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Polyelectrolyte-fluorosurfactant complex-based meshes with superhydrophilicity and superoleophobicity for oil/water separation

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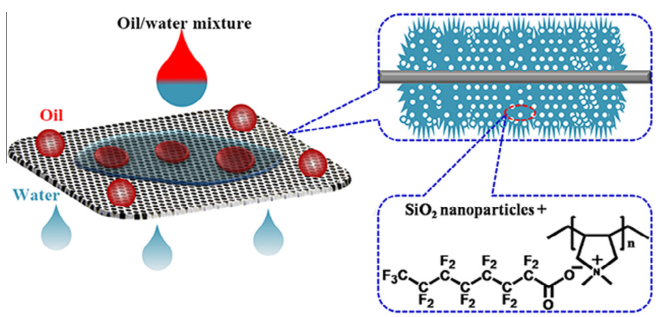
HIGHLIGHTS

- We fabricate the PFC-based mesh with superhydrophilicity and superoleophobicity.
- Water can pass through the mesh by gravity force while oils can be retained.
- Various oil/water mixtures can be separated using the prepared mesh.
- The oil/water separation function of the mesh keeps the long-term stability.

GRAPHICAL ABSTRACT



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ABSTRACT

To develop novel interface materials for oil/water separation, we describe a simple method to fabricate polyelectrolyte-fluorosurfactant complex-based meshes with superhydrophilicity and superoleophobicity both in air and underwater. The micro/nano-textured surface morphology, along with the interaction of hydrophilic groups and fluorinated alkyl chains, results in simultaneous superhydrophilicity and superoleophobicity. A water droplet can spread over the mesh surface with the contact angle of 0°, while a hexadecane droplet can roll off the mesh easily both in air and underwater. During oil/water separation process, water passed quickly through the mesh by the driving force of gravity and oils were retained above the mesh. As a result, various oil/water mixtures were separated using the mesh with the efficiency above 99.0%. Moreover, the performance stability of the prepared mesh was investigated using air plasma and corrosive aqueous solutions. After treatment, the mesh can keep the superhydrophilicity, superoleophobicity, and high oil/water separation efficiency. Therefore, this superhydrophilic and superoleophobic mesh would be a good candidate for oil/water separation to meet emerging needs in practical applications.

1. Introduction

The separation of oil/water mixtures has generated extensive attention because of the increase of industrial oil-polluted water and the frequency of off-shore oil spillages [1]. Traditional methods for the removal or collection of oils from oil/water mixtures generally used absorbent materials, but these materials also tend to absorb water, thereby lowering their efficiency [2]. Recently, inspired by functional interface materials with extreme wetting behaviors, various research groups have tried to develop superhydrophobic and superoleophilic materials for oil/water separation, which can cause water to run off the surface while allowing oil to permeate through [3]. These materials include polytetrafluoroethylene coated mesh [4], metal/metal oxide nanocrystals coated fabric [5], silicone nanofilament deposited polyester materials [6], carbon-based foams [7–9], and polymer-based sponges [10–12]. However, there are several drawbacks for superhydrophobic and

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superoleophilic materials to separate oil/water mixtures: (i) water usually settles below oil and against the surfaces owing to its higher density, forming a barrier layer that prevents oil permeation; (ii) they are easily contaminated and plugged by oils during separation process, culminating in a drop in the separation efficiency; (iii) the superhydrophobic property can be destroyed by illumination or corrosive oil-polluted water, leading to water permeation.

In view of the above problems, the most attractive approach to date appears to be the utilization of novel interface materials that can simultaneously display hydrophilicity and oleophobicity [13–15]. During oil/water separation process, water can pass through and the oil and oil-based contaminants are repelled [16]. More importantly, some damages caused by illumination or corrosive liquids could lead to form hydrophilic polar groups on the top of the surface, which may be favorable to water permeation and oil repellency [17]. Recently, inspired by the underwater self-cleaning property of fish scales, interfacial materials with superhydrophilicity in air and underwater superoleophobicity have been fabricated for oil/water separation [18–20]. However, due to only underwater oleophobic capability, when the oils are the first to contact the separation materials, oil fouling and permeation are still inevitable. Therefore, it would be desirable to develop a novel oil/water separation material with simultaneous superhydrophilicity and superoleophobicity both in air and underwater.

Polyelectrolyte-fluorosurfactant complexes (PFCs), owing to their hydrophilic groups and fluorinated alkyl chains, as one important class of interface materials with hydrophilicity and oleophobicity have received significant attention [21–23]. The hydrophilic PFCs are not consistent with the concept of traditional hydrophilic materials. The fluorinated alkyl chains orient toward the air–solid interface and localize hydrophilic groups of the polyelectrolyte in the near-surface region by electrostatic attraction. As a result, water molecules can responsively penetrate through defects in the fluorinated outermost layer toward the hydrophilic subsurface, while oil molecules are hindered by this top layer [24]. Although several types of hydrophilic and oleophobic PFCs have been synthesized, the report on the fabrication of PFC-based separation material with superhydrophilicity and superoleophobicity and its application for oil/water separation are seldom.

In the present study, we develop a simple method to fabricate the PFC/SiO_2-coated mesh with superhydrophilicity and superoleophobicity both in air and underwater. A water droplet can spread over the mesh surface due to water molecule penetration and 3D capillary effect, while a hexadecane droplet can remain the spherical shape with the contact angle greater than 150°. Various oil/water mixtures can be separated using the PFC/SiO_2-coated mesh only by the driving force of gravity. Moreover, the performance stability of the PFC/SiO_2-coated mesh was investigated using air plasma and corrosive aqueous solutions. The details of fabrication, characterization, and properties of the PFC-based separation material were described herein.

2. Experimental

2.1. Materials

Stainless steel meshes were purchased from a local hardware store. SiO_2 nanoparticles (average diameter ~20 nm), hexadecane, and paraffin oil were supplied from Sinopharm Chemical Reagent Co., Ltd., China. Vegetable oil was supplied by Luhua Group. Poly(diallydimethylammonium chloride) (20 wt%) and perfluorooctanoic acid were purchased from Sigma–Aldrich. Sodium perfluorooctanoate was prepared by the reaction of perfluorooctanoic acid with NaOH in water.

2.2. Fabrication of PFC/SiO_2-coated stainless steel meshes

Poly(diallydimethylammonium chloride) was firstly diluted to 1.0 mg/mL using deionized water, and then SiO_2 nanoparticles (0–0.4 g) were ultrasonically dispersed in the solution (100 mL), following by magnetic stirring for 2 h to absorb polyelectrolyte on the SiO_2 surface. Finally, sodium perfluorooctanoate (20 mL, 0.1 M) was added dropwise under stirring, making perfluorooctanoate anions coordinate to quaternary ammonium groups of poly(diallydimethylammonium chloride). The produces (PFC/SiO_2) were obtained by filtrating, rinsing, and drying. To fabricate PFC-based separation materials, the PFC/SiO_2 suspension (0.15 g/mL) was sprayed onto stainless steel meshes (pore sizes ~40 μm) with 0.2 MPa nitrogen gas using a spray gun (Shanghai, Lotus brand, No. 1). The thickness of the wet coatings was controlled by regulating the spraying time and the composition of nonvolatile constituents in the coating precursors. The thickness of the cured coating was about 5–15 μm.

2.3. Oil/water separation experiment of PFC/SiO_2-coated stainless steel meshes

Deionized water, 1 M HCl, 1 M NaOH, hexadecane, paraffin oil, and vegetable oil were used to prepare oil/water mixtures. The PFC/SiO_2-coated stainless steel mesh was fixed between two glass tubes with a diameter of 10 mm. Various oil/water mixtures were poured into the tube and the separation was achieved by the driving force of gravity. The water-based solution passed quickly through the mesh, while oils were kept in the upper glass tube.

2.4. Characterization

Scanning electron microscopy measurements were carried out using a JSM-7001F field-emission scanning electron microscopy (SEM, JEOL, Japan). X-ray photoelectron spectroscopy (XPS) analysis of the sample was performed on a PHI-5702 electron spectrometer using an Al Kα line excitation source. Contact angle and sliding angle measurements were performed using a Krüss DSA 100 (Krüss Company, Ltd., Germany) apparatus at ambient temperature. A 5 μL of deionized water was dropped on the mesh using an automatically dispense controller, and the contact angles were determined automatically by using the Laplace–Young fitting algorithm. Sliding angle was measured by tilting the mesh until a 5 μL of liquid droplet rolled off. Underwater contact angle was measured by placing a 5 μL of oil droplet (chloroform) onto the underwater PFC/SiO_2-coated mesh. The average contact angle and sliding angle values were obtained by measuring the sample at five different positions of the mesh. The images of oil/water separation process were captured with a traditional digital camera (Canon SX50 HS).

3. Results and discussion

The advantages of PFC-based separation materials with superhydrophilicity and superoleophobicity are fully demonstrated in Fig. 1a. When oil/water mixtures are poured onto separation material, water spreads over the surface and passes through the mesh by the driving force of gravity while the oil remains suspended on the water-wetted surface. Even if the oil is the first to contact the mesh surface, it can run off without leaving any contamination. In this work, to fabricate the superhydrophilic and superoleophobic materials, SiO_2 nanoparticles are chosen to construct the micro/nano-textured structure (Fig. 1b), and PFC synthesized by poly(diallydimethylammonium chloride) and sodium