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Porous reduced graphene oxide/phenolic nanomesh membranes with ternary channels for ultrafast water purification



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ABSTRACT

Graphene and its derivatives are attracting substantial interest in constructing laminated separation membranes for water purification. However, the long and tortuous interlayer pathways are unconducive to achieve ultrafast water permeation. Herein, we present a facile approach for the preparation of graphene-based membranes with shorter and straighter water pathways. Porous reduced graphene oxide (rGO) nanosheets are mixed with phenolic/polyether nanosheets, followed by vacuum filtration to form laminated structures and acid treatment to remove polyether. The obtained porous rGO/phenolic nanomesh membranes are endowed with ternary channels for water to permeate comprising the 30–60 nm pores of rGO nanosheets, the 9 nm mesopores of phenolic nanomeshes, and the sub-nanometer interlayer nanochannels. Moreover, the hydroxyl-containing phenolic nanomeshes can polymerize, enabling good hydrophilicity and tight structures of the membranes. Such membranes exhibit ultrafast water permeation while remaining high rejections. This work demonstrates a simple and efficient route to fabricate high-performance separation membranes by using two kinds of two-dimensional porous nanomaterials.

1. Introduction

Clean and safe water has become one of the scarcest resources worldwide due to the shortage and maldistribution of fresh water, population explosion, and industrial pollution [1,2]. Purifying and recovering the conventionally unavailable resources such as wastewater, seawater, and brackish water are inevitable for augmenting the water supply [3–6]. Among diverse water treatment technologies, membrane separation holding the merits of high efficiency, low energy consumption, and wide applicability is drawing substantial interest [7, 8]. High-performance membranes with desired nanostructures for advanced water purification are always pursued [9,10].

Two-dimensional (2D) graphene and its derivatives with atomic thickness, versatile functionality, and good flexibility and stability have been highlighted as building blocks for developing advanced separation membranes in recent years [11–13]. Graphene is composed of sp² hybridized carbon atoms in a hexagonal honeycomb arrangement, which

has been proved to enable faster water transport than traditional membranes [14]. Graphene oxide (GO) synthesized by oxidizing graphite possesses rich oxygen-containing groups and therefore excellent solution feasibility and processability, and shows great potential for constructing laminated membranes with tunable microstructures and chemical convertibility [15,16]. However, the oxygen-containing groups are capable of adsorbing water molecules, leading to the enlargement of the interlayer nanochannels between adjacent GO nanosheets [17,18]. As a result, GO membranes would suffer from declined solute rejection and disintegration of laminated structure. More typically, reduced graphene oxide (rGO) nanosheets with decreased number of oxygen-containing groups can guarantee stable interlayer nanochannels for precise rejection of solutes [19-21]. Nevertheless, the elimination of oxygen-containing groups narrows the interlayer nanochannels and sacrifices the hydrophilicity, resulting in insufficient water permeation through rGO membranes [22]. Therefore, there remains a high demand for designing graphene-based membranes with stable

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interlayer nanochannels for fast water permeation.

Governed by the Hagen-Poiseuille equation, shortening the length of water pathways inside the membranes emerges as one effective approach to increase the water permeation [23]. In pristine graphene-based membranes, water pathways mainly consist of the horizontal interlayer nanochannels and the vertical defect/edge-derived nanochannels [24]. Accordingly, small-flake GO nanosheets were exploited to engineer membranes with shorter and less tortuous pathways [25]. However, additional cross-linkers and intercalators were needed to stabilize the membranes, which partially occupy the interlayer nanochannels and hinder the water permeation [26]. Another strategy is creating through-plane pores to offer extra vertical water pathways [27]. For example, membranes stacked by nanoporous graphene can ensure good stability and high water permeance [28]. Unfortunately, nanoporous graphene was produced at high temperature and necessitated post-functionalization for redispersion, complicating the membrane fabrication processes. Alternatively, intercalating porous polymeric nanosheets has exhibited extensive advantages in building 2D laminated membranes with rich through-plane pores and customizable chemistry [29]. For instance, covalent organic framework nanosheets can not only provide additionally tunable through-plane porosity for improving water permeation, but also interact with GO and rGO through functional groups for enhancing stability [30-32]. Very recently, we developed phenolic nanomeshes with ordered through-plane mesopores by a glycerol-triggered 2D assembly method and explored the possibility of phenolic nanomeshes in tuning microstructure and interlayer chemistry of GO membranes for fast desalination [33,34]. However, the proportion of porous polymeric nanosheets dominates the separation performances since insufficient porous polymeric nanosheets brings limited improvement of water permeation whereas excessive porous polymeric nanosheets results in decreased rejections. Therefore, it remains a challenge to develop graphene-based membranes with short water pathways by simple methods for high-performance separations.

Herein, we present a facile strategy to prepare laminated graphenebased membranes with short pathways by combining porous graphene and porous polymeric nanosheets for ultrafast water purification. Porous rGO nanosheets are first synthesized by low-temperature hydrothermal reduction of GO and then stacked with phenolic nanomeshes to form porous rGO/phenolic nanomesh membranes (Fig. 1). Such membranes are featured with ternary water channels including the through-plane pores of rGO nanosheets and phenolic nanomeshes, and the interlayer nanochannels between rGO nanosheets. Moreover, the addition of phenolic nanomeshes can enhance the hydrophilicity and tighten the structures of the membranes. Consequently, membranes exhibit improved water permeations and good stability.

2. Results and discussion

2.1. Characterizations of porous rGO nanosheets and phenolic nanomeshes

The porous rGO nanosheets were synthesized by low-temperature hydrothermal reduction of GO nanosheets [35]. We first monitored the changes of chemical compositions to demonstrate the reduction of GO nanosheets after hydrothermal treatment. As shown in Fig. 2a, the peaks located at the wavenumbers of 3200 cm⁻¹, 1720 cm⁻¹, 1385 cm^{-1} , 1215 cm^{-1} , and 1060 cm^{-1} are ascribed to the vibrations of –OH, C=O, -COOH, C-OH, and epoxy C-O-C groups in GO nanosheets, respectively [36,37]. These peaks are greatly weakened after hydrothermal reduction, revealing the elimination of the oxygen-containing groups. Moreover, the *d*-spacing of GO nanosheets in dry state is calculated to be 8.2 Å according to the peak located at the 2θ of 10.8° (Fig. 2b). After hydrothermal treatment, a peak located at the 2θ of 25.8° is observed and corresponding to a decreased *d*-spacing of 3.4 Å because of the removal of oxygen-containing groups, revealing the successful reduction of GO nanosheets. The GO nanosheets are in the lateral size of 1–4 µm and the thickness of 1.1 nm (Fig. S1), which is indicative of the single-layered structure. After hydrothermal reduction, the rGO nanosheets show plenty of wrinkles and partially overlapped regions (Fig. S2). Importantly, the rGO nanosheets exhibit plenty of pores with a diameter of 30-60 nm (Fig. 2c). During the hydrothermal reduction process, the oxygen-containing groups turn to carbon monoxide, carbon dioxide, and water [11]. These species are removed from the basal plane and the edges of GO nanosheets, leading to the rGO nanosheets with porous structures [38].

To clearly observe the structures of phenolic nanomeshes, we first synthesized phenolic/F127 nanosheets via a glycerol-triggered 2D assembly method, and then removed F127 by soaking in 48 wt% H₂SO₄ at 95 °C for 6 h according to our previous work [33]. F127 serving as the soft template can interact with phenolics through hydrogen bonds and form micelles with phenolics as the shell. Viscous glycerol is able to wrap the phenolic/F127 micelles, leading to enhanced repulsive Coulombic interactions, good dispersity, and constrained motions of the micelles in liquid phases. Consequently, the phenolic/F127 micelles are directed to assemble and merge exclusively in the lateral direction to form phenolic/F127 nanosheets. After removal of the templating F127, phenolic nanomeshes with single-layered mesopores can be obtained. As shown in Fig. S3, the phenolic/F127 nanosheets exhibit a 2D morphology with sharp edges and a thickness of \sim 4 nm. After acid treatment, mesopores with average pore diameter of ~9 nm are uniformly distributed on the phenolic nanomesh (Fig. 2d). It should be mentioned that pure phenolic nanomeshes after acid treatment cannot



Fig. 1. Schematic illustration for the preparation of porous rGO/phenolic nanomesh membranes.



Fig. 2. Characterizations of the porous rGO nanosheets and phenolic nanomeshes. (a) FTIR spectra and (b) XRD patterns of GO and rGO nanosheets. TEM images of (c) the porous rGO nanosheets and (d) the phenolic nanomeshes.

be redispersed due to the polymerization of phenolics between neighboring nanomeshes. Therefore, phenolic/F127 nanosheet dispersion with excellent accessibility and processability was used for the preparation of the membranes.

2.2. Morphologies and chemical compositions of porous rGO/phenolic nanomesh membranes

The porous rGO/phenolic nanomesh membranes were fabricated by vacuum filtrating the mixed dispersion containing porous rGO nanosheets and phenolic/F127 nanosheets, followed by acid treatment to remove F127. The obtained porous rGO/phenolic nanomesh membranes are denoted as $PRGO/PN_x$, where x represents the volume proportion (%) of the phenolic/F127 nanosheet dispersion in the mixed nanosheet dispersion. Macroporous polyvinylidene fluoride (PVDF) membranes with good chemical stability were used as the supports. We first investigated the morphologies of the PRGO/PN50 membrane fabricated by filtrating 100 mL of the mixed dispersion before and after acid treatment. Before acid treatment, the PRGO/PN50 membrane exhibits a rough surface with some pits and bulges (Fig. 3a). The thickness of the PRGO/PN₅₀ layer is 303 nm (Fig. 3b). After acid treatment, the surface of the PRGO/PN₅₀ membrane becomes smoother and denser (Fig. 3c). Moreover, the thickness of the PRGO/PN50 layer is decreased to 249 nm (Fig. 3d). During the acid treatment process, F127 can be degraded and phenolics are subjected to further polymerization [39]. The denser surface morphology and the decreased thickness of the PRGO/PN50 layer are mainly because of the polymerization of the adjacent phenolic nanomeshes by forming methylene groups. That is, the structures of the porous rGO/phenolic nanomesh membranes are tightened after acid treatment. Notably, the membranes exhibit a less laminated structure, which is due to the van der Waals bonding-induced aggregation of the fold-edge rGO nanosheets [40,41] and the crispation of the flexible COF nanosheets [42].

The physicochemical properties of the PRGO/PN₅₀ membrane before and after acid treatment were further characterized. As shown in Fig. 3e, the PRGO/PN₅₀ membrane before acid treatment exhibits a peak located at the 2 θ of 26.7°, which is nearly unchanged (26.8°) after acid treatment. Correspondingly, the *d*-spacing of the porous rGO nanosheets in

the PRGO/PN₅₀ membrane before and after acid treatment is constant to be 3.3 Å. This demonstrates that the interlayer nanochannels between porous rGO nanosheets are unaffected by the acid treatment. Notably, the d-spacing of the porous rGO nanosheets in the PRGO/PN50 membrane is slightly smaller than that in pure porous rGO (3.4 Å) due to the physical compression effect of the phenolic nanomeshes [43]. As shown in Fig. 3f, the peaks located at the wavenumbers of 2875 cm⁻¹ and 1105 cm⁻¹ are ascribed to the stretching vibrations of C-H and C-O-C in F127, respectively [44]. These two peaks almost disappear after acid treatment, confirming the successful removal of F127. Meanwhile, the peaks located at the wavenumbers of 1450 cm⁻¹, 1175 cm⁻¹, and 870 cm⁻¹ represent the vibrations of –CH₂- in phenolics, the CF₂ and C–C in PVDF, respectively [39,45]. These peaks remain unchanged after acid treatment, verifying that phenolics and PVDF can tolerate the acid treatment conditions. Moreover, the characteristic peak of –OH located at the wavenumber of 3300 cm⁻¹ is slightly weakened after acid treatment because phenolics are further polymerized by consuming hydroxymethyl groups [46]. These results indicate that F127 is removed to create mesopores and phenolic nanomeshes are polymerized to tighten the structures of the membranes after acid treatment, while porous rGO nanosheets and PVDF supports remain stable. Moreover, the pure porous rGO membrane exhibits a water contact angle of 72° (Fig. 3g), which indicates a less hydrophilicity due to the elimination of the oxygen-containing groups after hydrothermal reduction. However, the intercalation of phenolic nanomeshes with oxygen-containing groups leads to a declined water contact angle of 47° (Fig. 3h). Therefore, the intercalation of phenolic nanomeshes can endow membranes with enhanced hydrophilicity than pure porous rGO membranes, which facilitates the water transport through the porous rGO/phenolic nanomesh membranes.

2.3. Separation performances of porous rGO/phenolic nanomesh membranes

We first examined the water permeances and the rejection rates to Congo red of the PRGO/PN₅₀ membranes before and after acid treatment. As shown in Fig. 4a, the water permeance and the rejection rate of the PRGO/PN₅₀ membrane before acid treatment are 2.3 L/(m²·h·bar)



Fig. 3. Characterizations of the PRGO/PN₅₀ membrane fabricated by filtrating 100 mL of the mixed dispersion. (a) Surface and (b) cross-sectional SEM images of the PRGO/PN₅₀ membrane before acid treatment. (c) Surface and (d) cross-sectional SEM images of the PRGO/PN₅₀ membrane after acid treatment. The scale bar in (a) applies to (a–d). (e) XRD patterns and (f) FTIR spectra of the PRGO/PN₅₀ membranes before and after acid treatment. Water contact angles of (g) the pure porous rGO membrane and (h) the PRGO/PN₅₀ membrane.

and 99.5%, respectively. After acid treatment, the water permeance of the PRGO/PN₅₀ membrane is greatly increased to 353.7 L/(m²·h·bar) while the rejection rate maintains 98.0%. During the acid treatment process, F127 is removed and rich through-plane mesopores are formed in phenolic nanomeshes. Consequently, plenty of short water pathways across phenolic nanomeshes are produced, leading to the increased water permeance of the membrane. The molecular size of Congo red is 2.6 nm × 0.7 nm, which is smaller than the diameters of pores in rGO nanosheets and phenolic nanomeshes. That is, the rejection of Congo red is mainly dominated by the interlayer nanochannels. Acid treatment has barely influence on the interlayer nanochannels, enabling the high rejection rate of the membrane.

Further, we measured the separation performances of the porous rGO/phenolic nanomesh membranes with varied proportions of phenolic nanomeshes. As shown in Fig. 4b, the pure porous rGO membrane exhibits a water permeance of 3.7 L/(m^2 ·h·bar) and a rejection rate of 99.6% due to the through-plane pores and the narrow interlayer nanochannels. After intercalating the phenolic nanomeshes, the water permeance of the PRGO/PN₁₀ membrane is increased to 60.4 L/(m^2 ·h·bar) due to the introduction of through-plane pathways through phenolic nanomeshes and the enhanced hydrophilicity. With further increase in the proportion of phenolic nanomeshes, the water permeance is gradually increased to 620.1 L/(m^2 ·h·bar) for the PRGO/PN₇₀ membrane because of the increased number of short through-plane water pathways. However, the rejection rate of the PRGO/PN₇₀ membrane is decreased to 90.6%. Notably, the pure phenolic nanomesh membrane

exhibits a low rejection rate of 27.2%. Therefore, excessive phenolic nanomeshes provide paths that allow solutes to permeate through the PRGO/PN₇₀ membrane, leading to decreased rejection rate. In addition, by simply adjusting the volumes of the mixed dispersion from 50 mL to 200 mL, we prepared the PRGO/PN₅₀ membranes with various thicknesses ranging from 130 nm to 580 nm (Fig. S4) and tested their separation performances. As shown in Fig. 4c, the membranes exhibit decreased water permeances and increased rejection rates with the increase in thicknesses. Membranes with higher thicknesses possess longer pathways and higher mass transfer resistances, leading to decreased water permeances and increased rejection rates [47].

Owing to the polymerization of phenolic nanomeshes during acid treatment process and the stable interlayer nanochannels between rGO nanosheets, the porous rGO/phenolic nanomesh membranes with tight structures are expected to show good separation performance stability. We evaluated the long-term stability of the PRGO/PN₅₀ membrane by continuously measuring the permeation fluxes and rejection rates within 24 h. As shown in Fig. 4d, in the initial 5 h, the permeation flux of the membrane is decreased due to the pressure-induced structural compaction. Afterward, the membrane exhibits stable permeation flux of 270 L/(m²·h·bar). Moreover, high rejection rates (>97%) are maintained during the test, indicating the good stability of the membrane. Therefore, the porous rGO/phenolic nanomesh membranes are promising in separating small molecules in practical applications.

We compared the separation performances of the porous rGO/ phenolic nanomesh membranes with other reported graphene-based



Fig. 4. Separation performances of the porous rGO/ phenolic nanomesh membranes. (a) Water permeances and rejection rates of the PRGO/PN₅₀ membranes before and after acid treatment. (b) Water permeances and rejection rates of the pure porous rGO membrane and the PRGO/PN_x membranes. (c) Water permeances and rejection rates of the PRGO/ PN₅₀ membranes with different thicknesses. (d) Permeation fluxes and rejection rates of the PRGO/ PN₅₀ membrane under long-term operations. (e) Comparison of separation performances of the PRGO/ PN₅₀ membrane with other reported graphene-based membranes. (f) Schematic illustration of the ternary water channels of the porous rGO/phenolic nanomesh membrane.

membranes. As shown in Fig. 4e and Table S1, the porous rGO/phenolic nanomesh membrane exhibits higher water permeance than most other membranes with similar rejection rates. The superior separation performance of the porous rGO/phenolic nanomesh membrane should be mainly attributed to the ternary water channels. As illustrated in Fig. 4f, water can transport across the membrane through the pores of rGO nanosheets and phenolic nanomeshes, and the interlayer nanochannels. Compared with other graphene-based membranes, the porous rGO/phenolic nanomesh membrane possess shorter and straighter water pathways, contributing to the superior water permeation. Meanwhile, the narrow and stable interlayer nanochannels between porous rGO nanosheets guarantee the high retentions to the solutes of the porous rGO/phenolic nanomesh membranes.

3. Conclusion

In conclusion, we demonstrate a facile strategy to prepare porous rGO/phenolic nanomesh membranes with shortened pathways for fast water permeation. Membranes are fabricated by reducing GO to synthesize porous rGO, laminating porous rGO and phenolic/F127 nanosheets to form stacked structures, and acid treatment to remove F127. The pores of rGO nanosheets and phenolic nanomeshes, and the interlayer nanochannels afford the membranes ternary water channels. Moreover, the intercalation of phenolic nanomeshes enhances the hydrophilicity of the membranes. Accordingly, membranes exhibit superior separation performances exceeding most graphene-based membranes. In addition, good long-term stability is achieved thanks to the stable interlayer nanochannels between rGO nanosheets and the tight structures of the membranes because of the polymerization of phenolic nanomeshes. This work provides a simple method to deliver

high-performance porous graphene-based membranes with short pathways and stable interlayer nanochannels, which can be extended to design membranes using other 2D nanomaterials.

CRediT authorship contribution statement

Qianqian Lan: Conceptualization, Methodology, Investigation, Writing – original draft, Visualization, Funding acquisition. Leyao Liu: Investigation, Visualization, Formal analysis. Yunchen Wu: Investigation. Chao Feng: Investigation. Kaiqin Ou: Investigation. Zicheng Wang: Resources. Yunpeng Huang: Resources. Yan Lv: Funding acquisition. Yue-E Miao: Resources. Tianxi Liu: Resources, Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.coco.2022.101216.

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