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Review article

Fabrication of hydrothermally reduced graphene oxide/chitosan composite membranes with a lamellar structure on methanol dehydration

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ABSTRACT

Reduced graphene oxide (rGO) has been prepared through hydrothermal reduction, an environmentally safe reduction of graphene oxide (GO). rGO is used to fabricate a highly compatible and orderly stacked lamellar structure of composite membranes with chitosan (CS). This method also facilitates a continuous large-scale fabrication of membranes. Conventionally, GO and CS are the preferred compounds for this type of fabrication because of their hydrophilic nature. Nevertheless, when they are mixed together, the occurrence of ionic complexation ($-COO^- H_3^+ N-R$) between the negatively charged carboxylate ions of GO and the positively charged protonated amines of CS create extreme membrane aggregation. Hydrothermal reduction is useful for preventing undesired ionic complexation from mixing rGO and CS because it can remove most carboxylate ions from GO. Consequently, the hydrophilic CS molecular chain is inserted in between the rGO laminates, improving the dispersion and enabling the rGO/CS to stack-up and self-assemble into a lamellar structure. Furthermore, excellent methanol dehydration can be observed through pervaporation, which is attributed to the selective water channels formed in the rGO laminates.

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1. Introduction

Combining nanofillers and polymeric materials created a new class of multifunctional materials known as polymer nanocomposites [1], which have been widely used in various fields such as electronics, biomedical technology, architecture, and aerospace technology [2–7]. Advancements in these fields depended largely on whether nanoparticles of various sizes and shapes were synthesized and assembled efficiently in special structural orientations [8]. Scientists examine materials with improved physicochemical properties that are dimensionally suitable in the field of nanoscience and technology. Compared with other commonly studied nanofillers, graphene as a nanofiller is relatively new [9] especially for membrane-based separations. It is a two-dimensional nanofiller with one-atom-thick planar sheet of sp^2-bonded carbon atoms that are packed in a honeycomb-like crystal lattice. Known as the thinnest material [10,11], graphene exhibits remarkable properties such as high thermal conductivity, strong mechanical properties, and excellent electronic transport properties [12–16]. However, graphene does not blend easily with organic polymers; thus, it does not form homogeneous composites [17,18]. Graphene oxide (GO), a graphite derivative, differs considerably from graphene in terms of characteristics, because GO contains oxygen in its functional groups such as hydroxyl, epoxide, diol, ketone, and carboxyl [19–21]. Therefore, GO sheets are strongly hydrophilic, and this property enables them to swell and disperse in water. The H-bonding and $\pi-\pi$ interaction of GO sheets helps to form nanochannels. It leads to the formation of a high-orientation lamellar structure of GO sheets that makes it to have an unimpeded permeation for desalination or separation processes [22–26]. However the GO interlayer spacing increases in wetted state affects the stability [19,20,27,28]. The addition of polymer may resolve the problem but aggregation occurs when the amount of GO is greater than 10 wt% of the polymer [29–34] and this remains as a challenge.

Scientists have drawn inspiration from nature and substantially contributed to the structure of materials [35–39]. A lamellar structure comprises of numerous well-stacked alternating layers of inorganic (e.g., calcium carbonate) and organic compounds (e.g., chitosan and protein). It is similar to a brick-and-mortar structure, which is multilayered and highly ordered. This composite material is strong and has a homogeneous composition. The inorganic layers impart strength, whereas the organic layers contribute to rigidity. Previous studies have fabricated membranes with well-stacked lamellar structures through several methods such as layer-by-layer [40–43], vacuum filtration [33,38], ice-templating [44,45], sintering [46], *in situ* growth [47,48], and sequential coating [49]. The current major challenges encountered in research on fabricating membranes with lamellar nanostructures are as follows: (1) determining the amount of inorganic compounds relative to that of organic compounds, (2) identifying the interaction between organic and inorganic interfaces, (3) achieving homogeneity of lamellar structures, (4) overcoming limitations on a continuous large-scale fabrication of membranes, and (5) the membrane stability [50].

However, mixing GO and CS, which are both hydrophilic, turned out to be challenging because of the severe aggregation in the fabricated polymer nanocomposite materials. The present study adopted an environment-friendly method—hydrothermal reduction—for fabricating a composite membrane (reduced graphene oxide/chitosan, rGO/CS) with a lamellar structure. This membrane nanostructure was achieved by varying the hydrothermal reduction time. Such an approach enabled a continuous fabrication of large-scale membranes, and its effective application could expedite the use of graphene-based polymer nanocomposites in real world applications. This study explored this type of well-stacked structure to understand the association between the membrane microstructure and its performance. Conventional practice involves selecting hydrophilic nanofillers and mixing them with homogeneous and hydrophilic polymers to ensure interfacial compatibility between the nanofiller and the polymer.

2. Experimental

2.1. Fabrication of the membrane support

A solution of 18 wt% polysulfone in N-methyl-2-pyrrolidone was prepared. This solution was cast onto a nonwoven polyester substrate by using a 200-μm casting knife. The cast membrane was precipitated in a bath of water. Then, the formed membrane was washed in a water bath overnight and stored for later use.

2.2. Preparation of composite membranes

GO was synthesized using the modified Hummers method [19–21]. The synthesized GO was ultrasonically dispersed in deionized water to prepare a 1 wt% GO suspension, which was aliquoted and hydrothermally reduced at 90 °C for various periods of time (0, 6, 12, 24, 48, and 72 h). The GO or rGO suspension was added to a 2 wt% CS (Aldrich-746134 $M_v = 40{,}000–60{,}000$) solution to form a 50 wt% GO or rGO (based on chitosan). The mixture was homogenized for 3 h and was then ultrasonicated for another 3 h to ensure that GO or rGO was dispersed well in the mixture. The GO/CS or rGO/CS mixture was cast on a PSf support layer by using a 100-μm casting knife. The resulting composite membranes were then dried at 110 °C in an oven for 40 min.

2.3. Pervaporation tests

The pervaporation performance of the GO/CS or rGO/CS composite membrane was determined in dehydrating a 90 wt% methanol—water mixture at 30 °C. The pervaporation process was performed as described previously [19,20]. The permeate was collected in a trap immersed in liquid nitrogen. The flux was calculated by dividing the permeate weight by the product of the membrane effective area and sampling time. The feed and permeate compositions were determined by gas chromatography (model 8700T, China).

2.4. Characterization of the solution and composite membranes

AFM, UV—Vis spectroscopy, and zeta potential were used to determine the thickness, dispersion properties, and surface charges of the GO and rGO suspensions, respectively. XPS was used to determine the oxidation of GO and rGO. ATR-FTIR was used to determine the surface compositions of the composite membranes. A rheometer was used to measure the viscosity of the prepared solutions. Water contact angle was measured to indicate the composite membrane surface hydrophobicity and hydrophilicity. SEM and TEM were used to describe the morphologies of the composite membranes. XRD was used to obtain the 2θ and calculate the interlayer spacing.

3. Results and discussion

3.1. Characteristics of GO and hydrothermally reduced rGO

The frequently employed method to reduce GO was by chemical [51] or high-temperature reduction [30]. By contrast, hydrothermal reduction is a GO modification process that facilitates control over the reduction levels without causing harmful environmental

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