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Superhydrophobic mGO/PDMS hybrid coating on polyester fabric for oil/water separation

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ABSTRACT

With the environment pollution deteriorating by industrial waste water and oil leak, superhydrophobic materials for oil/water separation have attracted more attentions and become a worldwide research hotspot. Herein, we propose a facile dipping-UV curing approach to fabricating superhydrophobic hybrid coating on polyester fabric for oil/water separation by utilizing (3-mercaptopropyl) trimethoxysilane modified graphene oxide (mGO) and vinyl-terminated polydimethylsiloxane (V-PDMS). With mass ratio of mGO to V-PDMS increasing, the roughness of the fabricated mGO/PDMS hybrid coating on polyester fabric correspondingly increased and the water contact angle (WCA) reached up to 157°, demonstrating excellent water repellency. Importantly, due to the formation of crosslinked PDMS network with mGO as crosslinking points, the fabric exhibited good thermal stability and chemical resistance. Furthermore, the superhydrophobic fabric also possessed high oil/water separation efficiency at 99.8%, and still kept at 98.4% even after 15 separation cycles. Our findings stand out as a new tool to fabricate superhydrophobic materials and coatings with graphene and its derivatives for oil/water separation, showing great potential in practical applications such as oil spill accidents and industrial sewage emissions.

1. Introduction

Inspired by lotus leaves [1], rose petals [2], water strides [3], and other various plants and insects [4–7] in nature, superhydrophobic materials with water contact angle (WCA) above 150° and sliding angle (SA) below 10° [8–10] have aroused much attention for their potential applications in self-cleaning [11,12], anti-icing [13,14], anti-fouling [15], drag reduction [16] and oil/water separation [17,18]. In the past two decades, with industrial waste water discharge and oil spill accidents increasing [19,20], the environment and ecology have been suffering from serious contamination. Therefore, to fabricate superhydrophobic materials for efficient oil/water separation is an important research direction worldwide.

Generally, hierarchical micro/nanostructures and low-surface-energy substance are considered to be the two key factors for constructing superhydrophobic materials [21–23]. Based on this principle, several representative methods have been developed to prepare superhydrophobic materials, including lithography [5,24], self-assembly [25,26], electrospinning [27,28], chemical vapor deposition (CVD) [29,30], sol-gel process [31,32], etching [33–35] and templating [36]. However, the harsh operating conditions, special equipment and time-consuming process limit their large-scale production and application.

Graphene and its derivatives have been favorably used in versatile composite materials to improve thermal, mechanical, chemical and electrical performances [37–39]. In recent years, due to the intriguing hydrophobicity, graphene has been consecutively proposed to fabricate superhydrophobic materials [40–42]. Javad et al. [43] fabricated a thermally exfoliated graphene film with controllable superhydrophobicity-superhydrophilicity by adjusting the relative proportion of acetone and water. After solvothermal reduction of the mixed dispersion of graphene oxide and PVDF, Li et al. [44] prepared a superhydrophobic and superoleophilic graphene/polymer aerogels with high absorption capacity for oils and organic solvents. By taking advantages of the low polarizability of perfluorinated carbons and the intrinsic conductive nature of graphene nanoribbons, Wang et al. [45] also prepared a perfluorododecylated graphene nanoribbon film with excellent anti-icing and deicing properties. In Li's study [46], graphene oxide was firstly treated with spark plasma sintering (SPS) and then reduced at 1050 °C for 1 min, the obtained SPS-reduced graphene oxide demonstrated a WCA of 153° and possessed an impressive bacterial antifouling and inactivation effect against Escherichia coli. From the above literatures, it is obvious that the incorporation of toxic fluorine-containing chemicals and high-temperature treatment with expensive equipment are usually necessary for the fabrication of graphene-based

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superhydrophobic materials and surfaces. Recently, our group [47] prepared a thiolated graphene-based superhydrophobic polyurethane sponge with high absorption selectivity and oil/water separation efficiency, and the thiolation process of graphene oxide to thiolated graphene was simple and low-cost. However, the adhesion between thiolated graphene and sponge skeleton still needs to be further strengthened in practical oil/water separation.

Herein, we propose a facile approach to fabricating superhydrophobic hybrid coating on polyester fabric for oil/water separation with graphene material. Firstly, graphene oxide (GO) was modified with (3-mercaptopropyl) trimethoxysilane (MPTMS) to achieve hydrophobic mGO with thiol groups. Secondly, the pristine polyester fabric was immersed into the acetone solution containing mGO, vinyl-terminated polydimethylsiloxane (V-PDMS), trimethylolpropane triacrylate (TMPTA) and photoinitiator Darocur 1173, and then exposed under UV light to form crosslinked mGO/PDMS hybrid coating on fabric. The as-fabricated coating on polyester fabric exhibited rough morphology and superhydrophobicity. Importantly, the superhydrophobic fabric possessed high oil/water separation efficiency at 99.8% and good reusability. Our method is simple, efficient and cost-effective, and has great potential in the treatment of oil spill accidents and industrial sewage emissions.

2. Experiment section

2.1. Materials

Graphite powder (325 mesh), sodium nitrate ($NaNO_3$), (3-mercaptopropyl) trimethoxysilane (MPTMS), trimethylolpropane triacrylate (TMPTA, 85%), 2-hydroxy-2-methylproplophenone (Darocur 1173), sodium chloride, hexane, ethanol and oil red O were all provided by Aladdin reagent Co., Ltd., China. Hydrogen peroxide (H_2O_2, 30%) was bought from Chinasu Specialty Products Co., Ltd., China. Potassium permanganate ($KMnO_4$), sulfuric acid (H_2SO_4, 98%), hydrochloric acid (HCl, 37%), sodium hydroxide, acetone, toluene, petroleum ether, dichloromethane and trichloromethane were all supplied by Guangzhou Chemical Reagent Factory, China. Vinyl-terminated polydimethylsiloxane (V-PDMS, average M_W = 6000) was purchased from Meryer (Shanghai) Chemical Technology Co., Ltd. Methylene blue was obtained from Tianjin Tianxin fine chemical development center (China). Polyester fabric (plain weave fabric, 120 g/m^2) was bought from local market. All chemicals were used as received without further purification, and deionized water was used for all the experiments and tests.

2.2. Preparation of MPTMS modified graphene oxide (mGO)

GO was synthesized from graphite powder according to the modified Hummers' method [47,48] (see Supporting Information). To achieve the modification of GO, 5 mL of MPTMS and 100 mL of deionized water were firstly added to a 500-mL three-neck flask equipped with a mechanical stirrer and a condenser pipe, and then the pH value was adjusted to 4–5 by adding HCl solution (1 mol/L). After that, 60 mL of GO aqueous solution (3.5 mg/mL) was added under stirring. Subsequently, the mixture was heated to 90 °C and kept for 6 h. Finally, the cooled mixture was filtrated, washed with plenty of deionized water and ethanol separately for three times, then dried at 50 °C for 12 h, and the black mGO was obtained for the next use.

2.3. Fabrication of superhydrophobic mGO/PDMS hybrid coating on polyester fabric

The schematic illustration for fabricating superhydrophobic mGO/PDMS hybrid coating on fabric is presented in Fig. 1. Typically, the pristine polyester fabric with suitable size (25 mm × 25 mm) was separately cleaned with ethanol and deionized water under sonication, and dried at 80 °C for 1 h. Next, a predetermined amount of mGO (e.g. the mass ratios of mGO to V-PDMS was varied at 0, 0.1, 0.25 and 0.5, respectively) was added into 10 g of acetone solution containing 0.3 g of V-PDMS, 0.03 g of TMPTA and 0.01 g of Darocur 1173, and sonicated for 30 min to form a homogeneous solution. Subsequently, the dried fabric was dipped into the acetone solution and sonicated for 30 min in the ice water bath to keep the temperature constant, then taken out and exposed under UV light (INTELLI-RAY 400, Uvitron International, Inc., U.S.A.) for 2 min with a distance of 15 cm between the sample and the center of UV light lamp. Thus, the superhydrophobic mGO/PDMS hybrid coating on fabric was obtained.

2.4. Stability evaluation of superhydrophobic mGO/PDMS hybrid coating on polyester fabric

The thermal stability of the superhydrophobic mGO/PDMS hybrid coating on fabric was evaluated by measuring the water contact angle (WCA) after being heated in the range of 30–150 °C with an increasing interval of 30 °C for every 6 h. To comprehensively evaluate the chemical stability, the superhydrophobic fabrics were separately immersed into various solutions including water, toluene, hexane, NaCl solution (1 mol/L), HCl solution (pH = 1) and NaOH solution (pH = 13) for different time, and then rinsed with ethanol and dried at 80 °C for WCA test. In addition, the mechanical stability was also studied via the abrasion test. The 800 mesh sandpaper was acted as the abrasion material, and the superhydrophobic fabric sample was pressed by a weight of 200 g in one direction, and the dragging distance was 15 cm for one cycle.

2.5. Oil/water separation

Oil/water separation test was carried out with a simple homemade filter device composed of two glass tubes and two metal clips. The fabricated superhydrophobic fabric acting as filter membrane was sandwiched between the two glass tubes, and then firmly fixed using metal clips. When oil/water mixture was poured into the upper tube, water was impeded in the tube owing to the water repellency of the fabric, while oil automatically penetrated through the fabric and was collected in the container under the glass tube. Several different kinds of light oil and heavy oil including hexane, toluene, trichloromethane, dichloromethane and petroleum ether were selected for separation test. The oil/water separation efficiency was calculated according to the following Eq. (1):

$$Separationefficiency = \frac{m_1}{m_0} \times 100\% \quad (1)$$

where m_0 and m_1 represented the mass of initial oil and collected oil, respectively.

2.6. Characterizations

The surface morphologies of the mGO and superhydrophoic fabric were observed on an EVO18 scanning electron microscope (SEM, Carl Zeiss Jena, Germany) at an acceleration voltage of 10.0 kV under high vacuum condition. Fourier transform infrared (FT-IR) spectroscopy was carried out on a Bruker Tensor 27 spectrometer (Bruker Optics, Germany) in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} and scanning times of 32, and samples were prepared by the potassium bromide (KBr) tableting method. Chemical compositions of GO and mGO were performed on a X-ray photoelectron spectroscope (XPS, Kratos Axis Ulra DLD, UK) equipped with Al Kα monochromatic X-ray source and three electron take-off angles (30°, 60° and 90°). The surface microstructure and roughness of the pristine and fabricated fabrics were analyzed with atomic force microscopy (AFM, Bruker Multimode 8, USA) in tapping mode with a scanning rate of 0.977 Hz in 3 μm × 3 μm scale. The grafting ratio of MPTMS on GO was