Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

An anomalous anion transfer order in graphene oxide membrane induced by anion-π interactions

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Content

PS1: Method

Synthesis of GO suspension. The GO suspension was prepared by a modified Hummers method[1,2]. Firstly, 3 g graphene powders, 2.5 g P_2O_5 powders, and 2.5 g $K_2S_2O_8$ powders were gradually added into 12 mL H_2SO_4. The mixed solution stirred continuously under 80 ^oC for 6 hours. Further, the mixed solution was diluted by deionized (DI) water, centrifuged, and washed with DI water. After drying, pre-oxidized graphite was fabricated. To further oxidize the pre-oxidized graphite, the concentrated H_2SO_4 and $KMnO_4$ diluted with DI water was applied, followed by the addition of 30% H_2O_2. The product was centrifuged and washed with 1:10 HCl aqueous solution and DI water sequentially to remove impurities. The concentration of GO suspension was about 5 mg/mL.

Preparation of GO and NaCl-controlled GO membrane. 80 μL of as-prepared GO suspension was diluted to fabricate the GO membranes on mixed cellulose ester substrates (MCE, 47 mm, 0.22 μm pore size, Jinlong company) via a vacuum filtration method. On the other hand, we also prepared the NaCl-controlled GO membranes with the interlayer spacing about 12.1 Å as we reported before to study the separation performance for anion in salt solution[2]. The as-prepared GO membranes were immersed in 0.25 mol/L NaCl solution for half an hour to fix the interlayer spacings. The membrane was washed three times with DI water to remove the salt ions on the membrane surface before the separation process.

Preparation of rGO suspension. The rGO suspension was fabricated by a facile amino-hydrothermal method[3], which is defined as AH-rGO. The GO suspension (5mg/mL) was diluted to 0.1 mg/mL with the volume of 50 mL using DI water and then 30 mL $NH_3 \cdot H_2O$ with a concentration of 14.79 mol/L was added into the GO suspension.

Afterward, the mixture was kept in a sealed container and heated in a water bath at 80 ^oC for 5 hours with magnetic stirring at 20 rpm. Then, the mixture was heat at 90 ^oC for 1 hour to remove excess $NH_3 \cdot H_2O$ and cooled at room temperature (25 ^oC), followed by sonication for 30 min. And AH-rGO membranes supported by the mixed of cellulose ester was fabricated by vacuum filtration method.

Separation performance of GO membrane for anions. All the evaluation of GO membranes were measured under 1 bar in a dead-end filtration device. The effective area of membranes in this experiment is 13.85 cm^2. The single ion filtration experiments were performed using 25 mL salt solutions (NaF, NaCl, NaBr and NaI) as feed solution with the salt concentration from 2 mM to 10 mM and 5 mL solution in draw side was collected to measure the concentration of anion. Additionally, we also measured the separation performance of halide anions for the GO membrane using binary halide anion mixtures (NaI/NaF, NaF/NaBr, NaBr/NaCl and NaI/NaBr). And the concentration of each halide anion was 10 mM.

The water permeation (J_w) and salt ions rejection (R) were measured using Eqs. (1) and (2), respectively.

$$J_w = \frac{V}{A \times \Delta t \times P} \quad (1)$$

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

where J_w is the pure water or salt water permeance (L m^{-2} h^{-1} bar^{-1}), V is the volume of the filtered salt solution (L). Δt is the permeation time (h) for salt solution separation, A is the effective membrane area, P is the pressure (bar) during the filtration process. C_p and C_f are the salt solution concentrations at feed side and draw side, respectively, which were measured by ion chromatograph (IC, Metrohm). Filtrates was obtained after 10 min in order to make sure the filtration system was steady. All the experiments were performed three times.

Characterization. The surface and cross-section of GO membranes were characterized by scanning electron microscope (SEM, ZEISS Gemini 300) and X-ray diffraction (XRD Siemens, 08DISCOVER). The anion concentration in solution was measured by ion chromatograph (IC, Metrohm). The zeta potential was tested with a Malvern Zetasizer Nano ZS90 instrument to characterize the surface charge of GO suspension. X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha) was used for analysing the elemental composition of the membranes. The absorption spectra were tested by UV-vis absorption spectroscopy (UV-1600, Mapada, China).

PS2: The permeability of the NaCl controlled GO membranes for various salt solution in binary systems

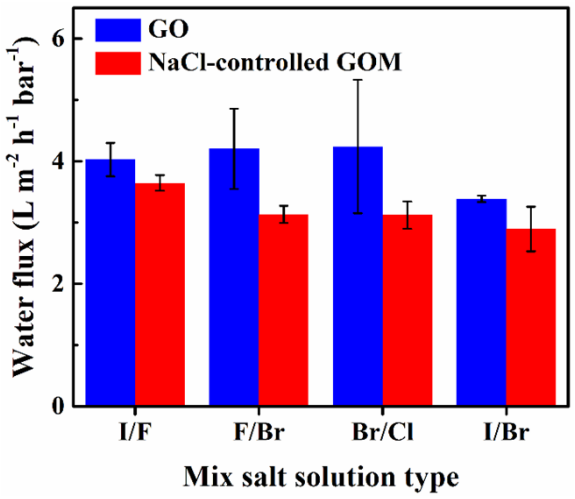

Fig. S1 Water flux of the GO membrane and the NaCl-controlled GO membrane.

PS3: UV-vis absorption spectroscopy of GO suspension

The UV absorption spectra of GO suspension and GO suspension mixed with NaF, NaCl, NaBr and NaI were presented in Fig. 3. The characteristic peak at ~ 230 nm was observed for pure GO solution, which was attributed to the π–π* from the aromatic double bond conjugate[2]. We observed that the intensity of GO in salt solution significantly decrease, indicating the conjugate double bonds of the aromatic group in GO were affected (Fig. 3). It has been reported that the strong cation-π interactions are responsible for the phenomenon. Further, we note that the intensity of GO mixed with NaF was slightly decreased than that of GO mixed with NaCl. Considering the same cations in the salt solution, we think the slight change can be attributed to the different of anions. In addition to the cations, it can be a weak anion-π interaction between anions and graphene sheets. Unfortunately, when we compared the UV absorption spectrum for GO mixed NaBr and NaI, there are the overlapping characteristic peaks for NaBr and NaI at ~ 230 nm (Fig. S2), which hindered our studies of anion-π interaction

between graphene sheets and those anions via UV absorption spectrum.

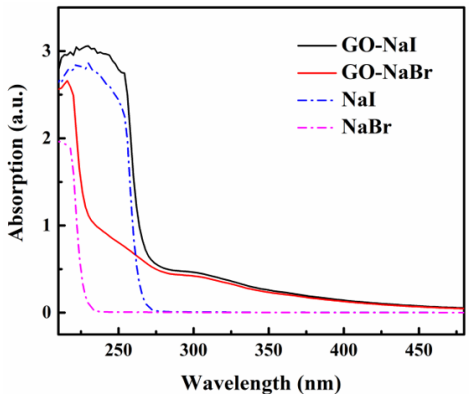

Fig. S2 UV absorption spectra of GO suspension (25 mg/L) 1:1 mixed with 0.025 mol/L salt solution (NaBr and NaI) diluted with 100 times.

PS4: XPS results of GO membranes

We used XPS to measure the oxygen-containing group distribution of GO membranes. Fig. S3a showed the survey XPS scans of the GO membranes. We found that there were no observable ion signals. The atomic concentration of C was 73.2% and O was 26.8%, respectively, indicating numerous oxygen-containing groups were introduced into the graphite during oxidation. Fig. S3b presented C1s XPS spectra for the GO membranes. Three peaks at 284.8 eV, 286.8 eV and 288.5 eV corresponding to C-C/C=C (58.42%), C-O/C-O-C (29.86%) and C=O (11.72%), respectively. We also measured the survey XPS scans of the AH-rGO membranes (Fig. S3c). The atomic concentration for C, O and N was 73.3%, 19.0% and 7.7%, respectively. Fig. S3d presented C1s XPS spectra for the AH-rGO membranes. Four peaks[3,4] at 284.8 eV, 286.8 eV, 288.5 eV and 284.5 eV corresponding to C-C/C=C (62.28%), C-O/C-O-C (24.66%), C=O (10.41%) and C-N (2.63%), respectively, indicating the GO suspension

was slightly reduced.

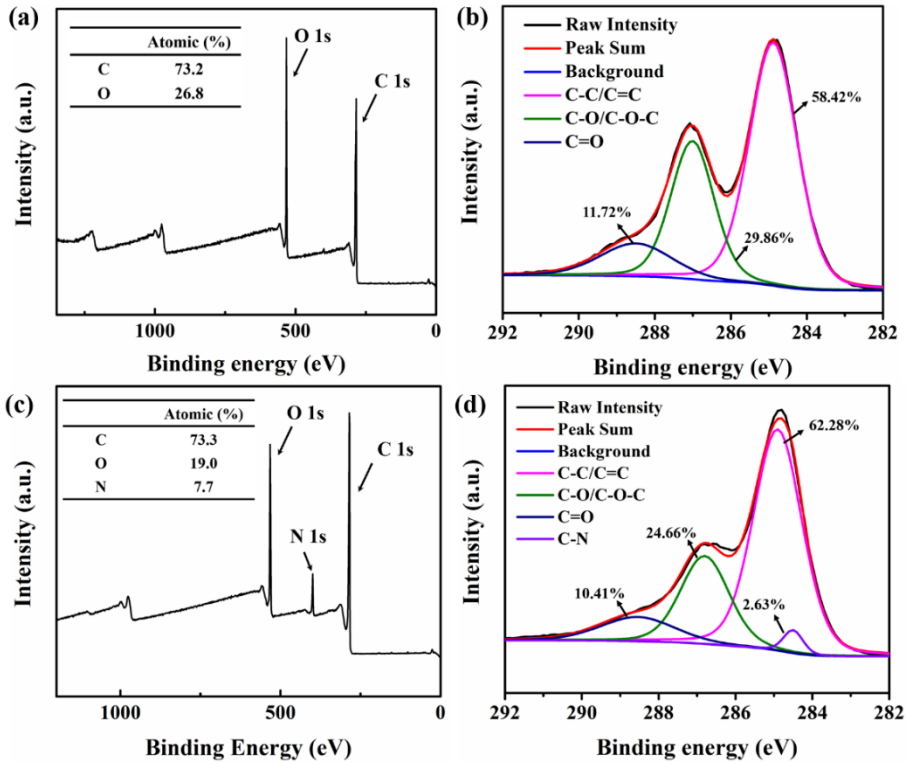

Fig. S3 (a) The full-scan XPS of GO membranes. **(b)** C1s XPS spectra of GO membranes; **(c)** The full-scan XPS of AH-rGO membranes. **(d)** C1s XPS spectra of AH-rGO membranes.

PS5: XRD pattern of the GO membrane

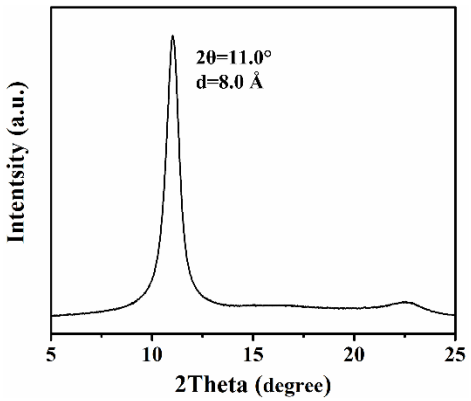

Fig. S4 XRD pattern for the GO membrane.

Reference

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