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Organosilane-functionalized graphene oxide for enhanced antifouling and mechanical properties of polyvinylidene fluoride ultrafiltration membranes

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ABSTRACT

Functionalized graphene oxide (f-GO) was synthesized by a simple covalent functionalization with 3-aminopropyltriethoxysilane (APTS). The hybrid polyvinylidene fluoride (PVDF) ultrafiltration membranes were then prepared by adding different ratios of graphene oxide (GO) and f-GO via phase inversion induced by immersion precipitation technique. Zeta potential demonstrated that covalent functionalization of GO with APTS was favorable for their homogeneous dispersion in organic solvents. SEM images showed that very large channel appeared in top-layer by the addition of additives. Furthermore, the PVDF/f-GO membranes exhibited superior hydrophilicity, water flux, BSA flux and rejection rate than nascent PVDF membranes and PVDF/GO membranes. Filtration results indicated that the fouling resistance parameters were significantly declined due to higher hydrophilicity of hybrid membranes. An atomic force microscope (AFM) analysis with a BSA-immobilized tip revealed that the adhesion forces between membrane and foulants increased in the following order: PVDF/f-GO < PVDF/GO < PVDF. After a ternary cycle BSA solution inner fouling process, PVDF/f-GO membranes exhibited higher water flux recovery ratio (*FRR*) value than that of PVDF/GO. Meanwhile, tensile strength and elongation-at-break of PVDF/f-GO membranes were increased by 69.01% and 48.38% compared with those of PVDF/GO membranes, which is believed to be attributed to the strong interfacial interaction between f-GO and matrix by covalent functionalization of GO. As a result, GO functionalization will provide a promising method to fabricate graphene-based hybrid membranes with effective reinforced permeation, antifouling and mechanical performance.

1. Introduction

Polymeric material polyvinylidene fluoride (PVDF) is commonly used in ultrafiltration membrane fields because of its good thermal stability, easily-controlled morphology and high porosity [1,2]. However, the application of PVDF in water treatment is restricted due to its hydrophobicity which leads to severe membrane fouling and decline of permeability [3,4]. Subsequently, considerable effort has been devoted to improving hydrophilicity and fouling resistant properties of PVDF membranes, including addition of additives (e.g. siloxane [5]and hydrophilic carbon materials such as carbon nanotubes [6]), chemical modification of surface and bulk membranes and preparation of amphiphilic polymer blends [7–9]. Recently, graphene derivates have also become ideal candidates for polymer reinforcement on account of their unique architecture and superior performance. Correspondingly, it can be incorporated into ultrafiltration membranes to optimize targeted properties, such as high water permeability, high salt rejection and better antifouling performance, by the solution-blending method [10,11]. In our previous work, we have also simply investigated the influence of low-dimensional carbon materials (including carbon nanotubes and graphene oxide) on permeation and antifouling performances of ultafiltration membranes [12,13]. However, graphene derivates themselves have their shortcomings in numerous applications. One is the homogeneous dispersion which is restricted due to their strong tendency to aggregation [14,15]. Thus, permeation and antifouling performances of graphene-based ultrafiltration membranes may be limited by the aggregation of graphene sheets. Another is that the incorporation of graphene in membranes may cause the decline of the mechanical

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strength of membranes, which is attributed to the bad interfacial interaction between graphene and polymer matrix [16,17]. As a result, the modification of graphene derivates for the improved performance of ultrafiltration membranes needs to be investigated on the basis of our previous work. Additionally, fouling mechanism and interaction behavior of membrane-foulant as well as the functional mechanism of additives in mechanical properties were not studied fully.

As we all know, covalent functionalization on the surface of graphene is one strategy for fabricating graphene-based polymer composites, which is an effective method to improve interfacial interaction between graphene and polymer matrix [16–18]. Graphene oxide (GO) has abundant functional groups on the surface including hydroxyl, epoxide and carboxyl [17], which provide the reactive site for covalent functionalization. Chemical functionality significantly alters Vander Waals interaction among nanofiller aggregates, making them easy to be dispersed in the polymer matrix. Moreover, functionalized GO can tightly intertwine with PVDF matrix due to their long polymer chains which are expected to penetrate into the matrix. As a result, the covalent functionalization not only makes the dispersibility of GO better but also enables the interfacial interaction between graphene and matrix stronger [17,19]. Hence, we can expect that integrating functionalized graphene oxide in membranes will enhance the hybrid ultrafiltration membrane antifouling performance and mechanical strength greatly. Besides, to the best of our knowledge, the antifouling performance ameliorated by GO functionalization has not been reported till now, and for the first time, the effects of long polymer chains on GO surface on the alleviative fouling behavior and enhanced mechanical strength for hybrid ultrafiltration membranes are investigated fully.

Based on our previous work, the present paper addresses the above-mentioned issue by introducing chemically functionalized GO which was modified by 3-aminopropyltriethoxysilane (APTS). Subsequently, the APTS-functionalized GO (f-GO) and GO with different ratios are incorporated into PVDF matrix via phase inversion induced by the immersion precipitation technique. APTS has a wealth of hydrophilic long polymer chains which can penetrate into and entangle with PVDF matrix. As a result, a significant improvement in membrane performance was achieved because of the better dispersion of f-GO in PVDF matrix as well as the strong interfacial interaction between them.

2. Experimental

2.1. Materials

The PVDF (FR904) was purchased from Shanghai 3F New Materials Co. Ltd. China. N,N-dimethylacetamide (DMAc, > 99.5%, reagent) and polyvinyl pyrrolidone (PVP) were purchased from Tianjin Weichen Chemical Reagent Co. Ltd. China. N,N′-dicyclohexyl-carbodiimide (DCC, 99%) and 3-aminopropyltriethoxysilane (APTS, 99%, 0.942 g m L^{-1}) were of analytical grade and obtained from Aldrich. Graphite powder, concentrated sulfuric acid (98%), sodium nitrate, potassium permanganate, 30% H_2O_2 solution and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Distilled water was used as the nonsolvent for polymer precipitation.

2.2. Preparation of graphene oxide and silane-functionalized graphene

Graphite oxide powders were prepared by improved Hummers' method [20]. Then the powders were suspended in pure water (1 mg ml^{-1}) and sonicated for 2.5 h to generate a GO suspension. Subsequently, the aqueous GO suspension was frozen into an ice cube in a refrigerator (258.15 K) for 8 h and then was freeze-dried using a FD-1A-50 lyophilizer (Boyikang Co. Ltd., China) with a condenser temperature of 223.15 K at an inside pressure of less than 20 Pa. After 48 h lyophilization and 48 h vacuum drying (318.15 K) process, low-density, loosely packed GO powders were finally obtained. As is well known, GO contains hydroxyl, carboxyl and carbonyl groups on their basal planes and edges, which could provide active sites to react with APTS, as illustrated in Fig. 1. Briefly, GO (100 mg) and DCC (50 mg, as cat.) were dispersed in APTS (50 ml) and followed by ultrasonication for 1 h, and the black and homogeneous mixture was stirred and heated to 348.15 K for 12 h. Afterwards, the resulting f-GO were centrifuged, washed with pure water and then dried under vacuum.

2.3. Preparation of membranes

All the membranes were prepared by classical phase inversion method using PVDF and PVP as solute material, DMAc as solvent, GO and f-GO as additives, and distilled water at room temperature as nonsolvent coagulation bath. GO or f-GO (0, 0.5, 1 and 2 wt% based on the weight of PVDF) was first imported into DMAc solvent (84 g), and then the solution was sonicated for 30 min (40 kHz) before addition of PVP (1 g) and PVDF (15 g) powders. Casting solution was then mechanically stirred at 323.15 K for at least 24 h. After fully degassing, the casting solution was spread onto clean glass plates with 200 μm gap and then immersed into coagulation bath (distilled water) for 30 min. After peeling off from glass plates, the resultant membranes were rinsed in distilled water before ultrafiltration tests. In order to identify these membranes easily, it was denoted as PVDF, P/GO and P/f-GO respectively.

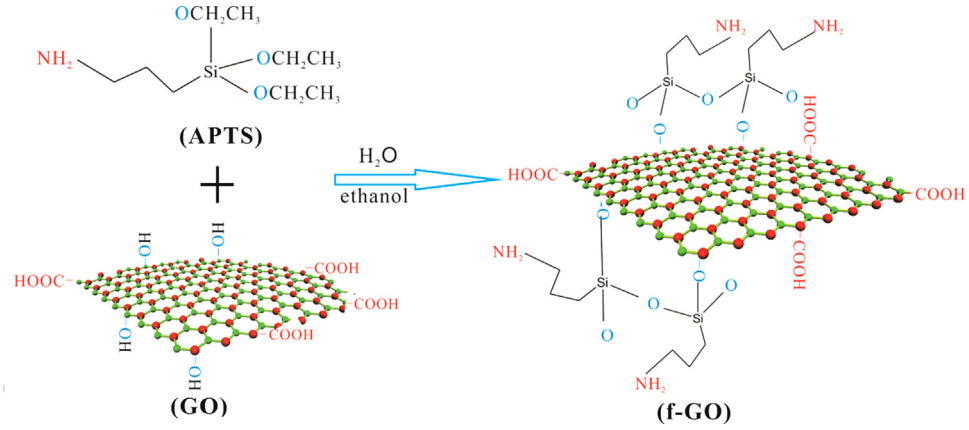

Fig. 1. Illustration of the reaction between GO and APTS.