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Processable graphene oxide-embedded titanate nanofiber membranes with improved filtration performance

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HIGHLIGHTS

- Graphene oxide embedded titanate fiber films with good processability are prepared.
- The content of graphene oxide sheets and thickness of films can be adjusted easily.
- Embedded graphene oxide sheets improve the filtration property of fibrous films.
- Such composite films also exhibit enhanced selectivity performance.

GRAPHICAL ABSTRACT

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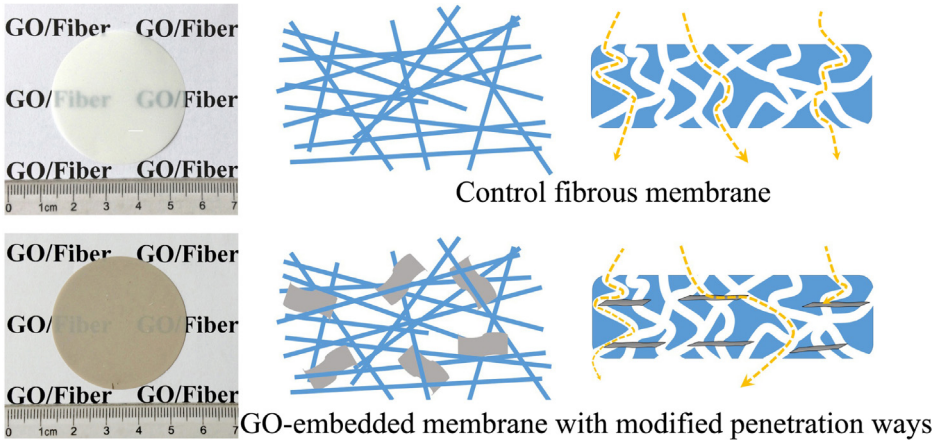

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ABSTRACT

Graphene oxide (GO)-embedded titanate nanofiber (TNF) membranes with improved filtration performance are prepared successfully by a two-step method including electrostatic assembly of GO and TNFs into hybrids and subsequent processing of them into membranes by vacuum filtration. The embedded contents of GO sheets in films and thickness of as-assembled films can be adjusted facilely, endowing such composite films with good processability. Owing to the skilful introduction of GO sheets, the pore and/or channel structures in these hybrid membranes are modified. By treating different dye solutions (Direct Yellow and Direct Red), the filtration properties of these membranes show that the introduction of certain amount of GO sheets efficiently improve the separation performance of the membranes. Interestingly, these

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GO-embedded TNF membranes also display superior selective separation performance on filtrating the mixture solutions of such two dyes, making these hierarchical membranes more flexible and versatile in water treatment areas.

1. Introduction

Inorganic fibrous membranes have been considered as promising separation membranes due to their large surface area, high chemical and thermal stability, large porosity and high permeability, etc [1–4]. Despite of these advantages, the interconnected and open channels in fiber-based films are relatively large [5–8], which makes such membranes suffer a lot from poor retention efficiency and selectivity, limiting their potential applications in separation fields, especially in organic wastewater purification [9–12]. Generally, the permeation properties of fiber membranes can be improved by surface modification (for example, adsorption properties) [13,14] and the structural adjustment of the pores/channels [15–17]. In addition to enhancing the adsorption capacity, modification of pore/channel structures could be an alternative and effective strategy to improve the retention ability of these films [18,19]. Unfortunately, restricted by the fiber structures and the disorder assembling process of these fibers, the size of the as-formed pores (channels) in fibrous membranes are still hard to be well controlled. Thus, how to construct desirable pore/channel structures that could appropriately improve the separation performance of fibrous membranes is still a big challenge.

Graphene-based sheets have recently been found to be promising building blocks in film areas owing to their unique two-dimensional structure and properties [20–23]. Apart from used as the main components in films (sometime as surface coating membranes) [24–28], these carbon sheets have also been considered as excellent additives to improve certain properties of the films, for example conductivity, film-formation, antifouling and so on [29–31]. Thus, if these carbon sheets are successfully added into inorganic fiber filtration membranes, may the channels of membranes be modified, and their separation performance be improved [32–35]? As Scheme shown in Fig. 1, when carbon sheets are introduced into fiber membranes, some of the interconnected and open channels in the as-obtained membranes may be segmented and cut off during the film assembly process, which would change the structure of these channels. Meanwhile, these embedded two-dimensional sheets could also increase the barrier area, which will delay substance permeation through the fiber membranes, improving the interception ability of these films. Accordingly, addition of graphene-based sheets could cause structural changes of these pores or channels in these inorganic fibrous films, which may affect the films' permeability and selectivity performance, resulting in improved filtration separation properties of these fibrous membranes.

Herein, we demonstrate a facile method to fabricate graphene oxide-embedded titanate ($H_2Ti_2O_7$) nanofiber (TNF) membranes with improved filtration separation properties. GO-embedded TNFs membranes are prepared by a two-step method including preparation of GO—$H_2Ti_2O_7$ nanofiber (TNF-GO) composites and assembling of them into membranes by simple vacuum filtration. The content of GO sheets and the thickness of films can also be adjusted facilely by our method. The separation performances of these GO embedded nanofibers membranes are investigated by filter organic dyes (Direct Yellow 50, Direct Red 80, or their mixed solutions). The results show that embedding GO sheets into these fiber membranes can efficiently improve the filtration separation performance of these TNF-GO membranes, which expands the potential applications of these hybrid filtration membranes in the film separation areas.

2. Experimental section

2.1. Preparation of GO, TNF and TNF-GO composites

GO sheets were prepared from purified natural graphite (Alfa-Aesar Co.) according to the method reported by Hummers and Offeman [36]. Then the as-obtained GO dispersion (1 mg/ml) was sonicated and centrifuged to remove un-exfoliated and larger sheets. TNF are prepared using modified hydrothermal method according to the previous reports [34,37]. First, tetra-*n*-butyl titanate (0.85 ml) was added in KOH solution (10 mol L^{-1}, 40 ml), which was stirred for 30 min to ensure a complete blending of the reactants. Then, the mixture was transferred to 50 ml Teflon-lined autoclave and was conducted at 200 °C for 24 h. The product was collected after the hydrothermal reaction and washed using HCl (0.2 M) and deionized water to remove any impurities.

The as-obtained GO sheets and TNF are used as precursors to prepare TNF-GO composites. In a typical experiment, GO dispersion (0.25 ml, 1 mg ml^{-1}) was added in titanate nanofibers suspension (50 mg of TNF dispersed in 50 ml of water) and the pH value was adjusted to around 6. Then, the as-formed slurry was stirred for 12 h at room temperature. Finally, the TNF-GO composites were centrifuged and washed with distilled water several times. Different usages of GO in TNF-GO composites were also prepared through the same process, and these samples are labelled as TNF-$GO_{x\%}$ (x%, mass ratios of original added GO sheets).

2.2. Film assembling and filtration test

Before membrane assembling, TNF and TNF-$GO_{x\%}$ composites (50 mg) were redispersed in HCl solution (0.2 M, 50 ml) for 2 days to form relatively stable suspensions. Then, TNF and TNF-GO membranes were prepared by vacuum filtration of the as-prepared suspensions through Poly(ether sulfones) filter membranes (47 mm in diameter, 0.2 μm pore size, Tianjin Jinteng). Distilled water was poured to wash these films. The filtration properties of our membranes were evaluated by filtering different dye solutions, including Direct Yellow 50 (45 ppm), Direct Red 80 (35 ppm), and their mixture with the same concentrations. After washed by distilled water, 100 ml of these dye solution was poured on the top of the as-formed membranes, which was then subjected to continuous vacuum suction for 30 min (with a pressure of around 1 bar) to allow the solution to flow through the membranes. The volume of filtrate was recorded to calculate of flux for filtration membranes. The resultant filtrate was examined by ultraviolet-visible (UV–vis) spectroscopy to calculate the relative concentration of filtrate ($(C_{filtrate}/C_{feed}) \times 100\%$) and retention rate ($(1\text{-}C_{filtrate}/C_{feed}) \times 100\%$). Furthermore, the adsorption capacities of TNF and TNF-GO films were obtained by stirring the as-prepared films in the dye solution for 30 min. After centrifugation, the solution was analysed by UV–vis spectroscopy ($(1\text{-}C_{adsorption}/C_{feed}) \times 100\%$).