membrane:

In a typical preparation process, graphite oxide, which was prepared by the modified Hummers method, was firstly dispersed in the N, N-dimethylformamide (DMF, analytical reagent，Guangfu Chemical Reagent Co. Tianjin, China) by sonication (JY92-N, a high-energy bench mounted ultrasonic disintegrator, Scientz Co. Ltd, China) at an output power of 100 W, and the obtained GO/DMF dispersion was used to replace the pure DMF solvent. Then, PES (PES 6020P, Mw=29000, BASF Co. ,Germany) and PEG (PEG2000, analytical reagent, Damao Chemical Reagent Co., Tianjin, China) was added into the above GO/DMF dispersion and stirred for 1 h at 60 °C to form the casting solution. During the membrane casting process, the obtained casting solution was cooled to room temperature, and subsequently spread with a casting knife on a glass plate and immersed into a given coagulation bath at 20 °C less than 30 s. A thin membrane was found to form on the glass plate, and after peeled off, the membrane was rinsed with water for 1 h and stored in water for at least a day before use.

Characterization of the membrane: Microscopic observations for the membrane surface and cross-sectional structure were conducted by a scanning electron microscope (SEM, Hitachi 4800,

Japan), and the wetting angle measurement was conducted by a contact-angle instrument (FM40 Easy drop, Kruss Gmbh, Germany). The thermal stability of the membrane is characterized by the differential scanning calorimetric (DSC) analysis using Rigaku Thermo Plus TG 8120. The mechanical properties of PES and PES/GO membranes were measured using a mechanical tester (DMA Q800 V7.4 Build 126) in tensile mode at room temperature.

Protein adsorption on PES/GO composite membrane: PES composite membrane**s** (30 mm in diameter) were put into a 1 mg/mL BSA (Purchased from Institute of Hematology, Chinese Academic of medical sciences, Tianjin, China) solution (5.0 ml) at 25 ^{o}C for 24 h. **T**he pH value of the solution was kept at 7.0 by phosphate-buffered solution. Coomassie brilliant blue was employed to determine BSA concentration. The apparent amount of adsorbed protein was calculated by measuring the concentration difference of BSA solution before and after contacting with the studied membranes.

Ultrafiltration experiments:

(1) Flux measurement: A dead-end stirred cell filtration system connected with a N_2 gas cylinder and solution reservoir was designed to evaluate the filtration performance of membranes. All ultrafiltration experiments were carried out using a filtration test cell (Model 8200, Millipore Co., USA) whose volume capacity was 200 mL. The effective area of the membrane was 28.7 cm^2. The operation pressure (1.5 times standard atmosphere pressure) in the system was maintained by nitrogen gas. All the ultrafiltration experiments were carried out at a stirred speed of 400 rpm and a temperature of 25$\pm$ 1 ^{o}C.

(2) Rejection of BSA: BSA solution with the concentration of 1 mg/mL was prepared at room temperature by dissolving a pre-weighed amount of BSA powder in phosphate buffer with the pH value of 7.0. The prepared membranes were used as the UF membrane. The absorbance of the permeated

solutions was analyzed by Ultraviolet–visible (UV-Vis) spectrophotometer (Persee Tu-1810) at wavelength 280 nm to calculate the protein concentration of the permeated solution. The fluxes of the BSA solution and the rejection rates of the BSA are shown in the Table S1.

2. Membrane characterization results

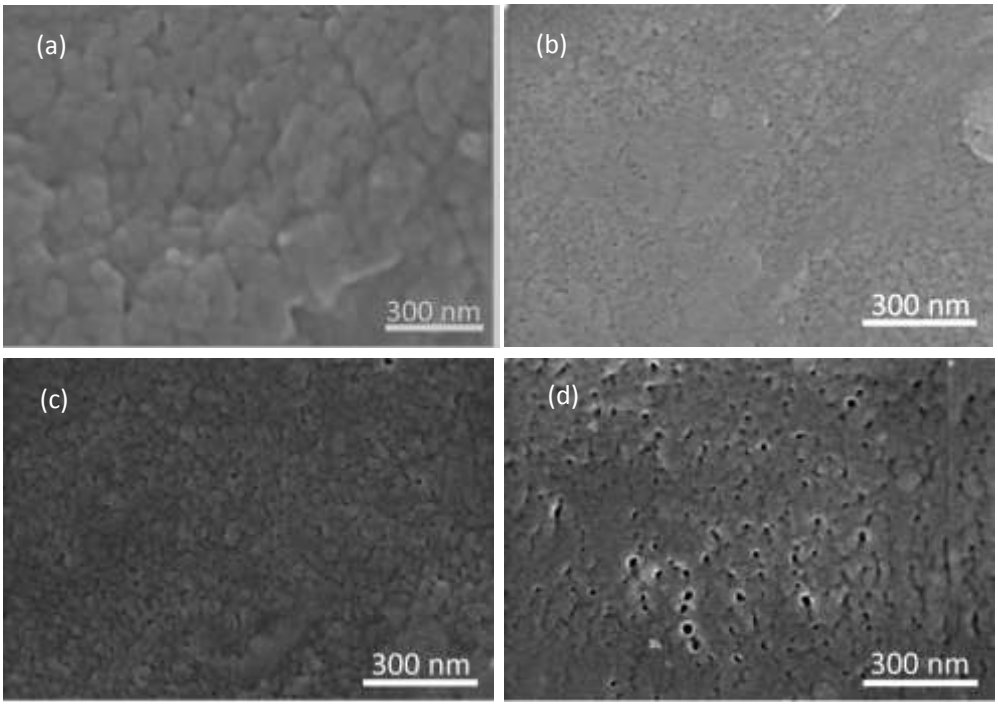

Fig. S1 SEM images of the PES/GO membranes with different GO concentrations in the parent dispersions. The concentration of GO for the (a)-(d) is 0, 1, 3 and 10 mg mL^{-1}, respectively. The composite membrane shows much smoother surface compared to the PES membrane which is possibly because the increased hydrophilicity of the GO/PES dispersion improves the contact of water and PES phase during the membrane formation process. Moreover, theses membranes with the GO fraction lower than 5 mg mL^{-1} show compact surface which is similar to that of pure PES membrane, indicating the pore structure of these membranes is slightly changed. In contrast, more defects on the surface of the membrane with the GO concentration of 10 mg mL^{-1} are observed, which should be ascribed to great structure changes of the membrane with high GO concentration, in accordance with the cross-sectional SEM images shown in Fig. 1.

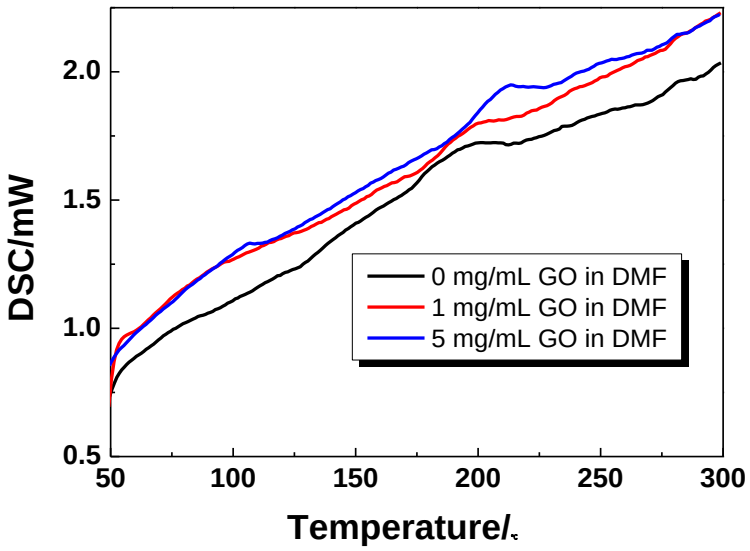

Fig. S2 DSC profiles for the PES/GO membranes with different GO concentrations in the parent dispersions. From the above profiles, we found that transition temperature of PES membrane increases with the GO incorporation (200 ℃ for a pure PES membrane and 220 ℃ for the membrane prepared with the GO concentration of 5 mg/mL in DMF), indicating the thermal stability is improved after the GO is incorporated in.

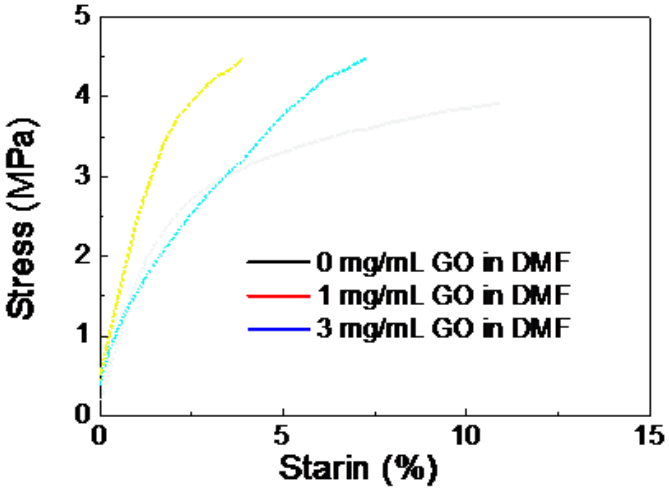

Fig. S3 Typical stress strain behaviors of PES/GO composite membranes prepared with different GO concentrations. It is obvious that the incorporation of GO has a significant effect on the mechanical behavior of the pure PES membrane from the typical stress-strain behaviors. The average values of percentage elongation before the fracture decrease with the increase of

GO concentration. This may be attributed to the interaction between GO nanosheets and the polymer matrix, which restricts the movement of polymer chains. The tensile strength shows an obvious improvement after the GO is added in.

Table S1 Fluxes of the pure water and the BSA solution of the membranes prepared with the DMF solutions with different GO concentration, and the BSA rejection rate is also shown.

Concentration of GO in DMF (mg mL^{-1})	Pure water Flux (L $m^{-2}h^{-1}$)	BSA solution Flux (L $m^{-2}h^{-1}$)	Rejection of BSA(%)
0	373.3	161.3	100
1	606.5	303.2	100
3	856.3	401.0	100
5	1076.4	579.2	100
10	1844.3	708.0	92.3

The pore size for the membrane with low GO concentration (less than 5 mg mL^{-1}) should be less than 5 nm because they shows the 100% rejection towards BSA that with the molecular size of about 3-4 nm[1, 2], while the membrane with high GO concentration (10 mg mL^{-1}) has larger pores indicated by the decreased rejection.

References:

1. D. Bulone, V. Martorana and P. L. San Biagio, *Biophys Chem*, 2001, **91**, 61-69.
2. R. X. Su, W. Qi, Z. M. He, Y. B. Zhang and F. M. Jin, *Food Hydrocolloid*, 2008, **22**, 995-1005.