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One-pot synthesis of robust superhydrophobic, functionalized graphene/polyurethane sponge for effective continuous oil–water separation

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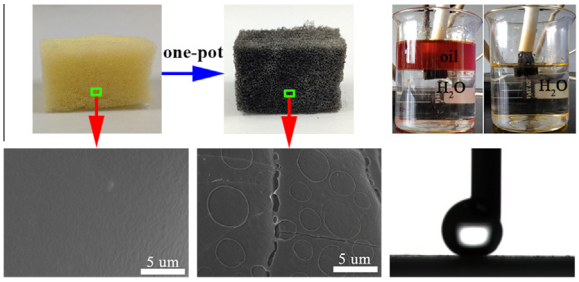
HIGHLIGHTS

- A one-pot processing technique was used to produce the modified sponge.
- The modified sponge possessed a superhydrophobicity.
- The modified sponge could act as a selective filter to continuously separate the oil.
- The modified sponge had a high oil–water separation efficiency.

GRAPHICAL ABSTRACT



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ABSTRACT

Graphene/polyurethane (PU) sponges with superhydrophobicity have been one-pot synthesized by solvothermal technique. The surfaces of interconnected pores within the PU sponges were modified with (3-Mercaptopropyl)trimethoxysilane and graphite oxide via a solvothermal treatment, allowing crater-like functionalized graphene layers to be formed as a substructure and attached firmly to the polyurethane skeleton. By forming such characteristic nano–micro substructures on the backbones of PU sponges, the graphene/PU sponges possessed a superhydrophobicity with WCA exceeding 160°. When applied in conjunction with a simple vacuum system, this sponge could act as a selective filter to continuously and effectively separate the oil from water. Because the functionalized PU sponge retained original PU structural integrity, the material was chemically robust and capable of separating oil up to 53,000 times of its own mass with high oil–water separation efficiency (>99.5%). The functionalized PU sponge and integrated oil–water separation system proposed in this study may provide a novel and practical methodology for industrious scale oil–water separation.

1. Introduction

Oil spillages from industrial accidents and leaking of oil tankers have caused serious ecological problems, and greatly affected the quality of human life. In many oil fields where the oil is depleted over the years of exploitations, water is injected into underground to displace oil from the reservoir, causing substantial water contamination in the extracted oil. Therefore there is an increasing demand for new materials that can effectively separate and collect oils from water. Until now, superhydrophobic meshes [1], polymer films [2], and other porous materials [3] have been used as filters that allow oil to penetrate through them, while keeping the water out of the materials. Because these previously reported efficient materials need to be regenerated before the next cycle of operation, so it is impossible for them be applied to separate oil from water continuously.

Commercial polyurethane (PU) sponges have attracted considerable interests in fields of absorption and removal of oils and

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organic solvents from water surfaces due to low density, high porosity, high absorption ability and low cost. However, PU sponges are naturally hydrophilic, which makes them inefficient to be used directly for selective removal of oils from water. Therefore, modifications are required to increase the surface roughness and decrease the surface tension in order to enhance the hydrophobicity of the PU sponges for more efficient oil–water separation. In a recently published work, TiO_2 nanoparticles was used to modify the chemical composition and to increase the roughness of the PU surface, thereby increasing the hydrophobicity of the modified PU sponge significantly [4]. A PU sponge incorporated with Fe_3O_4 nanoparticles, SiO_2 and fluoropolymer (FP) exhibited not only fast magnetic response but also a much improved hydrophobicity/oleophilicity [5]. More recently, superhydrophobic graphene-based materials with high oil absorption capacity and good reusability have also been reported [6,7]. Yu and coworkers applied two types of coupling agents to covalently bond the reduced graphene oxide onto the surface of polyurethane (PU) sponge [8]. In a multi-step synthesis, Li used graphene (GN) chemically modified with γ-methacryloxypropyl trimethoxy silane (KH-570), to form a composite with PU, and prepared sponge displayed superhydrophobicity and superoleophilicity [9]. However, in all these studies, reducing agents were required and multi-step reactions must be adopted in order to achieve a superhydrophobicity, limiting the large-scale manufacture of these materials [8–10].

Here a one-pot processing technique was used to produce (3-Mercaptopropyl)trimethoxysilane (MPS) functionalized graphene/PU sponge (FGN/PU sponge) with excellent superhydrophobicity. In order to simplify the following description, we defined MPS functionalized graphene/polyurethane sponge as FGN/PU sponge, and also defined MPS functionalized polyurethane sponge as FPU sponge. The functionalized networks of the interconnected PU skeleton synergistically enabled a characteristic nano–micro substructure to be constructed and a silylated surface chemical composition to be formed, both contributing substantially towards the much enhanced hydrophobicity. The facile synthetic process ensured the integrity of FGN/PU sponge structure, effectively strengthening the stability of the material against corrosion and erosion during continued affinitive oil absorption and filtration. The constructed sponge endowed with excellent selectivity and good oil absorption capacities, which can be widely used in absorbing various types of oil and organic solvents. Owing to its prominent superhydrophobicity, high porosity and high oil–water separation selectivity, it was possible to use this FGN/PU sponge in conjunction with an integrated vacuum system for continuous absorption and removal of oil pollutants from water with high efficiency. The functionalized sponge, together with the oil–water separation system displayed in this study may imply a novel methodology for large-scale oil–water separation.

2. Experimental section

2.1. Chemicals and materials

All chemical reagents were of analytical grade level, and there was no further purification. The deionized water was used to prepare all mixed solutions. The PU sponge used as a basic material for modification was obtained from by Alibaba Enterprise. MPS were purchased from Aladdin Chemistry Co. Ltd. Graphite oxide was offered by Sinopharm Chemical Reagent Co. Ltd, Shanghai, China. Hydrochloric acid (HCl) was obtained from Shanghai Linfeng Chemical Reagent Co. Ltd, China.

2.2. Material synthesis

FGN/PU sponges were successfully synthesized via a one-pot process using a dip-coating and solvothermal route, without the need of using reducing agents and multi-step reactions. In a typical synthesis process, 2 mL of (3-Mercaptopropyl)trimethoxysilane (MPS) was mixed with 40 ml of water, then 36% hydrochloric acid solution was gradually added into the mixture until a pH between 4 and 5 was reached. Then, 40 mL of graphite oxide (GO) dispersion (3 mg mL^{-1}) was thoroughly mixed by ultrasonic method with the as-obtained MPS/hydrochloric acid solution. Next, 1 g of the pure PU sponges were placed in the solution, sealed in the teflon lined container and heated at 95 °C for 6 h, to efficiently fulfill the hydrolysis and reduction process. Finally, the FGN/PU sponges were dried in a vacuum oven and the residual solvents were removed at 50 °C. The fabrication procedure and mechanism for the FGN/PU sponge were schematically shown in Fig. 1.

2.3. Characterization

Raman spectra were recorded from 500 to 4000 cm^{-1} on a Labram Aramis. The Bruker D8 advanced diffractometer (Bruker D8 Super Speed) with Cu Kà radiation was used for the X-ray diffraction (XRD) analyses, and the scanning area was from 5° to 80° of 2θ. The surface functional groups of samples were tested by a Bruker Vector 22 FTIR spectrometer within the wave number from 400 to 4000 cm^{-1}. Field-emission scanning electron microscopy (FESEM, Model-S4800) was used to observe the morphology of the sponge, coated with a thin layer of gold prior to SEM observation. Transmission electron microscopy (TEM) images were taken with Model Tecnai 12. Samples for TEM observations were prepared by dropping the solutions of samples on the copper grids and drying in air. The instrument (SL200B, Solon Tech. Co. Ltd) was to test the water contact angles (WCAs) at room temperature, in order to determine the hydrophobic properties of the material. WCAs on all samples were measured for ten times and average value taken. Thermogravimetric analyses (TGA) were carried out between 45 °C and 600 °C under nitrogen atmosphere, using a Model TA2100, (TA Instruments, USA). The PHI QUANTERA II spectrometer was used for X-ray photoelectron spectroscopy (XPS) analysis.

2.4. Oil-absorption experiments

The modified sponge was put into the oil. After 5 min, the absorbed oil was collected by squeezing the saturated absorbed sponge, and the desorbed sponge can be used in the cycle test. The mass of modified sponge was recorded before and after absorption test. All tests were carried out at room temperature. The Q was reckoned with the following formula:

$$Q = (m_e - m_0)/m_0$$

where m_0 and m_e are the mass of FGN/PU sponges before and after the absorption test, respectively.

3. Results and discussion

Fig. 2 shows Raman spectra of pure PU sponge, GO and FGN/PU Sponge. Compared with pure PU sponge in Fig. 2a, the characteristic D band and G band appeared in Fig. 2c. Besides, the intensity of D band relative to G band of FGN/PU sponge is significantly higher than that of graphite oxide (Fig. 2b), suggesting that GO has been converted into graphene [11].

The XRD diffraction patterns of GO, PU sponge and FGN/PU sponge were displayed in Fig. 3. As shown in Fig. 3a, GO had a typ-