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Bio-inspired durable, superhydrophobic magnetic particles for oil/water separation

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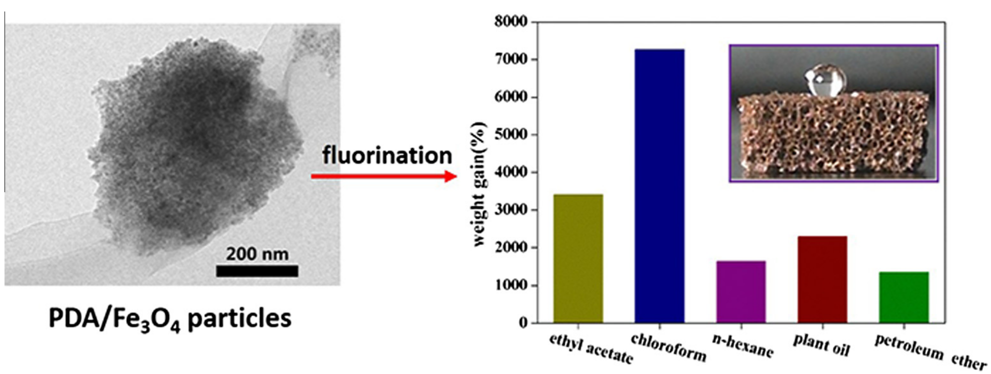
GRAPHICAL ABSTRACT



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ABSTRACT

In the present study, superhydrophobic and superoleophilic microparticles with magnetic property were fabricated by combining the oxidation and self-polymerization of dopamine and formation of Fe_3O_4 nanoparticles on the surface of the polydopamine (PDA) particles, followed by modification with low surface energy material. The modified PDA/Fe_3O_4 particles showed high water repellency with contact angle (CA) measured at 153.7 ± 1.6° and high oil affinity. The superhydrophobic microparticles preserved high water CA after aging test, showing excellent durability. The microparticles were employed to effectively remove oil from water in different routes. Superhydrophobic sponge was prepared by modifying with the achieved microparticles. The sponge exhibited high absorption capability of oil, with weight gains ranging from 1348% to 7268%. The results suggest this work might provide a promising candidate for oily pollutants/water separation and transportation.

1. Introduction

In the last years, superhydrophobic materials have drawn more and more attention in many areas due to their amazing properties. As well known, lotus leaf is a typical kind of superhydrophobic material in nature, which can clean away dusts easily when water droplets roll down from the surface. This self-cleaning property of lotus leaves is ascribed to the surface micro structures (micro papillae with nano protrusions) and surface chemical composition (plant wax) [1–3]. It is necessary to obtain proper roughness and low surface energy for the preparation of superhydrophobic materials. Many different methods have been utilized for the purpose, including layer-by-layer (LBL) self-assembly, chemical etching, gelation technique, phase separation and electrospinning, etc.

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[4–9]. However, these approaches exist lots of disadvantages such as relatively complex fabrication procedures, weak stability in harsh environment and low adaptability. Thus, there is a lasting demand for superhydrophobic materials with good stability, simple fabrication process and high adaptability.

Moreover, superhydrophobic materials have been found important application in the field of oil/water separation. Over the past decades, water pollution caused by oil spillage and chemical leakage have been threatening the marine life and the ecosystem seriously. Oil spill cleanup is a grand worldwide challenge currently [10–12]. It has been well revealed that the introduction of superhydrophobicity to solid can effectively absorb oil from water. For example, Gu et al. fabricated Janus hybrid membranes through grafting polystyrene (PS) and poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA) from different sides of CNT membranes. This membranes can selectively absorb some organic solvents from water [13]. Li et al. constructed a series of hierarchical rough surfaces via layer-by-layer self-assembly using different sized SiO_2 nanoparticles. The surfaces after the treatment of low surface energy material showed superhydrophobicity. In addition, some of the surfaces could separate oil/water with an efficiency of above 99% and have good durability [14]. An equally interesting area is the bio-imitation of the adhesive proteins of marine organisms. Inspired by bioadhesion, Messersmith's group addressed that dopamine was a structure mimic of the mussel adhesive proteins, which could polymerize and deposit on almost all kinds of surfaces [15]. Moreover, the resultant polydopamine (PDA) could act as a platform for secondary reactions which endowed it with wide applications, including surface wettability alternation [16].

Herein, this article presents a facile method to superhydrophobic and superoleophilic microparticles with good durability. Under the nature inspiration, PDA/Fe_3O_4 microparticles were prepared by the help of the metal binding ability of the catechols presented in the PDA, in order to mimic the hierarchical structure of lotus leaf. After modification, the PDA/Fe_3O_4 micro particles preserved high water repellency. Due to the presence of the Fe_3O_4 nanoparticles, the modified PDA/Fe_3O_4 microparticles not only could be used in oil/water separation, but also oil transportation driven by magnetic force. Superhydrophobic sponge were prepared by introduction of the microparticles to a sponge and high absorption capability of the achieved sponge was revealed. Moreover, the sponge could separate oil from water by a gravity-driven process. These findings offer a simple and versatile strategy to prepare superhydrophobic magnetic particles which could engage in oil/water separation in various paths.

2. Experimental section

2.1. Materials

Dopamine hydrochloride was purchased from Sigma–Aldrich. Tris(hydroxymethyl)aminomethane (Tris) (99.9%) and 1H,1H,2H,2H-perfluorodecanethiol were purchased from Aladdin. $FeCl_3{\cdot}6H_2O$, $FeCl_2{\cdot}4H_2O$, $NH_3{\cdot}H_2O$ (25%), n-hexane, ethyl acetate, petroleum, chloroform and hydrochloric acid (37%) were purchased from Sinopharm Chemical Reagent. PU sponges and plant oil were obtained locally. All of the reagents were used as purchased without more purification.

2.2. Preparation of superhydrophobic PDA/Fe_3O_4 particles

Synthesis of PDA/Fe_3O_4 particles: Dopamine hydrochloride (60 mg) was dissolved in a 30 mL mixed solution which was prepared by mixing Tris–HCl buffer solution (pH = 8.5) and ethanol (V_{water}:$V_{ethanol}$ = 3:2). After stirring for more than 3 days, the product was centrifuged, washed with deionized water and frozen dried. Then PDA particles (10 mg) were dispersed in 40 mL deionized water. The mixed solution (60 mL) of $FeCl_2$ (0.3 mmol) and $FeCl_3$ (0.6 mmol) was added to the PDA suspension under stirring. Ammonia (5 mL) was then dropped into the suspension of PDA. After 24 h, the product was centrifuged and washed with deionized water, and then frozen dried [15,17].

The modification of the PDA/Fe_3O_4 particles: The PDA/Fe_3O_4 particles were dispersed in 30 mL n-hexane by sonication. Then 30 μL 1H,1H,2H,2H-perfluorodecanethiol was added to the PDA/Fe_3O_4 suspension under stirring. After 24 h, the product suspension was filtrated and dried.

2.3. Preparation of the superhydrophobic sponges

A piece of PU sponge (1.0 cm ∗ 1.0 cm ∗ 0.8 cm) were ultrasonically cleaned with ethanol and distilled water for 30 min. Then the sponges were dried in an oven at 60 °C. The PDA/Fe_3O_4 particles were dispersed in n-hexane. Then the cleaned sponge was immersed in the above suspension under stirring for 24 h, followed by drying in an oven at 60 °C.

2.4. Characterization

Morphology observations were conducted on a scanning electron microscope (SEM, S-4700, 20 kV) and transmission electron microscope (TEM, H-800, 200 kV). X-ray diffraction (XRD) patterns were measured by a XRD-2500VB2+PC (Rigaku). Water contact angles (CAs) were measured by a contact angle measuring device (JC2000DF) with 3 μL water droplets as indicators.

3. Result and discussion

The PDA particles with diameter about 500 nm were prepared by the oxidation and self-polymerization of dopamine from a 2.0 mg/mL dopamine solution (Fig. 1a). PDA can be used as a versatile platform for secondary reactions and act as a reducing agent because there are many quinone–hydroquinone-types in its chains [17–19]. It can effectively prevent the oxidation of $FeCl_2$. The Fe_3O_4 nanoparticles were generated when ammonia was added into the mixed solution of $FeCl_2$, $FeCl_3$ and PDA particles. In the solution, PDA formed stable complexes with Fe_3O_4. Moreover, iron(III) formed metal catecholate bond, which was highly covalent with both σ- and π-donor bonding [20]. As a result, the Fe_3O_4 nanoparticles were immobilized on the surface of the PDA particles. The size of the Fe_3O_4 nanoparticles were about 50 nm. The PDA particles and Fe_3O_4 nanoparticles together formed a two-tier structure in resemblance to the lotus leaf as shown in Fig. 1b and c. In addition, the result of XRD also demonstrated the surface of PDA particles was coated with a layer of Fe_3O_4 nanoparticles. The diffraction peaks at 18.30°, 30.10°, 35.45°, 43.09°, 53.46°, 56.98°, 62.57°, 74.03° were corresponding to (1 1 1), (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), (4 4 0) and (5 3 3) planes of cubic Fe_3O_4 (Fig. 1d) [21,22].

The PDA/Fe_3O_4 particles were modified with 1H,1H,2H,2H-perfluorodecanethiol to achieve hydrophobic ability by simple immersion. The thiol groups could react with the catechol/quinone groups of PDA in a manner analogous to the reaction between thiols and metals (Fig. S1) [15]. Thus, monolayers of fluoroalkanes were formed on PDA/Fe_3O_4 surfaces. The chemical composition of the modified particles was confirmed by XPS spectra (Fig. S2) and FTIR spectra (Fig. S3). The PDA/Fe_3O_4 particles exhibited superhydrophobicity after the treatment. The image of a water droplet on the surface constructed by the modified PDA/Fe_3O_4 particles is exhibited in Fig. 2a. The wettability of the treated PDA/Fe_3O_4