Ultrathin Graphene Nanofiltration Membrane for Water Purification

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Introduction

In the coming decade, the lack of clean water is a formidable challenge because of rapid population growth, extended droughts and fast growing demands. Nanofiltration technology is now widely used in drinking water and waste water treatments due to its low energy cost and simple operational process, in which the properties of nanofiltration membranes (NFMs) are of vital importance. Hence, an ideal NFM would be made by a polymeric NFM-like solution-based simple process, and simultaneously combine the fine attributes of both membranes. However, to access such a NFM is still a big challenge unresolved hitherto.

Here, we designed and fabricated ultrathin (22–53 nm thick) graphene membranes with 2D nanochannels by the simple filtration-assisted assembly strategy, using base-refluxing reduced GO (brGO) and successfully applied them as NFMs for water purification. Accompanied by the relative high pure water flux (as high as 21.8 L m^{-2} h^{-1} bar^{-1}), the resulting ultrathin graphene nanofiltration membranes (uGNMs) showed high retention rates for organic dyes and moderate retention rates for salts, and the rejection mechanism of separation process for 2D nanochannels was discussed or the first time.

Flux for water and other liquids

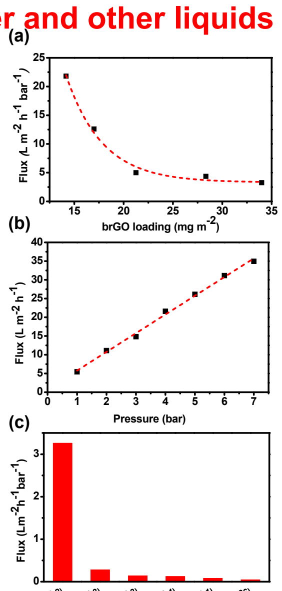


Figure *a) Variations of pure water flux as a function of brGO loading coated on the membranes. The pressure applied here was 1 bar. b) Water flux versus pressure applied on the uGNM with a brGO loading of 28.3 mg m^{-2}. c) Flux for various liquids as a function of their polarities under a pressure of 5 bar. The polarities were listed in the parenthesis behind each the name of the liquids. The uGNM used here had a brGO loading of 34.0 mg m^{-2} .*

Characterization of base-refluxing reduced GO (brGO)

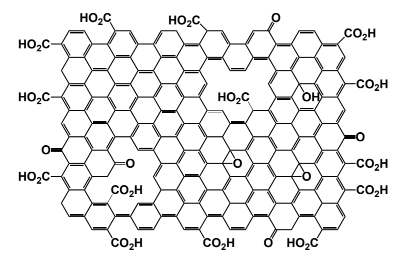


Figure *Schematic representation of a brGO graphene sheet with a certain amount of holes and most of the oxidized groups are located on the edges and the periphery of the holes on it. Note that the real graphene sheets extend further than depicted.*

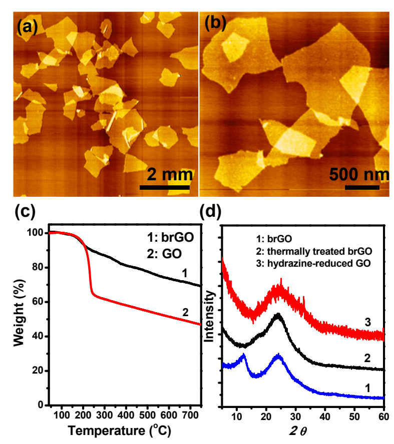


Figure *a,b) AFM images of brGO sheets dispersed on a mica. c) Thermogravimetric analysis in nitrogen of GO and brGO. d) XRD patterns of base-refluxing reduced GO (or brGO), hydrazine-reduced GO, and thermally treated brGO at 220 °C in vacuum.*

Characterization of the ultrathin graphene nanofiltration membranes (uGNMs)

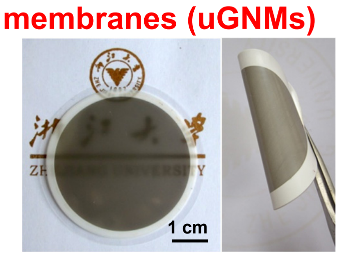


Figure *Digital photo of an uGNM coated on an AAO disk (left) and a twisted uGNM coated on a PVDF membrane (right).*

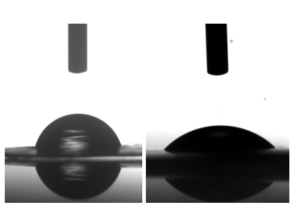


Figure *Digital photos of water drops on an uGNM (left) and a GO film (right), and the water contact angles are 70º and 43º respectively.*

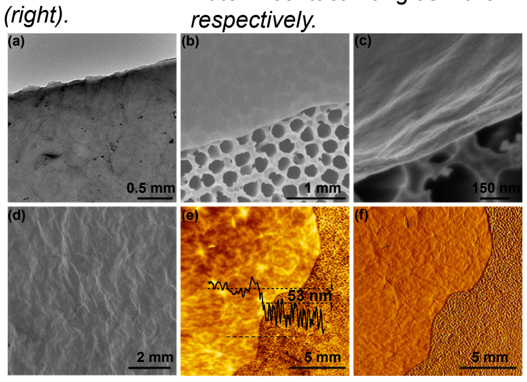
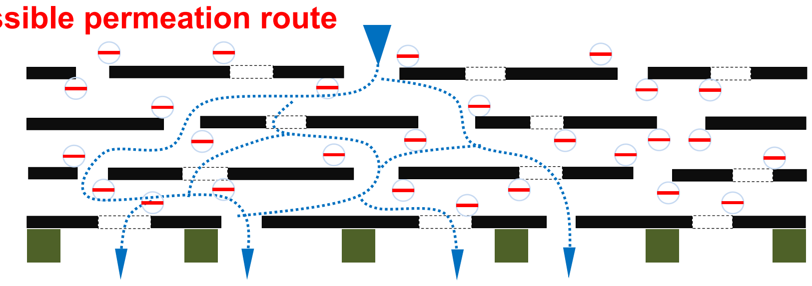


Figure *a) TEM image of a free standing ultrathin graphene membrane on a copper mesh. The edges of the graphene sheets could be distinguished clearly from the dark lines in the image. b) SEM image (top view) of the coating of an uGNM on an AAO disk. The top half of the image shows the uniform and smooth coating of brGO sheets, whereas the bottom half shows the porous structure of the bare AAO disk. c) Amplified SEM image (top view) of the coating of an uGNM on an AAO disk with more details about the surface morphology and the cross-section. The top half of the image shows the coating of brGO sheets, whereas the bottom half shows the bare AAO disk. d) SEM image (top view) of the surface morphology of an uGNM deposited on a mixed cellulose ester membrane with pore size of 0.22 mm, indicating the relatively smooth surface of the uGNM. The loading of all these uGNMs was 34 mg m^{-2}. e) AFM height and f) phase images of an uGNM coated on an AAO disk (pore size 200 nm). The right part of the image shows the bare AAO support, while the remaining parts shows the surface morphology of the uGNM.*

Schematic view for possible permeation route



Scheme *Water molecules go though the nanochannels of the uGNMs and the holes on the graphene sheets and at last reach the pores of supporting membranes. The blank squares present the holes on the graphene sheets (black line). The edges of the brGO and the periphery of the holes are negatively charged.*

Retention for dyes and salts

Table *Retention of organic dyes for uGNMs with different brGO loadings and brGO layer thickness*

brGO loading (mg m^{-2})	thicknes s (nm)	Pure water flux J_0 (L m^{-2} h^{-1} bar^{-1})	MB[a]			DR 81[a]		
			retention (%)	J/J_0 (%) [b]	C/C_0 [c]	retention [a] (%)	J/J_0 (%) [b]	C/C_0 [c]
14.1 [d]	22	21.81	99.2	90.0	1.27	99.9	89.6	1.31
17.0 [e]	26	12.62	99.7	91.1	1.30	99.8	89.7	1.33
21.2 [e]	33	5.00	99.7	89.4	1.32	99.9	87.2	1.33
28.3 [e]	44	4.37	99.6	90.4	1.33	99.9	95.8	1.34
34.0 [e]	53	3.26	99.8	95.0	1.36	99.9	95.6	1.35

[a] The concentration of feed dye solution C_0 was 0.02 mM. [b] The ratio of permeate flux of the dye solution J to the pure water flux J_0. [c] Concentration ratio of upper stream (C) when the permeation volume was 10 mL to the original feeding solution (C_0, 35 mL). [d] The applied pressure was 1 bar. [e] The applied pressure was 5 bars.

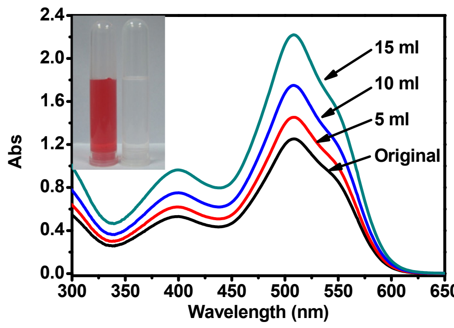


Figure *UV-vis absorbance changes of upper stream of DR 81 solution when the permeation volume was 5, 10, and 15 mL under the pressure of 5 bar. Inset: the photographic image showed the color change of 0.02 mM DR 81 solution (left) and the collected filtrate (right). The uGNM used here had a brGO loading of 28.3 mg m^{-2}.*

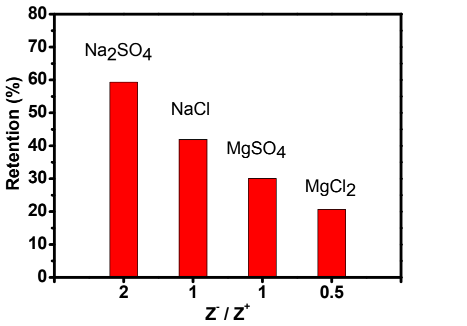


Figure *Retention measured for four different salt solutions (0.02 M) with different ion valences. The uGNM used here had a brGO loading of 34.0 mg m^{-2}, and a pressure of 5 bars was applied.*

Conclusion

In summary, dried, ultrathin, and robust graphene nanofiltration membranes were firstly fabricated from brGO by vacuum assisted assembly strategy. The brGO sheets stacked with each other forming sub-1-nm sized 2D nano-capillaries, and the hydrophobic carbon nanochannels favor high water flux. The uGNMs showed excellent performance for retention of organic dyes, especially for the charged dyes, based on the mechanism of physical sieving and electrostatic interaction. The Donnan exclusion dominated the salt rejection of the graphene membranes. The uGNMs are extremely thin, and less than 35 mg of brGO is needed for making a square meter membrane.

References and notes

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