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A superhydrophobic/superoleophilic sponge for the selective absorption oil pollutants from water

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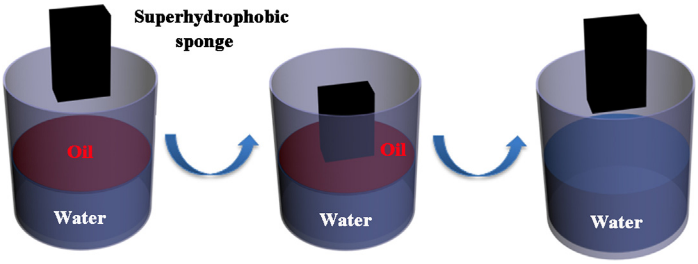
HIGHLIGHTS

- A superhydrophobic/superoleophilic sponge was fabricated by a facile method.
- The PVDF-HFP was used to solve the limited adhesion problem.
- After compression tests, no particles detached from the superhydrophobic sponge.

GRAPHICAL ABSTRACT



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ABSTRACT

Fabrication of robust superhydrophobic porous materials for oil removal is of great importance for industrial applications. However the poor adhesion between porous substrate and superhydrophobic coatings severely hinders their use in practical application. Herein, we fabricated a robust superhydrophobic and superoleophilic CNTs-SiO_2 coated polyurethane sponge for the selective absorption of oils from water. The mechanical stability of the resulting sponges was investigated by a compression test, and the result demonstrated that it still showed excellent elasticity and mechanical stability after repeated compression test. By combining its wettability and porosity, the as prepared sponges can fast and selectively absorb various kinds of oils from water. More importantly, the superhydrophobic sponge could be reused in oil–water separation for many cycles without losing its high oil absorption capacity. The study provides a fast and simple approach for removal of oils from water.

1. Introduction

With the increasing of industrial oily wastewater and the frequent oil spill accidents, there is a growing requirement to develop novel materials that are able to effectively absorb, remove, and transfer oil spills from water [1,2]. To achieve this goal, there has recently been a significant amount of research directed toward achieving superhydrophobic and superoleophilic textured surfaces [3–9]. Although these previously developed materials are effective in oil/water separating, they cannot be applied to separate oils from water in oil spill accidents, because the polluted water should firstly be collected and then filtered. Therefore, demand of development oil/water separating materials with high oil-absorption capacity, selectivity, and low cost is highly imperative.

In previous reports, three dimensional porous materials have been applied for the absorption and removal of various kinds of oils and organic solvent from water [10–14]. Tai et al. reported a facile method to fabricate graphene-based sponges for separation and

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absorption of oils from water [15]. Wu et al. synthesized a sponge-like bulk material with high structural flexibility and robustness [16]. More recently, Pan et al. described a novel and general method for fabricating ultralow-density magnetic foams possessing superhydrophobicity and superoleophilicity for efficient oil–water separation [17]. Nevertheless, the practical applications of the above mentioned oil/water separating materials are limited by complicated synthesis procedures and expensive precursors.

Generally, superhydrophobic surfaces can be achieved by combining appropriate surface roughness with hydrophobic materials. Polyurethane sponge is a kind of commercially available 3D porous material with porous structure and large internal surface area, which has been used for fabricating superhydrophobic absorbents in oil–water separation [18–21]. For recycle use of such superhydrophobic sponges, the adhesion between the coatings and the sponge skeletons needs special care. In this paper, we present a simple and inexpensive dip-coating method for the fabrication of a superhydrophobic and superoleophilic CNTs-SiO_2 coated polyurethane sponge. The resulting sponge exhibited high absorption capacity, high selectivity, and robustness, when they were employed as absorptive materials for collecting oils from water. The specific wettability of this CNTs-SiO_2 coated polyurethane sponge suggests its potential applicability in oil/water separation and oil-spill cleanup.

2. Experimental

2.1. Material

The PU sponge was purchased from a local store and used as received. Pristine multiwall CNTs with a diameter of 8–15 nm and a length of about 50 μm was purchased from Chengdu organic chemicals Co., Ltd., China (synthesized by a CVD process; purity > 99.9%). Silicon dioxide nanopowder (particle size: 10–20 nm), perfluorotetradecanoic acid, and poly(vinylidene fluoride-hexafluoro-propylene) (PVDF-HFP, $M_w \sim 400{,}000$) were obtained from Aldrich and used as received. Water (18.2 MΩ cm) was purified with a Millipore Simplicity system and used for all experiments.

2.2. Sample preparation

2.2.1. Preparation of modified nanoparticles and PVDF-HFP solution

1.5 g SiO_2 and 1.5 g CNTs were immersed in piranha solution for 12 h (H_2SO_4 and 30 wt% H_2O_2 in a 3:2 volume ratio) [22] and washed with distilled water and ethanol until the pH was near 7. PVDF-HFP solution was prepared by dissolving PVDF-HFP (0.5 g) in acetone (40 ml).

2.2.2. Preparation of superhydrophobic and superoleophilic sponge

Modified CNTs and SiO_2 were dispersed in 150 ml anhydrous ethanol, which was then subjected to ultrasonication for 30 min. The PU sponge was dipped into PVDF-HFP solution and then CNTs/SiO_2 suspension. After cured in an oven (140 °C, 0.5 h), and blowing off particles with poor adhesion, the resulting sponge was immersed in anhydrous ethanol containing perfluorotetradecanoic acid (4 g/L) for 1 h. The resulting sponge was dried at 80 °C for 1 h to obtain superhydrophobic samples.

2.2.3. Oil-removal from artificial sea water and oil absorption capacity measurement

The artificial sea water was prepared by dissolving 25 g sodium chloride (NaCl), 1.14 g calcium chloride ($CaCl_2$) and 0.7 g potassium chloride (KCl) in 1 L deionized water. The removal of oil from artificial sea water was carried out by dipping the superhydrophobic sponges into oil–water mixtures. The oil absorption capacity was calculated using the following formula: $Q = (m_w - m_d)/m_d$, where Q is the oil absorption capacity of the superhydrophobic sponge, m_w is the weight of the sponge after absorption, and m_d is the weight of the sponge before absorption. In typical absorption measurements, coated sponges were placed on the surface of various oils (pump oil, and rap oil) and organic solvents (chloroform, hexane, acetone, ethanol, methanol, ethyl acetate), then left for saturated absorption, and finally weighed immediately to avoid evaporation of solvents or oils.

2.3. Characterization

Contact angle (CA) was measured with 10 μl droplets of water using a Krüss DSA 100 (Krüss Company, Ltd., Germany) apparatus at ambient temperature. X-ray photoelectron spectra (XPS) was obtained on an ESCALAB250xi spectrometer equipped with a focused monochromatic Al X-ray source (1486.6 eV). The morphology of the surface was observed by field-emission scanning electron microscope (JEOL JSM-6701F FESEM). The optical images were captured by a digital camera (Canon).

3. Results and discussion

Fig. 1a shows the photograph of pure (white color) and CNTs-SiO_2 based (black color) sponges after being placed on water.

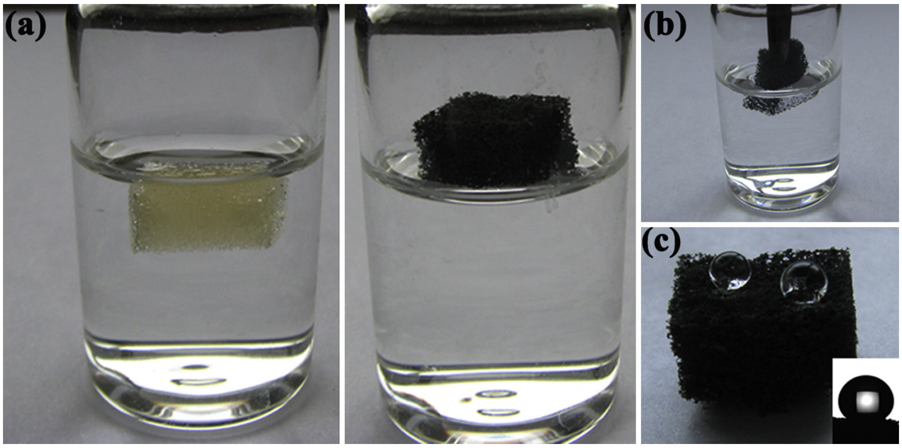

Fig. 1. Photograph of the pristine (white color) and the superhydrophobic sponge (black color) after being placed in water (a). Superhydrophobic sponge partially immersed in water by a force (b). Optical image and contact angle profile (c) of a water droplet placed on the superhydrophobic sponge.