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Full Length Article

Achieving enhanced hydrophobicity of graphene membranes by covalent modification with polydimethylsiloxane

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ABSTRACT

In this study, the graphene oxide was covalently modified by amino terminated polydimethylsiloxane (PDMS) through amidation reaction. And the membranes of the graphene oxide (GO), reduced graphene oxide (RGO) and PDMS-covalently modified graphene were prepared respectively by a vacuum filtration method, and the wettability of these membranes were investigated. Infrared spectroscopy, Raman, X-ray diffraction, X-ray photoelectron spectroscopy, and thermogravimetry analysis combined with dispersion ability indicated that PDMS chains were successfully grafted on the surface of graphene oxide sheets. The morphology of the prepared membranes had smooth surface and well-stacked structure in the cross-section indicated by the scanning electron microscope and EDS-mapping. The contact angle measurements indicated that the PDMS-modified graphene membrane with water contact angle 129.5° showed increased hydrophobicity compared with GO and RGO membranes.

1. Introduction

Graphene, a novel two-dimension (2D) nanomaterial made up of carbon atoms which assemble into the structure of honeycomb lattice of single-atom-thick, has received considerable attention in material science [1–4]. However, pristine graphene tends to restacking and disperses poorly in the solvents, which constrains its processability and applications. Graphene oxide (GO) sheets as derivatives of graphene are heavily oxidized and show improved dispersibility due to the oxygen-containing groups located on the basal plane and at the edge of GO sheets [5–7]. Consequently, GO sheets provide many reaction sites for versatile further chemical modification with the presence of oxygen-containing groups [8,9]. The multifunctional property enhancements of the functionalized GO made it possible to generate nanocomposites which may create many new applications of graphene-based materials.

Moreover, the graphene and graphene oxide-based membranes have been demonstrated to have great applications in many fields [10–15]. The macro-devices assembled by graphene sheets performed well in the field of wearable electronics, supercapacitor and membrane science [10,16]. The GO-based papers or membranes have demonstrated to be effective barriers for gas and liquid separation and several breakthroughs have been achieved [15,17,18]. For instance, Geim et al. found that a GO membrane allowed unimpeded percolation of water while the diffusion of other molecules was blocked by reversible narrowing of the capillaries in low humidity [15]. However, when the GO paper or membrane were used continuous in aqueous condition, it undergoes a disassemble process owing to the interaction between GO laminate and water molecule. Thus, planar polymeric or ceramic hollow fibers were used as substrate [19–21]. In other cases, membranes based on GO/polymer hybrid materials which fabricating through covalent or noncovalent interaction between GO and polymer matrix not only showed improved mechanical properties but also exhibited higher permeability, selectivity and excellent antifouling property [18,22,23]. In addition, the hydrophilic characteristic of GO membrane limited its application where organic solvents were preferred. Reduced GO membrane prepared by thermal deoxygenated or chemical reduction is suitable for the demand of hydrophobic interface [24,25]. Polymer modification of GO is another method to endure GO to be hydrophobic surface [26]. For example, Liu group reported that polyhedral oligomeric silsesquioxane (POSS) was covalently attached to the GO sheets and the resulting films exhibited increased water contact angle and performed well in the separation of oil/water [27,28]. Polydimethylsiloxane (PDMS) is commonly used as hydrophobic materials and many end-

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functionalized PDMS products are commercially available which makes them attractive for macromolecule grafting researches [29–32]. Therefore, the modification of GO with PDMS might be another way to control the wettability of GO-based membranes.

In this study, PDMS covalently modified GO sheets (GO-*g*-PDMS) was synthesized through the amidation reaction between amino-terminated PDMS and acyl chloride GO, and the product was extensively characterized. Through vacuum filtration method, the GO, RGO and GO-*g*-PDMS membranes were prepared. The morphologies of the surfaces and cross-sections of all membranes were characterized. In addition, hydrophobicity and hydrophilicity of all membranes were investigated.

2. Experimental

2.1. Materials

Graphite powder (98%, J&K Scientific Co.), anino-terminated Polydimethylsiloxane (NH_2-PDMS-NH_2) (J&K Scientific Co.), hydrogen peroxide (A.R., Bodi Chemical Co., China), hydrazine solution (A.R., 80%, Bodi Chemical Co.) and ammonia solution (A.R., 25–28%, Chongqing Chemical Co.) were used as received. Thionyl chloride ($SOCl_2$, A.R., Bodi Chemical Co.), N,N-dimethylformamide (DMF, A.R., Kelong Chemical Co., China), and propylamine (A.R., Bodi Chemical Co.) were used after distilled.

2.2. Synthesis processes

2.2.1. Preparation of GO

GO sheets were prepared by Hummers method according to a previous work described in detail elsewhere [33]. Briefly, graphite (3 g), $NaNO_3$ (1.5 g) were added to H_2SO_4 (69 ml, conc. 98%) in a 500 ml three-neck flask with stirring in an ice bath. Then $KMnO_4$ (9 g) was slowly added to the mixture and the temperature was controlled to be lower than 10 °C for 1 h. Then flask with solution was transferred to an oil bath at 35 °C and stirred for 3 h. Then the deionized water (140 ml) was slowly added to the solution, and the temperature of oil bath increased to 98 °C and maintained at this temperature for 30 min. The reaction was terminated by addition of a large amount of solution of deionized water with 10 wt% HCl followed by treatment of 30 wt% H_2O_2 solution. Then the mixture changed into brilliant yellow color. The mixture was then dialyzed for a week. Then, the yellow brownish suspension was centrifuged at 8000 rpm after sonication for 2 h to eliminate un-exfoliated graphitic plates. Finally, centrifugally sedimentated GO powder was dried under vacuum.

2.2.2. Preparation of GO-COCl

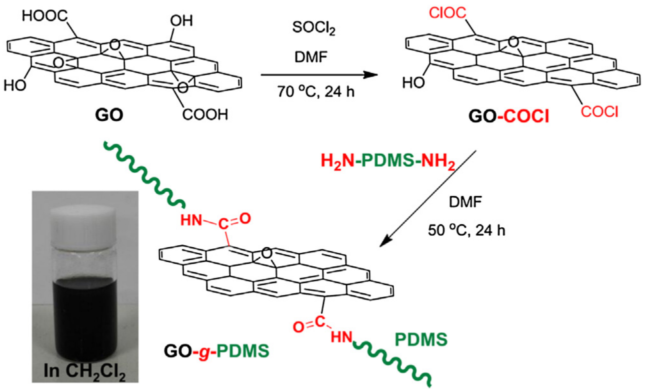
The prepared GO (10 mg) was dispersed in anhydrous DMF (5 ml) with the aid of ultrasonication for 3 h. Afterwards, 20 ml of $SOCl_2$ was slowly added and the mixture was refluxed at 70 °C for 24 h. The chlorinated GO (GO-COCl) was obtained by centrifugation and was purified with anhydrous DMF for five times.

2.2.3. Preparation of GO-g-PDMS

The GO-COCl (10 mg) dispersed in anhydrous DMF (40 ml) was added to the PDMS solution in anhydrous THF/DMF (30 ml). Then the mixture was cooled to 0 °C and anhydrous triethylamine (2 ml) was added dropwise to the reaction mixture. Afterwards, the reaction mixture was maintained at 50 °C for 24 h. Finally, the GO-*g*-PDMS was obtained by filtration and washed with THF for 5 times, and re-dispersed in dichloromethane (CH_2Cl_2) for further use.

2.2.4. Preparation of reduced GO dispersion (RGO)

RGO dispersion was prepared according to Li's report [25]. In a typical process, GO dispersion (30 mg) was mixed with hydrazine solution (21 mg) and ammonia solution (0.1 ml) in a 50 ml glass vial. Then vial was put in a water bath (95 °C) for 1 h under stirring.



Scheme 1. Schematic illustration of the synthesis of GO-*g*-PDMS with the macrograph of the GO-*g*-PDMS well dispersed in dichloromethane.

2.2.5. Preparation of GO, RGO and GO-g-PDMS membranes

All the membranes were prepared by vacuum filtration method using glass fluid filter with a 0.45 μm microporous filter membrane. In addition, another GO membrane was fabricated by solvent evaporation with GO dispersion in glass culture dish in an air-circulating drying oven.

2.3. Characterization

Gel permeation chromatography (GPC) experiments were conducted on a Waters 2410 instrument equipped with a Waters 2410 RI detector, with pure THF as eluent (1.0 ml/min). The calibration curve was obtained with linear polystyrenes as standards. Deriving from the GPC curve of PDMS, the M_n of PDMS was 5800 g/mol and PDI is 1.35. Fourier transform infrared (FTIR) spectra was conducted on Nicolet 6700 spectrophotometer (Thermal Scientic, USA) in attenuated total reflection mode at resolution of 0.5 cm^{-1}. Thermal gravimetric analysis (TGA) was performed on a Netzsch TG 209 F1 instrument under a nitrogen atmosphere at the heating rate of 10 °C/min from 30 to 800 °C. X-ray photoelectron spectroscopy (XPS) was carried on an XSAM800 (Kratos Company, UK) with Al $K\alpha$ as radiation ($h\nu$ = 1486.6 eV). WAXD with X' pert Pro MPD (Philips Company, Netherlands) was conducted to determine the crystalline property of GO and GO-*g*-PDMS. Raman measurement was performed on InVia (Renishaw Company, Britain) at 532 nm. Scanning Electron Microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) measurements were employed to observe the surface, cross-section morphology and element mapping of GO, RGO and GO-g-PDMS membranes with Inspect F (FEI Company, USA) at 20 kV. The water contact angle measurements of GO, RGO and GO-*g*-PDMS were carried on a contact angle tester (DSA 30, Kruss Company, Germany) by dropping deionized water on the surface of the membranes. Atomic force microscopy (AFM, Anasys Company, USA) samples were prepared by casting a drop of solution under spin coating, and conducted using tapping mode to investigate the morphology and height.

3. Results and discussion

3.1. Synthesis and characterization of GO-g-PDMS

As shown in Scheme 1, the modification of GO with PDMS was processed through the "grafting to" method with the reaction between amino-terminated polydimethylsiloxane (NH_2-PDMS-NH_2) and acyl chlorinated GO which was similar to our previous