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Fabrication of a loose nanofiltration candidate from Polyacrylonitrile/Graphene oxide hybrid membrane via thermally induced phase separation

Zhongyong Qiu, Xiaofei Ji, Chunju He*

The State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai, 201620, PR China

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ABSTRACT

It is still a challenge to design and fabricate a robust nanoporous membrane in large scale and of fundamental importance for practical application. Here, a robust three/two-dimensional polyacrylonitrile/graphene oxide (PAN/GO) homogeneous nanoporous membrane is fabricated in large scale via thermally induced phase separation method, which guarantees the membrane with high mechanical strength and selective separation properties. Differing from conventional nanofiltration (NF) membrane with high rejection to both salt and dye, the resulting hybrid membrane is relative loose, which shows outstanding performances, i.e. high dye rejection and low salt rejection, high permeability and antifouling properties, acting as a promising candidate for dye/salt fractionation. The incorporation of 0.2 wt% GO endows membrane with excellent performance, where high tensile strength, high water permeability (33 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$), selectivity (100% to methyl blue, 99.8% to acid red 18, 26.7% to magnesium sulfate and 10.9% to sodium chloride and flux recovery ratio of 84.4%) are perfectly balanced. Its homogeneous structure and high strength guarantee long term use without the peeling of thin active layer as encountered by conventional NF membranes. The successful fabrication of such a hybrid membrane provides an attractive opportunity for loose NF membrane preparation with performance enhancement in a feasible way for practical application.

1. Introduction

Currently, an ongoing dye waste-water pollution crisis resulting from dyeing and finishing process industry has become a major threat to environment and human health [1]. As compared with traditional disposal methods, i.e. adsorption and degradation, which are usually non-destructive, inefficient or expensiveive [2], membrane technologies have played a prominent role as an effective way for water treatment and recycling. Among them, ceramic ultrafiltration and microfiltration membranes have received attention due to the effective sorption properties of different clays as sorbents for the removal of cationic dyes from waste water, which have limited adsorption capacity. When adsorption saturation is achieved, the membrane pores get blocked continuously and the rejection and flux rate decrease quickly [3]. The coupling cathodic electro-Fenton reaction to membrane filtration for dye degradation required electrochemically reactive carbon graphite membrane as cathode [4], while the chemical structure of final degradation product would be not clear. For nanofiltration (NF) membrane, the sieve effect and Donnan exclusion effect should be noticed which block dye molecules with larger kinetic radii, endowing the membranes with high transport channels for water molecules, reliable dye recovery and high capacity [5]. Apart from common NF membranes with high rejection to both dye and salt, a relatively “loose” NF membrane, as designed to own high dye rejection and low salt rejection, is necessary since the addition of salts during dye synthesis and dyeing process impairs the quality of dye products and spoils dye recovery respectively [5,6]. However, conventional methods, i.e. surface coating and interfacial polymerization, offer dense NF membrane with high salt rejection, low strength and performance deterioration due to the poor interfacial binding force between the support layer and the active layer [7,8]. Therefore, it is of great importance to explore a relative “loose” NF membrane with high mechanical strength, eligible stability and suitable selective performance.

Recent development in polymer-inorganic hybrid membranes has led to progress in NF membrane [9,10], which provides an effective way to prepare nanoporous membranes with 2D or 3D pores where both the pore size and the area of the membrane could be controlled. A polymer membrane with 3D pores can be obtained by phase separation process in a convient way, which offers practical applications. 2D-configured graphene oxide (GO) nanosheets with large negatively-

* Corresponding author.
E-mail address: chunjuhe@dhu.edu.cn (C. He).

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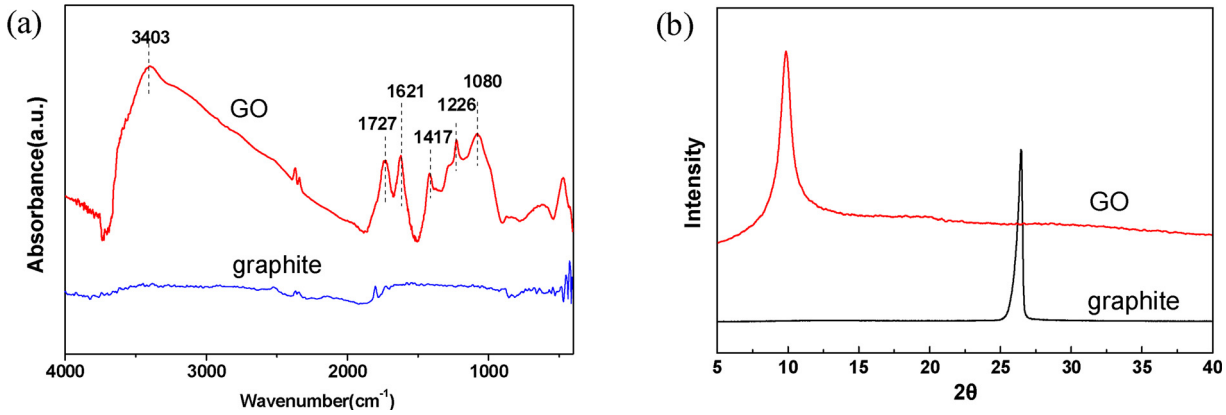

Fig. 1. Characterizations of GO: (a) FTIR spectrum of synthesized GO. (b) XRD patterns for graphite and GO.

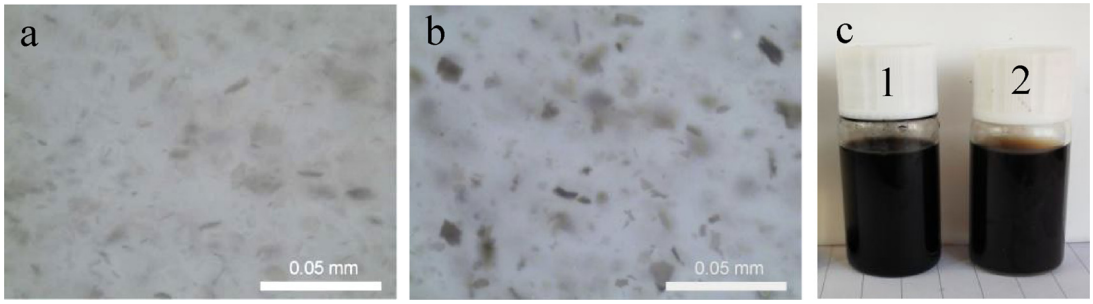

Fig. 2. Optical micrographs of the GO/PEG-400 system.
(a) by direct mixing; (b) by solvent-exchange method. (c) digital picture of GO dispersion after a month storage: (1) GO/PEG-400 dispersion, and (2) GO/water dispersion.

charged specific surface area and high packing density of the lamellar nanochannels construct water channels with high selectivity against solutes [11–14]. Polymer/GO hybrid membranes have been prepared by phase immersion precipitation process, vacuum filtration-assisted assembly, dip-coating and layer-by-layer self-assembly methods, which possess enhanced permeability, selectivity, antifouling and mechanical properties for NF [15–18]. However, state-of-the-art methods restrict its practical application due to large size inhomogeneity, weak bonding force between the active layer and the support, and weak mechanical properties of membrane.

As compared with these approach, the thermally induced phase separation (TIPS) way offers membrane with uniform pore size, low tendency to defect formation and excellent mechanical properties, which is essential for long service life. In a typical TIPS process, a polymer is dissolved in a diluent that serves as a solvent for polymer only at high temperature. Then, the homogeneous polymer–diluent system will separate into two phases upon cooling. After solidification of the polymer phase and extraction of the diluent phase, pores are formed [19,20].Although phase immersion precipitation process is another well-known fabrication method for porous membrane, quick inter-diffusion rate between solvent and non-solvent during phase immersion precipitation process often offers fragile asymmetric structures with a restricted pore size range and reduced mechanical strength [21]. Some polymers including polyethylene, polypropylene, poly(vinylidene fluoride) and polyacrylonitrile have been reported for membrane formation through thermally induced phase separation process [22–25]. However, the pore size of these membranes is large, i.e. in the range of tens to hundreds of nanometers. Therefore, designing a robust nanoporous membrane by the thermally induced phase separation would be a promising way.

Here, a robust 2D/3D-GO/polymer homogeneous nanoporous membrane is constructed via thermally induced phase separation in large scale, endowing the resulting membrane with high mechanical strength, high rejection to dye, low rejection to magnesium sulfate and sodium chloride in contrast to conventional NF membranes. Its homogeneous structure guarantee long term use without the peeling of thin active layer as encountered by conventional NF membranes. The well-dispersed GO improves the hydrophilicity, permeation, rejection, strength and antifouling performance of the hybrid membrane. So a large-scale homogeneous membrane with symmetric 2D/3D structure is obtained, which provides an efficient way to prepare NF membranes as the cutting edge of creating the next generation of NF membranes due to its promise of overcoming the trade-off relationship between structure stability and separation performance.

2. Experimental

2.1. Materials

Graphite powder (3500 mesh) was purchased from Nanjing XF Nano Material Tech Co, Ltd. Potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2, 30% in aqueous solution), hydrochloric acid (HCl, 35%), sulphuric acid (H_2SO_4, 98%), phosphoric acid (H_3PO_4, 85%), polyethylene glycol-400 (PEG-400), glycerol, ethanol, methyl blue, acid red 18 and inorganic salts were purchased from Sinopharm Chemical Reagent Co, Ltd. PAN powder ($M_n = 1.5 \times 10^4$ g/mol) was synthesized in our laboratory.

2.2. Preparation of graphene oxide (GO)

GO was prepared from graphite powder by modified Hummers' method [26]. Briefly, graphite (3 g) was mixed with H_2SO_4 (135 ml) and H_3PO_4 (15 ml) in an ice bath at 0°C, $KMnO_4$ (21 g) was dropped slowly over a period of an hour and stirred for additional 2 h under the temperature below 4°C. The system was heated to 50°C for 20 h, deionized water (500 ml) with 30% aq. H_2O_2 (20 ml) were then added