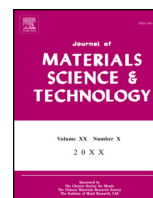




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Reduced graphene oxide/metal oxide nanoparticles composite membranes for highly efficient molecular separation

Khalid Hussain Thebo^{a,b}, Xitang Qian^{a,c}, Qinwei Wei^{a,c}, Qing Zhang^{a,c}, Hui-Ming Cheng^{a,d}, Wencai Ren^{a,*}

^a Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China

^b University of Chinese Academy of Sciences (UCAS), 19 A Yuquan Road, Shijingshan District, Beijing 100049, China

^c School of Materials Science and Engineering, University of Science and Technology of China, 72 Wenhua Road, Shenyang 110016, China

^d Tsinghua-Berkeley Shenzhen Institute (TBSI), Tsinghua University, 1001 Xueyuan Road, Shenzhen 518055, China

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ABSTRACT

Graphene oxide (GO) membranes play an important role in various nanofiltration applications including desalination, water purification, gas separation, and pervaporation. However, it is still very challenging to achieve both high separation efficiency and good water permeance at the same time. Here, we synthesized two kinds of GO-based composite membranes *i.e.* reduced GO (rGO)@MoO₂ and rGO@WO₃ by *in-situ* growth of metal nanoparticles on the surface of GO sheets. They show a high separation efficiency of ~100% for various organic dyes such as rhodamine B, methylene blue and evans blue, along with a water permeance over 125 L m⁻² h⁻¹ bar⁻¹. The high water permeance and rejection efficiency open up the possibility for the real applications of our GO composite membranes in water purification and wastewater treatment. Furthermore, this composite strategy can be readily extended to the fabrication of other ultrathin molecular sieving membranes for a wide range of molecular separation applications.

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1. Introduction

Nanofiltration (NF) membranes with nanometer sized pores play an important role in a wide range of applications such as desalination, water purification, food processing, pharmaceuticals, hemodialysis and petrochemicals [1–5]. The current available commercial membranes have a poor solvent resistance and a thick skin layer with a broad pore size distribution, leading to low permeance and poor rejection rate. Developing high-performance separation membranes, which have proper pore size, shape and number of diffusion channels, is highly desired.

Recently, graphene oxide (GO) has been widely demonstrated to be one of the most promising filter materials for desalination and waste water treatment applications [6–11]. First, GO can be readily dispersed in an aqueous medium to form well-dispersed aqueous solution without the help of any surfactants or stabilizing agents, which makes it very easy to assemble into membranes [12,13]. Second, the carbon atoms bonded to oxygen atoms in the form of epoxy, hydroxyl and carboxyl groups tend to form distorted

regions due to the high proportion of sp³ C–O bonds (40%). As a result, nanoscale wrinkles and structural defects are produced in the basal plane of GO sheets, which provide primary passages for water transport in GO membranes. Although the pure GO membranes show excellent rejection to various molecules [7], however the water permeance is usually very low [7,12,14–18], typically smaller than 70 L m⁻² h⁻¹ bar⁻¹.

In GO sheets, the oxygen functional groups provide many reactive handles for a variety of surface-modification reactions, which can be used to develop a series of functionalized or composite membranes to significantly improve the performance in various applications [19–29]. For instance, by integrating with various functional materials such as carbon nanotubes, metal-organic frameworks, layered double hydroxides zeolite, metal oxide, clay, nanoparticles and polymers, the resultant GO composite membranes have been widely used in energy storage and conversion, catalysis, and biomedical applications [24–29]. Recently, various rGO based composite membranes [30–33] have also been developed as NF membranes. Unfortunately, most of them suffer from either low rejection or low water permeance [30,32,33].

Here, we synthesized two kinds of rGO@metal oxide nanoparticle composite membranes, rGO@MoO₂ (~800 nm) and rGO@WO₃ (~1000 nm) by *in-situ* growth of metal nanoparticles on the sur-

* Corresponding author.

E-mail address: wcren@imr.ac.cn (W. Ren).

face of GO sheets. The membranes show high separation efficiency of ~100% for various organic dyes molecules such as rhodamine B (RB), methylene blue (MLB) and evans blue (EB), together with a water permeance over $125 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. The high water permeance and rejection efficiency enlighten the great potential of our GO composite membranes in water purification, wastewater treatment and other environmental applications.

2. Experimental

2.1. Fabrication rGO@MoO₂ composite membranes

The GO sheets were prepared by using a modified Hummers method [34]. The rGO@MoO₂ composites were synthesized according the previously method [35]. A GO aqueous dispersion (100 mL, 3.0 mg mL^{-1}), phosphomolybdic acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$) solution (100 mL, 15 mM), and DI water (100 mL) were first mixed together with continuous magnetic stirring. Then, hydrazine hydrate (1.25 mL, 80 wt%) was added into reaction mixture to reduce GO sheets. Initially the reaction mixture was sonicated for 3 h and then kept at room temperature for 3 h more. After that, it was filtrated by vacuum filtration, and washed with DI water and ethanol for three times, and dried in vacuum at 80 °C to get rGO@MoO₂ composites. Finally, certain amount of rGO@MoO₂ composites were fully dispersed in DI water with stirring up for 24 h at 70 °C, and then filtrated through the polyether sulfone (PES) membrane in a vacuum filtration assembly to fabricate composite membranes. The thickness of the membranes was controlled by the concentration and volume of composites in the dispersion.

2.2. Fabrication of rGO@WO₃ composite membranes

The rGO@WO₃ composites were synthesized by using a hydrothermal process [36]. First, 1.0 g of Na₂WO₄·2H₂O and 0.2 g NaCl were added into 40 mL GO dispersion (10 mg/mL) and continuously stirred for 4 h. In addition, hydrochloric acid (3.0 M) was added to reaction mixture to maintain the pH value up to 2. After that, the obtained mixture was placed into a Teflon-lined autoclave and kept at 180 °C for 12 h. Note that the GO sheets were reduced during this hydrothermal process. The black precipitate obtained was washed with DI water and ethanol several times to get rGO@WO₃ composites. Finally, certain amount of rGO@WO₃ composites were fully dispersed in DI water with stirring up for 24 h at 70 °C, and then filtrated through the PES membrane in a vacuum filtration assembly to fabricate composite membranes. The thickness of the membranes was controlled by the concentration and volume of composites in the dispersion. For comparison, pure rGO membranes were also prepared following the same procedure by using pure GO dispersion as raw material and hydrazine as reducing agent.

2.3. Membranes characterization

The morphology of rGO composite membranes were characterized by scanning electron microscopy (SEM, Nova NanoSEM 430, 15 kV/10 kV/5 kV). The chemical composition was characterized by X-ray photoelectron spectroscopy (XPS) on an ESCALAB250 microscope (150 W, spot size 500 μm) using Al Kα radiation; all spectra were calibrated to the binding energy of adventitious carbon (284.6 eV). Fourier Transform Infrared Spectroscopy (FTIR) was used to identify the bonding between GO sheets and MoO₂/WO₃ on Bruker Tensor 27. X-ray diffraction (XRD) patterns were acquired with a XRD diffractometer (D-MAX/2400) using Cu Kα radiation (λ = 0.154 nm). Raman spectra of the membranes were taken using a LabRAM HR800 (632.8 nm He-Ne laser, spot size ca. 1 μm², 100 × objective lens). The thicknesses of membranes were

measured by Bruker DektakXT Stylus Profiler (Germany). UV–vis spectra for the dyes were measured on a UV–vis–NIR spectrophotometer (Varian Carry 5000).

2.4. Separation performances of the membranes

The water permeance and dyes separation of the membranes were measured on a home-made dead-end vacuum filtration device with an effective area of 14.51 cm² under pressure difference of 1.0 bar at room temperature. 250 mL feed solution was used in the measurements. First DI water was used to test the pure water permeance of the membrane, and then different organic dyes solutions were used to test the rejection performance at a pressure of 1.0 bar. The permeance J ($\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) and rejection R (%) were calculated according to Eqs. (1) and (2), respectively:

$$J = \frac{V}{A\Delta tP} \quad (1)$$

$$R = 1 - \frac{C_p}{C_f} \times 100\% \quad (2)$$

where V (L) is the volume of permeated water, A (m²) is the effective membrane area, Δt (h) is the permeate time, P (bar) is the pressure difference, and C_p and C_f are the concentration of permeate and feed solution, respectively.

3. Result and discussion

3.1. Characterization of rGO composite membranes

The morphology and structure of rGO composite membranes were first characterized by SEM. It can be seen that some nanoparticles are attached on the surface of the GO sheets for both the rGO@MoO₂ and rGO@WO₃ composite membranes (Fig. 1(a), (b)). Due to the spacing of such nanoparticles, the composite membranes show irregular layered structure (Fig. 1(c), (d)), which is different from the well-aligned and tightly compact pure GO/rGO membranes [12,14]. Raman measurements confirm the formation of rGO@MoO₂ and rGO@WO₃ composites. As shown in Fig. 1(e), GO membranes show two distinctive peaks at about 1360 and 1600 cm⁻¹, which are assigned to the D and G band of GO, respectively. In contrast, the rGO@MoO₂/rGO@WO₃ composite membranes show Raman bands of both GO and MoO₂/WO₃ (Fig. 1(e)). The Raman peaks observed at 990 and 820, 665, 329, and 282 cm⁻¹ correspond to the Mo=O stretching, O–Mo–O stretching, O–Mo–O bending, and O–Mo–O wagging vibration modes of MoO₂, respectively. The Raman peaks at about 706 and 810 cm⁻¹ are attributed to the O–W–O stretching mode of WO₃.

We then used XRD to characterize the structure of the GO, rGO@MoO₂ and rGO@WO₃ membranes (Fig. 1(f)). The GO membrane shows a strong XRD peak at 11.5°, indicating an intersheet distance of 0.76 nm. For the rGO@MoO₂ composite, all the XRD peaks indicated by Miller indices can be indexed to monoclinic MoO₂ (cell parameters, $a = 5.60 \text{ \AA}$, $b = 4.86 \text{ \AA}$, $c = 5.54 \text{ \AA}$, $\beta = 119.37^\circ$), and no XRD peaks for impurities such as phosphates and other MoO₃ are observed, indicating the pure and high crystalline MoO₂. Similarly, the strong and sharp XRD peaks of rGO@WO₃ membranes indicate that they contain pure and high crystalline WO₃. In both rGO@MoO₂ and rGO@WO₃ membranes, it is important to note that the GO-membrane-related XRD peak at 11.5° disappears and no rGO-membrane-related XRD peak around 24° is observed. This indicates that the rGO sheets are well separated by metal oxide nanoparticles, consistent with the SEM observations, which leads to much larger intersheet distance than pristine GO membranes. Such larger distance is beneficial for the water permeance.

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