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A multifunctional graphene-based nanofiltration membrane under photo-assistance for enhanced water treatment based on layer-by-layer sieving

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ABSTRACT

Nanofiltration (NF) provides an effective strategy for rejecting large organic molecules. However, attaining high permeability, antifouling ability and good selectivity simultaneously still remains a crucial task for existing NF technologies. Herein, we built a photo-assisted multifunctional NF membrane assembled with g-C_3N_4, TiO_2, carbon nanotubes (CNTs) and graphene oxide (GO), in which CNTs not only expand the interlayer space between neighbored graphene sheets, but also enhance the stability and strength of GO layer. Benefiting from the photo-assistance, our NF membranes show an enhanced water flux (~16 L m^{-2} h^{-1} bar^{-1}), while keep a high dye rejection (~100% for Methyl Orange). The photo-assisted NF membranes also display good rejection ratio for salt ions (i.e., 67% for Na_2SO_4) due to the layer-by-layer sieving. Meanwhile, the NF membrane coupled with photocatalysis exhibits a multifunctional characteristic for the efficient removal of ammonia (50%), antibiotic (80%) and bisphenol A (82%) in water. Besides, the performance of integrated system is also tested by treating the real aquaculture wastewater to evaluate its practical application ability. The lost flux of the fouled membrane is effectively recovered by the photochemically assisted process. Hence, this work mitigates the longstanding challenge of GO-based NF membranes in large-scale application by integrating photocatalysis and nanofiltration technologies.

1. Introduction

Increasingly dwindling water resources have stimulated the development of advanced water treatment technologies that can afford clean and fresh water by the more eco-friendly and energy-saving strategies [1]. Nanofiltration (NF) technology has been widely used in the drinking water and waste water advanced treatments because of its relatively low energy consumption and simple process handling, in which the properties of NF membranes are of vital importance [2]. Graphene oxide (GO) has been reported as attractive materials for developing a novel class of NF membranes with extraordinary separation performance on account of their highly ordered 2D nanochannels between two graphene sheets [3]. Conventional GO-based NF membranes (CGNMs) are relatively effective (rejection $>$ 85%) in nanofiltration process for sieving molecular weights between 200 and 1000 g mol^{-1} due to its pore size around 1 nm, nevertheless it is difficult for CGNMs to reject pollutants with sizes smaller than membrane pores, such as ammonia, antibiotics and endocrine disrupting chemicals which are normally present in the surface water owing to its single separation function [4]. Unfortunately, these pollutants adverse for size exclusion separation seriously threaten the ecological safety and human health even at trace levels because of their persistence, toxicity, and bioaccumulation [5]. Although pressure-driven CGNMs exhibit the potential for the rejection of various charged ions, a trade-off between flux and ions rejection limits their further applications [6]. Meanwhile, the C-GNMs are not effective for the rejection of salt ions (rejection < 50%) [4]. Moreover, CGNMs with low water flux are difficult for achieving large-scale application ($<$ 10 L m^{-2} h^{-1} bar^{-1}) [2,7]. Currently, attaining high flux usually suffers from the high operating pressure in nanofiltration process, which results in a high energy cost. In addition, membrane fouling is also a universal and costly problem for CGNMs that generally causes deterioration in membrane performance, especially decreased permeating flux. Therefore, advances in the design and synthesis of multifunctional NF membranes that not only are able to offer high flux, high retention and good antifouling ability, but also are affordable and convenient for practical application would have tremendous impact in water supply with high quality.

Construction of multifunctional NF membranes depends on the structural tailoring and the introduction of functional layers. Recently, photocatalytic technologies have been extensively used in combination

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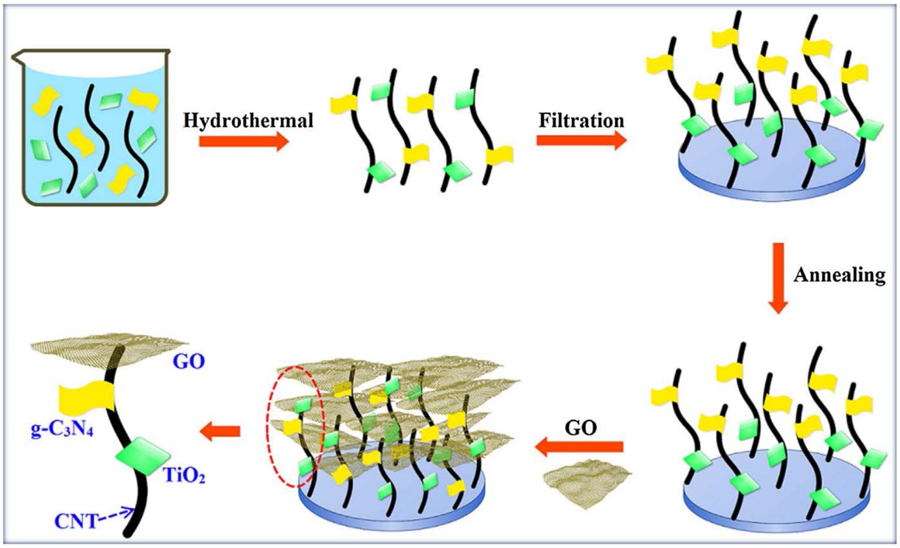

Scheme 1. Schematic illustration of the overall steps used in the preparation of GO/CN/TiO-CNT membranes.

with membrane processes to alleviate membrane fouling and further extend the practical applications of membranes [8–12]. During this integrated process, photocatalytic degradation of organic contaminants that can not be retained by size exclusion separation prevents them from permeating through the membranes. Simultaneously, the inherent membrane fouling is also mitigated due to the efficient decomposition of pollutants by photocatalysis. Based on the mechanism of photo-induced hydrophilicity [13], introducing the photocatalytic technologies into the CGNMs can efficiently enhance the hydrophilia of membrane surface, which is favorable to improving water flux. Generally, Donnan exclusion mechanism is used for explaining the rejection performance of charged CGNMs [14]. The abundant photogenerated charges are generated by the attractive heterostructure of g-C_3N_4 (CN) and TiO_2 (TiO), and these charges on the membranes will increase the rejection of co-ions (ions with the same charge as the membrane) in water according to Donnan theory. If these fascinating photochemical functions can be introduced into CGNMs, the additional photochemical functions will promote the physicochemical functions that are not available by size or charge exclusion alone. This might be an alternative approach to solve the issue of single separation function of CGNMs.

Carbon nanotubes (CNTs) provide a unique 1D nanochannel for water transporting. Intensively theoretical calculations predict that the permeation of water through the CNT is extremely fast [15,16]. And Hinds experimentally proved the water flux through aligned multi-walled CNTs over 4 orders of magnitude larger than conventional hydrodynamic flow prediction [17]. Undoubtedly, aligned CNTs forming a stereochemical structure are fine channels for liquid flowing. Thanks to the low resistivity and mass density, large specific surface area and good chemical stability, CNTs are used as conduits for transporting and storing electrons from photoirradiated photocatalyst [18,19]. In addition, owing to the bridging of CNTs, the interlayer space between neighbored graphene sheets is expanded, which is advantageous to the water flux. Meanwhile, the strong noncovalent π–π interactions between CNTs and GO are also beneficial to enhancing the stability and strength of GO layer.

To effectively make a balance between flux and rejection of NF membranes and overcome the defect of single separation function of CGNMs, we design a multifunctional NF membrane system with both high flux and high rejection by CNTs-bridged the g-C_3N_4/TiO_2 nanosheets and GO layers under photochemical assistance for the first time. Different from the CGNMs, the plentiful photogenerated charges on the membrane forming a reinforced Donnan potential are beneficial to the high ions rejection of membranes. A high water flux is also supposed because of the photoinduced hydrophilicity of g-C_3N_4/TiO_2 relying on the formation of surface defects upon light illumination and Hagen – Poiseuille theory. Meanwhile, the “grafting” of CNTs into the interlayers of GO skin layers and membrane support can increase the interlayer spacing from below one nanometer to several nanometers, which is conducive to the water transporting. Furthermore, the self-assembly of CNTs, thin g-C_3N_4 and TiO_2 nanosheets tends to forming a 3D nanoporous network, contributing to attaining high membrane porosity. The present study provides a new strategy for the design of high-performance multifunctional GO-based NF membranes and also provides a better understanding of the enhanced transport and rejection mechanism of photo-assisted GO-based NF membranes. Besides, the efficient antifouling ability of the GO-base NF membranes is also demonstrated under the photochemical assistance.

2. Experimental

2.1. Assembly of GO/CN/TiO-CNT membrane

100 mg of CN/TiO-CNT photocatalyst (see supporting information) was dispersed in 200 mL pure water (Millipore, 18 MΩ Cm) under assistance of ultrasonification. To obtain the uniform distribution of the nanoporous mat, the dissolved photocatalyst suspensions (50 mL) above were filtrated stepwise (5 mL each time) through the alumina membrane support with the assistance of a vacuum [20]. After filtration, the CN/TiO-CNT membrane was annealed in a flow of argon (40 sccm) at 500 °C for 2 h at a heating rate of 2 °C min^{-1}. Graphene oxide (GO) was synthesized by modified Hummers' method through oxidation of graphite powder [21]. Then GO was decorated on to the CN/TiO-CNT membranes via the filtration method to construct nanoscale channels. Briefly, 20, 40, 60, 100 and 150 mL of GO solution (5 mg L^{-1}) was filtrated stepwise on the CN/TiO-CNT membranes by the vacuum pump, denoted as GO/CN/TiO-CNT_1, GO/CN/TiO-CNT_2, GO/CN/TiO-CNT_3, GO/CN/TiO-CNT_4 and GO/CN/TiO-CNT_5 membranes, respectively. The schematic diagram of the preparation of GO/CN/TiO-CNT membranes is shown in Scheme 1.

2.2. Characterization

The morphological structure of GO/CN/TiO-CNT membrane was analyzed using scanning electron microscopy (SEM; Quanta 200 FEG) and transmission electron microscopy (TEM, FEI-Tecnai G^2 F30). The crystallinity of the sample was determined by X-ray diffractometer (XRD, EMPYREAN, PANalytical) using a diffractometer with Cu Kα radiation. The specific surface area was measured via an Automated