Photocatalytic self-cleaning carbon nitride nanotube intercalated reduced graphene oxide membranes for enhanced water purification

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HIGHLIGHTS

- Self-cleaning g-C_3N_4/rGO nanofiltration membranes were prepared.
- Organic dyes can be efficiently removed by an integrated process.
- 1D g-C_3N_4 NT intercalated rGO membrane exhibits relatively competitive performance.
- Self-cleaning mechanism of the membranes is established.

ARTICLE INFO

ABSTRACT

Crumpled laminar nanostructures with nanoscale water transport channels constructed by two-dimensional (2D) reduced graphene oxide nanosheets (rGO NS) have been considered as a promising membrane separation layer for water purification. However, efficient tuning of rGO laminar structures with enhanced membrane performance remains challenging. In this work, we report a novel 1D graphitic carbon nitride nanotube (g-C_3N_4 NT) intercalated rGO nanofiltration (NF) membrane with enhanced photo-induced self-cleaning performance. The g-C_3N_4 NT photocatalyst could not only enlarge the rGO interlayer spacing for improved water permeability, but also endow the composite membrane with visible-light photocatalytic activity for efficient removal of organic dyes from polluted water. Our g-C_3N_4 NT/rGO membrane exhibits superior water permeability (4.87 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$) and synergetic Rhodamine B (RhB) removal rate ($> 98\%$) for long-term operation, compared with pristine rGO membrane and 2D g-C_3N_4 NS intercalated rGO membrane prepared by the same method. The RhB removal mechanism on the as-prepared composite membranes under integrated photocatalytic filtration process is presented. Our findings offer new insights into designing and tuning laminar structures of photocatalytic graphene-based NF membranes for enhanced water purification.

1. Introduction

Potable water production and wastewater reuse are essential for the sustainability of modern civilization [1]. Currently, mainstream water purification technologies remain high cost and energy intensive, thus efficient and cost-effective alternatives are required for society's ever-increasing water demand [2]. Membrane separation technologies are gaining attention for sustainable water supply since they are energy-efficient, environmentally benign and economical [3]. Nanofiltration (NF) is a pressure-driven membrane process exhibiting high retention rate for small molecules (with molecular weights ranging from 200 to 1000 Da) and relatively low energy consumption, resulting in increasing adoption for industrial wastewater purification [4–7].

However, development of state-of-the-art NF membranes with well-defined nanostructures and excellent selectivity, high permeate flux and antifouling properties, remains challenging. Two-dimensional (2D) graphene-based nanomaterials have drawn broad attention due to their excellent properties including distinct electron and thermal mobility, high mechanical strength, good capacity for microbial disinfection, ease of chemical or physical modification and high specific surface area [8–10]. Graphene and its most important derivative, graphene oxide (GO), exhibit similar properties, but GO holds many oxygen-containing functional groups distributed on the nanosheet (NS). To date, numerous GO-based membranes have been fabricated with laminar separation structures for gas separation, pervaporation, and pressure-driven filtration [11–14]. 2D GO NS has been regarded as a promising building

block for the construction of new generation NF membranes with laminar nanostructures [6,15–17].

Although GO-based NF membranes have been successfully developed in recent years, there remains many technical challenges to be overcome for fabricating even high-performance membranes [18–21]. Pristine GO used for liquid separation generally needs to be chemically modified due to its intrinsic water dispersion characteristic [22]. Cross-linking GO laminates [23,24] and reduced GO (rGO) [25] are the simplest ways to enhance the water stability of GO-based membranes. However, chemical modification often changes the GO laminar structure. The water transport channel of GO laminates are formed by face-to-face (van der Waals' force) and edge-to-edge (electrostatic repulsive force) aligned GO NS and the reduction of GO can eliminate the oxygen-containing groups and narrow the water transport channels leading to a sharp decline in water permeability of the membrane [26]. To create water transport channel in GO-based laminar structure, Wang et al. used attapulgite (APT) nanorods as fillers for constructing NF membranes [27]. For the purpose of preparing robust and high performance NF membranes, most researchers applied both strategies, i.e. reduction of GO and intercalation with nano-spacers into the laminar structure. For examples, Zhang et al. intercalated metal organic framework (MOF), UiO-66-(COOH), into ultrathin rGO to prepare enhanced NF membranes for water purification [28]. Halloysite nanotubes (HNTs) and self-assembled 5, 10, 15, 20-tetrakis (1-methyl-4-pyridinio) porphyrin (TMPyP) molecules were attempted to be intercalated into rGO laminates for the purpose of tuning nanochannels [29,30]. Intercalating nano-spacers into rGO laminar structure has been proved to be an efficient strategy for enlarging water transport channels of rGO-based membranes, but very few intercalations can facilitate the rGO membrane with other desirable properties [31–35].

Recently, graphitic carbon nitride (*g*-C_3N_4) has attracted tremendous interest as a metal-free and visible-light photocatalyst owing to its good light-harvesting capability, high chemical stability, simple preparation and low cost [36,37]. Unlike most metal-containing photocatalysts that need expensive metal precursors for synthesis, *g*-C_3N_4 photocatalyst can be facilely prepared by thermally polycondensing cheap N-rich precursors, such as dicyanamide, cyanamide, melamine, and urea. The only disadvantage for *g*-C_3N_4 is less visible light response and high electron-hole recombination [38]. Coincidentally, *g*-C_3N_4 usually shows relatively low visible-light photocatalytic activity, but the introduction of rGO can efficiently promote an improvement [39]. Many studies have shown that graphene-based materials could conjugate well with nano-photocatalysts to enhance light absorption and charge separation of the heterostructure for improved photo-responsivity [40,41]. Graphene and *g*-C_3N_4 possess similar carbon networks and sp^2 conjugated π structures [42,43], which makes them the most compatible materials to form composites. The combination of *g*-C_3N_4 and rGO would enhance visible light absorption, overcome grain boundary effects of *g*-C_3N_4 and facilitate electron transfer and charge separation across the composite interface.

The concept of photocatalytic *g*-C_3N_4/rGO composite membranes was first proposed in 2014. Zhao et al. [44] attempted to intercalate 2D *g*-C_3N_4 NS into the rGO laminar structure to enhance cellulose acetate microfiltration (MF) membranes. They found that the composite membrane showed enhanced efficiency for the removal of organic contaminants from surface water under visible-light irradiation. In 2017, Li et al. [45] developed a polydopamine (PDA) modified *g*-C_3N_4 NS/rGO membrane which was used for efficiently separating oil-in-water emulsion and removing methylene blue (MB) dyes simultaneously when irradiated by visible light. To the best of our knowledge, these two studies are the only reports on photocatalytic *g*-C_3N_4/rGO composite membranes. They revealed that *g*-C_3N_4/rGO composite membranes have great potential in enhanced water purification, but there is still much scope for the improvement. For example, NF membranes can remove dye contaminants more efficiently, and intercalating different dimensions of *g*-C_3N_4 photocatalyst can optimize the *g*-C_3N_4/

rGO composite structures and consequently improve membrane performance. Among various nanostructured *g*-C_3N_4, it was evident by one of our recent studies that 1D *g*-C_3N_4 nanotube (NT) materials exhibited much better photocatalytic performance compared with its bulk and NS structures [46]. Many researchers believe that morphological control of *g*-C_3N_4 is an effective method to tune the specific surface area, light-induced carrier migration distance and active centers for enhancing its photocatalytic performance [47]. Recent experimental and theoretical studies have also confirmed the superior photocatalytic activity of *g*-C_3N_4 NT under visible light and a series of *g*-C_3N_4 NT-based photocatalysts with enhanced hydrogen generation rate were reported [48–50].

In this work, 1D *g*-C_3N_4 NT and 2D *g*-C_3N_4 NS were prepared as photocatalytic nano-fillers. *g*-C_3N_4 NT/rGO and *g*-C_3N_4 NS/rGO composites were then fabricated by intercalating *g*-C_3N_4 NT and *g*-C_3N_4 NS into a rGO laminar structure, respectively. The structure and corresponding properties of the prepared nanocomposites were well understood by various characterization methods. The influence of different dimensional intercalation on the rGO laminar structure and on the resultant membrane performance regarding water transport and Rhodamine B (RhB) removal were compared. Finally, the self-cleaning mechanism of the as-prepared composite membranes was described.

2. Materials and methods

2.1. Materials

Graphene oxide (GO) water dispersion (4 mg/mL) was purchased from Graphenea Corporation. Melamine (99%), tris(hydroxymethyl) aminomethane (Tris, ACS reagent, ≥99.8%), ethylenediamine (≥99.8%), hydrochloric acid (ACS reagent, 37%), anhydrous ethanol and dopamine hydrochloride (≥99%) were purchased from Sigma Aldrich. Rhodamine B (RhB) was obtained from Alfa Aesar. Commercial cellulose acetate (CA) membranes (diameter: 47 mm; pore size: 450 nm) were purchased from Sterlitech Corporation. All chemicals were used as received. Deionized (DI) water (18.2 MΩ·cm^{-1} at 25 °C) used throughout this study was generated by a Milli-Q system.

2.2. Synthesis of g-C_3N_4 NS and g-C_3N_4 NT

5 g of melamine powder was calcined at 550 °C for 2 h in static air to form bulk *g*-C_3N_4. *g*-C_3N_4 nanosheets (NS) were then exfoliated from the bulk dissolved in ethanol by ultrasonic treatment for 1 h. *g*-C_3N_4 nanotubes (NT) were synthesized by a modified water-induced morphological transformation process [46]. Briefly, the as-synthesized *g*-C_3N_4 NS were then heated at 350 °C for 10 min with a heating rate of 10 °C/min. The hot powder was rapidly transferred into an ice-water bath. *g*-C_3N_4 NT were finally obtained by filtration and drying at 120 °C for 12 h under vacuum.

2.3. Synthesis of g-C_3N_4/rGO composites

The details of synthesis and characterization of GO and rGO are present in the Supporting Information. *g*-C_3N_4 NS/rGO and *g*-C_3N_4 NT/rGO composites were synthesized through a facile physical adsorption process. 30 mg *g*-C_3N_4 NS or *g*-C_3N_4 NT were added into 1 mg/mL rGO solution (100 mL) under vigorous stirring for 24 h, respectively. After that, the mixtures were kept for 2 h and the well-dispersed *g*-C_3N_4/rGO composites were collected before use. The collected composites were dried under vacuum at 60 °C for 12 h.

2.4. Assembly of g-C_3N_4/rGO composite membranes

Disc-type CA membranes were used as substrates. Prior to membrane assembly process, the substrate was pre-treated with poly-dopamine (PDA) to enhance the adhesive force between the substrate