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Highly efficient oil-in-water emulsion and oil layer/water mixture separation based on durably superhydrophobic sponge prepared via a facile route

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ABSTRACT

The fabrication of the materials with special wettability being capable of removing oil layer on water surface and oil droplets in oil-in-water emulsion is an important issue for water pollution. So far, it still remains challenging to explore a simple, facile, environmentally friendly approach for achieving this goal. Herein, inspired by the adhesion of marine mussels, the polydopamine (PDA) coating with hierarchical structure was directly fabricated onto the surface of melamine (MF) sponge by facile self-polymerization in dopamine solution. Then, a superhydrophobic and superoleophilic sponge was successfully obtained after the modification by dodecanethiol (DDT) at ambient temperature. The as-prepared sponge can selectively separate a series of oil droplets in oil-in-water emulsion with high efficiency (transparency: 76.6–93.8%) and absorb various oils or organic solvents up to 45.2–98.6 times of its own weight. Moreover, in conjunction with a vacuum system, great amounts of oils up to 20 times its own weight can be effectively separated from water surface within 1 s by the sponge. Due to low cost, simple process, and easy accessibility, the as-prepared sponge has potential applications in oil-in-water emulsion separation and oil spill cleanup.

1. Introduction

The oil leakage and unintentional discharge of organic pollutants from industry have made crisis to ecological environment. It has become an urgent issue to solve the oil spill accidents and the increase of industrial organic pollutants (Wang et al., 2015a). Currently, the most prevailing methods for the cleanup of spilled oils and organic pollutants include in situ burning (Buist et al., 2011), chemical dispersion (Kujawinski et al., 2011), mechanical extraction (Hokkanen et al., 2016), and so on. However, these technologies would cause secondary environmental and ecological issues as well as high energy consumption and non-portable operation. Recently, various functional materials with superhydrophobic-superoleophilic properties has attracted a lot of attention for the reason that they can selectively separate oils from water surface and oil/water emulsions without secondary pollution. Superhydrophobic materials based on different substrates, such as metal meshes (Gunatilake and Bandara, 2017), cotton textiles (Zhang et al., 2016), kapok fiber (Wang et al., 2017b), carbon nanotubes (Fard et al., 2016), membranes (Liu et al., 2016), and foams (Wang and Zheng, 2017; Wang et al., 2017a, 2017b), have been applied to oil/water separation. However, the fabrication of majority of these materials involves complicated process and single function. Especially, there are very little materials that possess dual functions of separating oil from water surface and absorbing oil droplets in oil/water emulsion simultaneously. Therefore, the exploitation of superhydrophobic materials to meet these requirements is extremely necessary.

In recent years, three-dimensional (3D) polymer sponge with low cost, high porosity, light weight, and favorable elasticity, has caused great concern for their potential of application in the fields of oil/water separation. Because of the high hydrophilicity, the sponges cannot selectively absorb oils and organic solvents from water, which greatly influences their oil/water separation efficiency. So, superhydrophobic modification of the sponges have been developed by various methods, including chemical etching (Zhang et al., 2013), organosilane coating (Ke et al., 2014), chemical reduction (Wang and Wang, 2017), hydrothermal route (Wang et al., 2017a), and modification with nano-materials (Ag, Fe_3O_4, SiO_2, or CNTs-SiO_2) (Li et al., 2014; Kharissova et al., 2015; Wang and Geng, 2015; Beshkar et al., 2017) to improve the water repellency. Despite this, many methods have some disadvantages such as complicated procedure, high cost, requirement for special equipments and strong corrosive etchants, and thus preventing their practical applications. More importantly, most of obtained sponges can only

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remove oils from water surface, but unable to break the oil-in-water emulsion, which is significant for their practical applications in oil/water separation because of the complexity of oily wastewater environment. Therefore, developing superhydrophobic-superoleophilic material with easily scalable preparation process, and favorable demulsification ability, may bring great opportunity to ease environment pressure from large-scale oil contamination in water.

Polydopamine (PDA), containing catechol and amine functional groups, can virtually adhere to all types of substance surfaces with a strong binding interaction, which is quite useful for modifying the surfaces or as an excellent platform to immobilize functional groups or nanoparticles (Lee et al., 2007; Hong et al., 2012). Based on these features, the PDA coating has been used for fabricating superhydrophobic materials for oil/water separation recently (Cao et al., 2013). To obtain hierarchical structures, the common route in various approaches is to decorate nanoparticles under the effect of PDA adhesion. For instance, Zhu et al. prepared magnetically superhydrophobic sponge by directly and robustly immobilization of Fe_3O_4 nanoparticles under oxidation of dopamine (Zhu and Pan, 2014). In previous study, we also prepared superhydrophobic cotton fiber for selective sorption of the oils on water surface via the combined use of SiO_2 nanoparticles and PDA (Wang et al., 2015b). The introduction of nanoparticles plays a key role in the formation of superhydrophobic surface. If the aggregation of PDA can directly result in hierarchical surfaces in the absence of any additional nanoparticles, the fabrication of superhydrophobic surface will become much easier. In this paper, a superhydrophobic and superoleophilic MF sponge was fabricated via one-step formation of hierarchical PDA coating and subsequently hydrophobic modification. Because of high hydrophobicity, ultralow density, high porosity, and excellent mechanical stability as well as elasticity, the as-prepared sponge exhibits superior removal capability for both oil droplets in oil-in-water emulsion and oil layers from water. The oil sorption capacity, sorption rate, and recyclability of the as-prepared sponges for different oils were studied. The results indicate that the as-prepared sponges have excellent separation effect for the dispersed oil droplets in water and the oil layer in water, satisfactory selectivity, outstanding recyclability, and good chemical durability. Furthermore, when applied in conjunction with a vacuum system, a series of oil pollutants on water surface can be continuously separated and collected by the sponge. To the best of our knowledge, there is no report on the use of superhydrophobic MF sponges with only simple PDA deposition for removing oil droplets in oil-in-water emulsions. This work may provide a facile, convenient and low-cost path toward the treatment of oily wastewater and oils spillage accidents.

2. Experimental section

2.1. Materials

MF sponge was received from market, Yinchuan, China. Dopamine hydrochloride (chemically pure) was purchased from Nanjin Aoduo Biotechnology Co., Ltd., China. DDT (chemically pure), $NH_3{\cdot}H_2O$ (28 wt %), methanol, ethanol, n-octanol, THF, DMF, paraffin oil, n-hexane, chloroform, and toluene (analytical grade) were supplied by Sinopharm Chemical Reagent Co., Ltd., China. Gasoline and diesel were provided by the local station, Yinchuan, China.

2.2. Preparation of superhydrophobic sponge

Before use, MF sponges were ultrasonically treated with deionized water and ethanol for 20 min and dried at 60 °C. The fabrication process of superhydrophobic sponge is illustrated in Fig. 1a. In the typical experiment, dopamine hydrochloride (12.64×10^{-3} M) and MF sponges (2 × 2 × 2 cm) were added into the ethanol/water mixture (v:v, 8:2). The pH value of solution was adjusted to 8.5 by adding ammonia aqueous solution. Then, the above system was stirred at 30 °C for 12 h, the obtained sponges were taken out and rinsed with plenty of distilled water and ethanol several times. After drying, the PDA-coated MF sponges were placed in DDT solution (2 mM) to treat for 8 h at room temperature. Finally, the superhydrophobic MF sponge was successfully obtained.

2.3. Measurements of oil sorption property

A piece of dried sample (W_i) weighed beforehand was placed in a beaker containing oils at room temperature. The sample was taken out from the oil after 5 min. The oil sorption capacity of the sample was determined by weighing the samples before and after the sorption, and calculated by the following formula:

$$Q = (W_t - W_i)/W_i$$

where Q is the oil sorption capacity of the sorbents calculated as grams of oil per gram of sample, W_t is the weight of sorbent with oil (g), W_i is the initial weight of sorbent (g). All oil sorption capacity was tested three times, and an average value was used.

The sorption kinetics of samples was investigated by repeating the previous measurements at different time intervals. Micron-sized oil droplets in water (emulsions) were obtained by vigorously stirring the mixture of oil and deionized water (V_{oil}:V_{water}, 1:10) for 20 min. The removal of oil droplets from emulsion was performed by agitating the as-prepared sponge in emulsions for a certain time, and then the milky emulsions will become colorless and transparent.

2.4. Characterizations

Water contact angle measurements were carried out using a Krüss DSA 100 (Krüss Company, Ltd., Germany) apparatus at ambient temperature, and the volumes of probing liquids in the measurements were approximately 5 μL. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet NEXUS FTIR spectrometer using KBr pellets. The micrographs of samples were examined using SEM (JSM–5600LV, JEOL). Before SEM observation, all samples were fixed on aluminum studs and coated with gold.

3. Results and discussion

3.1. Surface wettability of as-prepared sponge

The wettability of the as-prepared sponges was evaluated via contact angle measurement. As can be seen from Fig. 1b, the pristine MF sponge displays hydrophilic property with a contact angle of nearly 0°. After the PDA coating, the sponge becomes brown and more hydrophilic with a water contact angle of 0° (Fig. 1c), which also exhibits faster water wetting rate than pristine sponge. After the modification of DDT for the PDA-coated sponge, the sponge demonstrates prominent water repellency with a water contact angle of 158°, as shown in Fig. 1d. This means that the surface wettability of the sponge transforms from hydrophilic to superhydrophobic. Besides, the wettability from the inside of the sponge was also investigated (Fig. 1e). It can be seen the blue-colored water droplets exhibit a large contact angle on the surface of the dissected sponge (θ = 156°). So, both the surface and the inside of as-prepared sponge turn into superhydrophobic after the modification. For the PDA-coated MF sponge without the modification of DDT, a stream of water can wet the surface easily (Fig. S1a, Video S1). In case of DDT-immersed sponge without PDA coating, the water jet shows low rolling angle and slow rolling rate, and the surface can still be wetted by the water droplets (Fig. S1b, Video S2). In comparison, the sprayed water that falls onto the surface of the PDA/DDT modified sponge present spherical shape, which quickly bounce off the sponge surface without leaving any residual trace (Fig. 1f, Video S3). This finding implies the crucial role of PDA nanoparticles in creating superhydrophobic surface. The further comparison on the water repellency of