Supporting Information for

Graphene Oxide/Polyamide-Based Nanofiltration Membranes for Water

Purification

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References

1. Results and discussion

1.1. Characterization of GO

The TEM of GO (Fig. S1a) has a clear layered structure. The wrinkled structure is observed on the GO surface, and most of them exist as a single layer. Fig. S1b shows the FTIR spectrum of the GO sample and graphite powder. Compared with graphite, the absorption peak intensity increases at 3420 cm^{-1}, which is attributed to the bending vibration of -OH on the GO surface[1]. The peaks at 1715 and 1053 cm^{-1} are attributed to the C=O tensile vibration of the carboxyl group and the C-O tensile vibration in the plane, respectively. It can be seen that oxygen-containing functional groups exist on the surface of GO. The XRD pattern (Fig. S1c) shows the clearly defined (001) peak (2=11°) of typical GO [2]. Using the Bragg equation [3], the GO layer spacing is 0.8 nm. The D and G characteristic peaks are shown in the Raman spectrum (Fig. S1d) correspond to the disordered and ordered structures of GO, respectively. The intensity ratio between the two characteristic peaks is related to the average size of the graphene sp^2 domain [4], indicating that the prepared GO has certain defects.
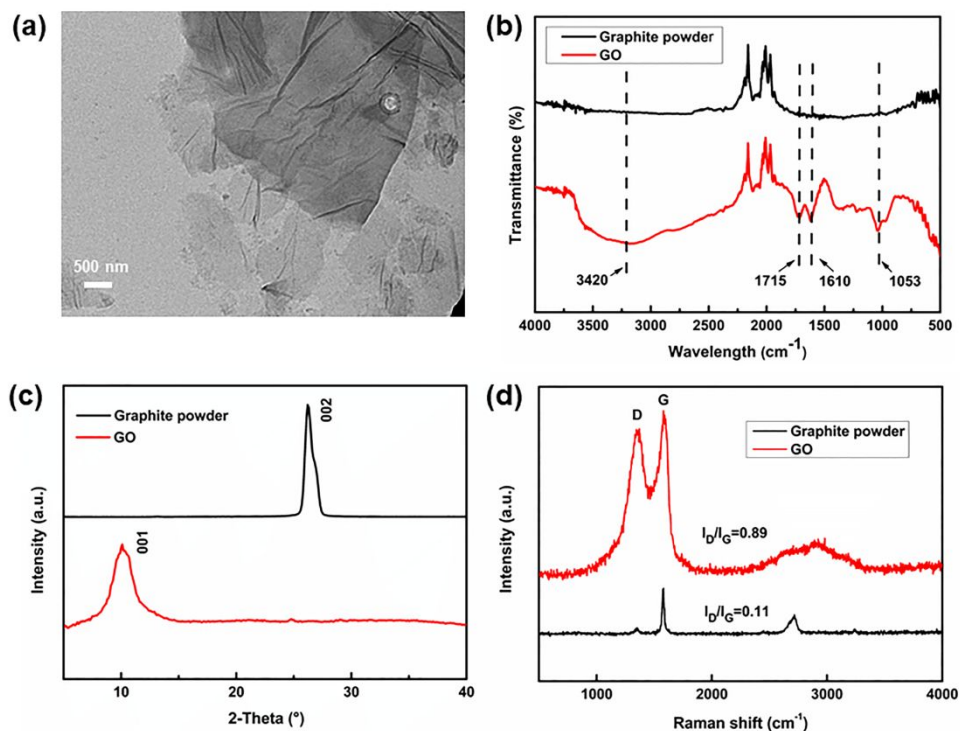
Fig. S1. TEM image of GO (a); FTIR spectrum of GO (b); XRD spectrum of GO (c); Raman spectrum of GO (d).

The results in Tab. S1 show that the O/N atomic ratio of the TFC/G0 surface is 1.01, which proves the good formation of the PA layer.. With the application of the electric field, the O content of the NF film increases, while the Cl content decreases. Compared with the NF film without electric field treatment, the C-O bond content of TFC/G0.3-DC is increased. The above results further confirm that the number of -COOH groups in the PA layer has increased. When polyamide is modified by an electric field, the acid chloride is more easily hydrolyzed to form -COOH.

Tab.S1. Element contents of NF membranes tested by XPS atomic survey.

| Sample | Atomic composition (%) | | | | O/N atomic ratio | Surface chemical bonds ratio | |
	C	N	O	Cl		C-O Content (%)	C=O Content (%)
TFC/G0	73.4	11.8	11.9	1.6	1.01±0.03	25.2	74.8
TFC/G0.3	73.3	11.7	12.4	1.4	1.06±0.033	25.7	74.3
TFC/G0.3-DC	72.7	11.9	13.4	0.9	1.13±0.035	27.4	72.7

The divalent salt separation performance of the membrane has been compared with the NF membrane reported in the literature (Fig. S2).
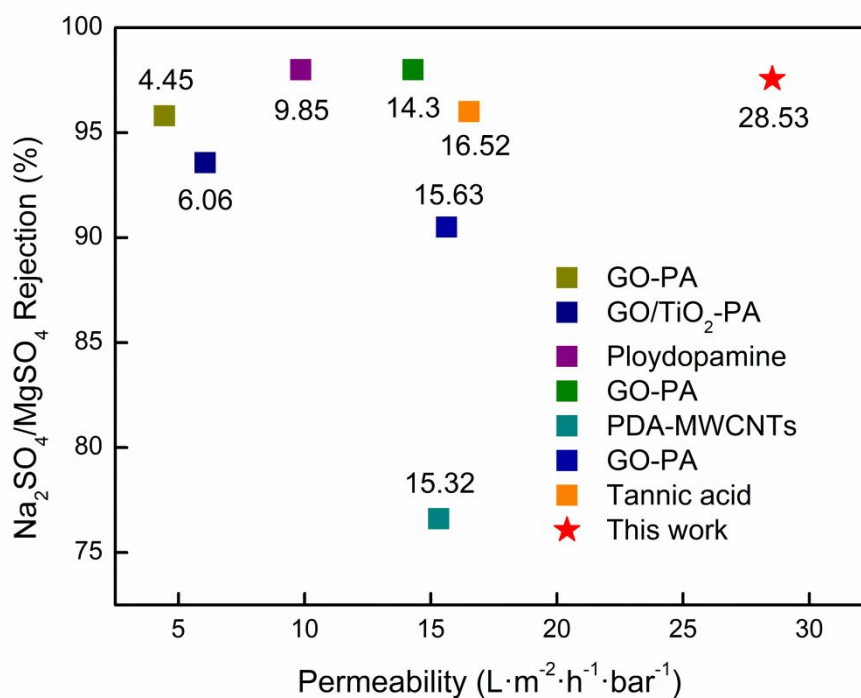
Fig. S2. Comparison of salt separation performance and water flux with NF membranes reported in the literature [5-11].

The mechanism of action of the PA layer is shown in Fig. S3. The surface of the PA layer is negatively charged in the sulfate solution (1000ppm, pH=6.3). Because of the size effect and the Donan effect, the SO_4^{2-} in the feed liquid is rejected. According to the results of Zeta potential, the PA layer to which the electric field is applied has a more substantial negative charge at pH=7, also more negative charge enhanced the antifouling performance for the negatively charged foulants.
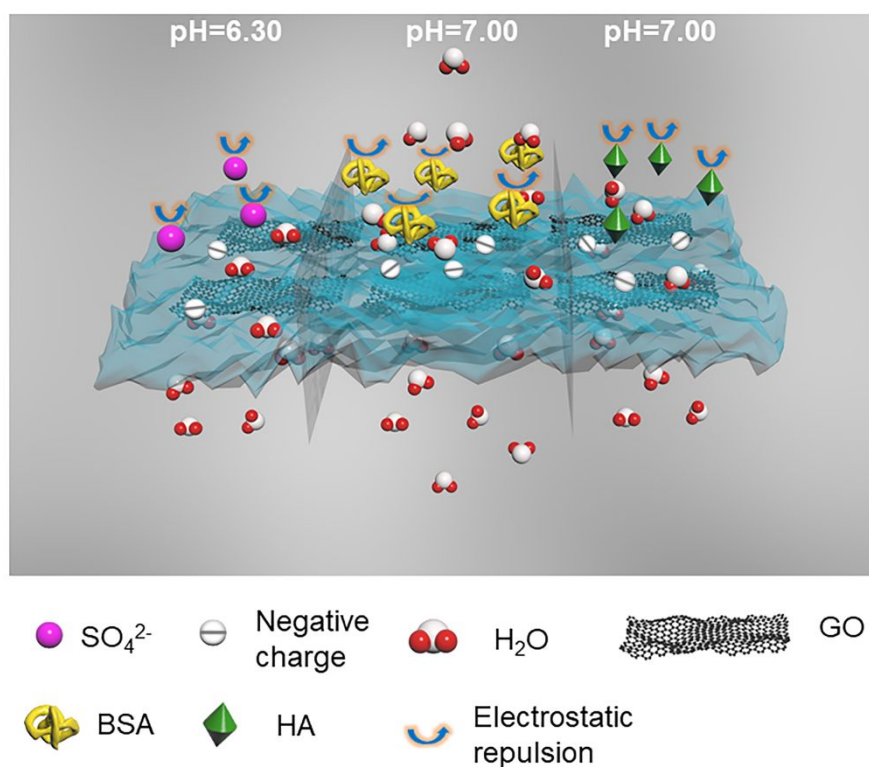

Fig. S3. Mechanism of sulfate interception and Anti-fouling in PA layer.

Reference

1. Safarpour, M.; Arefi-Oskoui, S.; Khataee, A., A review on two-dimensional metal oxide and metal hydroxide nanosheets for modification of polymeric membranes. *J. Ind. Eng. Chem* **2020,** *82*, 31-41.

2. Wang; Zhouyou; Zhang; Xiwang; Zeng; Xiangkang; Meng; Na; McCarthy; David, Highly dispersed TiO_2 nanocrystals and carbon dots on reduced graphene oxide: Ternary nanocomposites for accelerated photocatalytic water disinfection. *Appl. Catal. B* **2017**.

3. Chen, L.; Shi, G.; Shen, J.; Peng, B.; Zhang, B.; Wang, Y.; Bian, F.; Wang, J.; Li, D.; Qian, Z., Ion sieving in graphene oxide membranes via cationic control of interlayer spacing. *Science Foundation in China* **2017**.

4. Shen, J.; Li, T.; Yu, L.; Min, S.; Na, L.; Ye, M., One-step solid state preparation of reduced graphene oxide. *Carbon* **2012,** *50* (6), 2134-2140.

5. Lai, G. S.; Lau, W. J.; Goh, P. S.; Ismail, A. F.; Tan, Y. H.; Chong, C. Y.; Krause-Rehberg, R.; Awad, S., Tailor-made thin film nanocomposite membrane incorporated with graphene oxide using novel interfacial polymerization technique for enhanced water separation. *Chem. Eng. J* **2018**, S1385894718304741.

6.   Safarpour, M.; Vatanpour, V.; Khataee, A.; Esmaeili, M., Development of a novel high flux and fouling-resistant thin film composite nanofiltration membrane by embedding reduced graphene oxide/TiO$_2$. *Sep. Purif. Technol* **2015,** *154*, 96-107.

7.   Ang, M. B. M. Y.; Ji, Y.-L.; Huang, S.-H.; Lee, K.-R.; Lai, J.-Y., A facile and versatile strategy for fabricating thin-film nanocomposite membranes with polydopamine-piperazine nanoparticles generated in situ. *J. Membr. Sci* **2019,** *579*, 79-89.

8.   Xie, Q.; Zhang, S.; Hong, Z.; Ma, H.; Zeng, B.; Gong, X.; Shao, W.; Wang, Q., A novel double-modified strategy to enhance the performance of thin-film nanocomposite nanofiltration membranes: Incorporating functionalized graphenes into supporting and selective layers. *Chem. Eng. J* **2019,** *368*, 186-201.

9.   Zhao, F.; Ji, Y.; Weng, X. D.; Mi, Y.; Gao, C., High-Flux Positively Charged Nanocomposite Nanofiltration Membranes Filled with Poly(dopamine) Modified Multiwall Carbon Nanotubes. *ACS Appl. Mater. Interfaces* **2016,** *8* (10), 6693.

10. Wang, Z.; Huiyuan, L.; Na, M.; Meipeng, J.; Huanting, W.; Xiwang, Z., Graphene oxide incorporated thin film nanocomposite membrane at low concentration monomers. *J. Membr. Sci* **2018,** *565*, 428-434.

11. Zhenhua; Lü; Feng; Haiyan; Xiru; Zhang; Sanchuan; Meihong; Liu; Congjie, Composite nanofiltration membrane with asymmetric selective separation layer for enhanced separation efficiency to anionic dye aqueous solution. *J. Hazard. Mater* **2019**, *368,* 436-443.