Fabrication of Superhydrophobic-Superoleophilic Cement-Coated Meshes and Their Applications for Oil/Water Separation

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Abstract. Extreme wettability materials have shown great ability in dealing with oily industrial wastewater emission and oil spill accidents. Whenas, most of the addressed materials are technically sophisticated or inclined to involve corrosive or toxic chemicals. Herein, we fabricated an easy fabricated, low cost and robust material for oil/water separation. The superhydrophobic-superoleophilic (SOO) cement-coated meshes were made simply by dipping copper mesh in cement paste and surface modification. The micro/nanostructure and low surface energy endowed the mesh with great superhydrophobicity and superoleophilicity in air. The mesh had great oil absorption ability and high separation efficiencies for various oils. They were also admirably recyclable and durable. The meshes could be used to separate oil/water mixture at least for 20 cycles with high separation efficiency, and showed respectable superhydrobocity after being bent for 30 times. This simply fabricated, low cost and robust material will have great potential to be used in industrial wastewater treatment and oil spill in seawater.

1. Introduction
The large amount of oily industrial wastewater emissions and the frequent occurrence of oil spills not only aggravate the situation of water scarcity but also threaten the survival of aquatic organisms[1, 2]. Therefore, how to solve the problem of oil pollution in water effectively has become a hot issue in modern society. Traditional methods including burning, oil containment fences[3], oil containment absorption[4, 5] and biodegradation[6] are generally ineffective facing with serious oil spills, and the separated oil or water are not reusable[7, 8]. Recently, materials with extreme wettability have attracted increasing attention for oil/water separation due to the different interface effects of oil and water. These super-wetting materials can be obtained by adjusting surface micro/nanostructures and surface energy,[8-10] and can be classified into two main categories, i.e., absorption material and filtration material. Compared with adsorption method[11-15], filtration can be used as a final process of separation because the separated oil or water is almost pure. Extreme wettability materials for filtration are usually fabricated on three kinds of substance materials, i.e., metal meshes, textiles/fabrics, and polymeric membranes.[16] Because it is mechanically strong and easy to react with other chemicals, metal meshes became the most widely studied substances. The most typical and simple preparation method of extreme wettability metal mesh is chemical immersion[17-22], for example, Song et al.[18] fabricated a superhydrophobic mesh by immersing stainless mesh in an aqueous solution of 1 M CuCl₂ and 1 M HCl, and then modified by stearic acid. The mesh shows
superior water repellence and superoleophilicity, thus have high separation efficiency for oil/water mixture. Similarly, Wang et al.[23] fabricated a superhydrophobic and superoleophilic mesh by immersing commercial copper mesh in 4.0 M HNO$_3$ solution and modified by 1-hexadecanethiol. Although chemical immersion is a simple method and the fabricated meshes have excellent separation effects, it always contains corrosion or toxic chemicals that can cause secondary environmental pollution. In addition, a large amount of other methods were addressed, including chemical vapor deposition[24], spray-coating[25-27], sol-coating[28], electrospinning[29], electrochemical deposition[30, 31] and layer-by-layer assembly methods[31]. Feng et al.[32] fabricated a superhydrophobic and superoleophilic stainless steel mesh by spraying a homogeneous emulsion containing Teflon, adhesive, dispersant, et al. on the surface in 2004. Li et al.[33] fabricated a pH controllable coating by synthesizing polydimethylsiloxane, 2-hydroxyethyl methacrylate and poly (2-(dimethylamino) ethylmethacrylate). However, these methods mentioned above, were almost technically sophisticated, high operation cost, poor corrosion resistance and contain corrosive or toxic chemicals as well. Surely, many researchers have realized the problem, and developed new materials[34, 35], but technically simple and low production cost filtration materials are still solely needed.

Portland cement, a common material of architecture, was found superhydrophilic. Here, we fabricated superhydrophobic-superoleophilic (SOO) cement-coated meshes for oil/water separation simply by dipping copper mesh in the paste of cement, water and silicane, and then by low surface energy modification. The meshes showed great superhydrophobicity and superoleophilicity in air, and had great oil absorption ability. The SOO cement-coated meshes had high separation efficiencies for various floating oils and also were admirably recyclable and durable. This simply fabricated, low cost and robust material has great potential to be used in industrial wastewater treatment and oil spill in seawater.

2. Experimental Section

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2.1. Materials

Ordinary portland cement (PO 42.5) was bought from Guangdong Tapai Co., Ltd. (China). Cu meshes were purchased from Shanghai Hengxin Wire Mesh Co., Ltd. (China). Aqueous silicane (DC-30) was bought from Dingsheng New Materials Co., Ltd. (China). Hexane was bought from Sigma-Aldrich (USA). Diesel was purchased from a local gas station. Peanut oil was purchased from Luhua Co. (China) and lubricating oil was bought from CNPC.

2.2. Preparation of the SOO Cement-coated meshes

Cu meshes were firstly cut into circular pieces with diameter of 50 mm, then were washed in detergent, anhydrous ethanol and water, and were dried by absorbent paper. In the meanwhile, a paste composed of aqueous silicane, water and PO 42.5 with mass ratio of 1:1:2 was stirred adequately. Then Cu meshes were immersed in the paste for 30 s, and then pulled out with the velocity of 0.02 m/s. After dried absolutely at room temperature, the mesh was modified by 0.05 M ethanol solution of fluoroalkylsilane for 1 h, and after dried at room temperature, the SOO cement-coated mesh was prepared.

2.3. Oil/Water Separation

The SOO cement-coated mesh was fixed between two acrylic tubes with similar inner diameter of 36 mm with clamping devices. In order to help oils touch the surface of the SOO cement-coated meshes, the device was tilted 20°, and a mixture of 20 mL oils and 5 mL water were used for the separation. The water and oils in the mixtures were dyed differently for better distinguishing. The relevant properties of hexane, diesel, peanut oil and lubricating oil are listed in table 1. After separation, the separated oils were collected to evaluate the separation efficiencies.
Table 1. Properties of oils used in the experiments

| Oil            | Hexane | Diesel | Peanut oil | Lubricating oil |
|----------------|--------|--------|------------|-----------------|
| Density at 25°C [g/cm³] | 0.65   | 0.84   | 0.92       | 0.84            |
| Surface tension at 20°C [mN/m] | 17.9   | 28.3   | 34.5       | 40.1            |
| Kinematic viscosity at 40°C [cSt] | 0.42   | 4.33   | 39.6       | 74.4            |

2.4. Characterization

CAs (contact angles) and SAs (sliding angles) of water and oils were measured by an optical contact angle meter (Krüss, DSA100, Germany) using about 5 μL water or oil droplets at room temperature. Surface morphologies of cement meshes were observed by a field emission scanning electron microscope (SEM, JSM-6360LV, Japan). The purity of the separated oils and collected water were examined by Fourier transform infrared spectrum (FTIR, ThermoFisher 6700, America). The separated oils were examined by the FTIR to verify whether it contained water. For the separated water, tetrachloromethane was used to extract the oils in the water, and the absorbance intensity around 2954 cm⁻¹, 2920 cm⁻¹ and 2852 cm⁻¹ were used for calculating the oil contents. The separation efficiency \( R \) was calculated by the following equation,

\[
R \, (\%) = \left( \frac{M_a}{M_b} \right) \times 100\% 
\]

where \( M_a \) was the mass of the original oil in the oil/water mixture, and \( M_b \) was the mass of the separated oil.

3. Results and Discussion

The morphologies of the ordinary Cu meshes and the SOO cement-coated meshes are shown in figure 1(a) to 1(f). The surface of the ordinary Cu mesh was very smooth, but in contrast, the surface of the SOO cement-coated mesh was lumpy. There were lots of triangle-shaped pores and different size of protrusions in the mesh. The longest side of the triangle-shaped pores was around 250 μm, and the surface of the protrusions was covered by lots of leaf-shaped nanostructures. The micro-nanostructures and the low surface modification enabled the SOO cement-coated mesh to have great superhydrophobicity and superoleophilicity. And the triangle-shaped pores could help oil droplets pass through the mesh easily.

The excellent superoleophilicity of the cement-coated mesh is shown in figure 2(a) and 2(b). Droplets of hexane spread rapidly and completely on the SOO cement-coated meshes, and the water contact angle was almost 0°. In contrast, figure 2(c) shows the superhydrophobicity of the cement-coated meshes. The water droplets were almost spherical, and the contact angle was ~ 154°. The SOO
cement-coated mesh showed great water repellence when immersed in blue water while the ordinary Cu mesh was dyed blue as shown in figure 2(d). Figure 2(e) and 2(f) shows the touching, detacting and rolling off processes of water droplets on the SOO cement-coated meshes, demonstrating the superhydrophilicity and ultralow water adhesion of the meshes.

Due to the excellent superhydrophobicity and superoleophilicity, the cement-coated meshes showed superior absorption ability of various oils, as shown in figure 3. When the SOO cement-coated meshes were put onto the hexane/water mixture, diesel/water mixture, peanut oil/water mixture and lubricating oil/water mixture, they all absorbed the oils rapidly, and the 20 mm × 20 mm SOO cement-coated mesh could absorb at least 5 mL oil, indicating the excellent absorption ability of the meshes. The SOO cement-coated meshes still had good hydrophobicity after absorbing oils, thus could floating on the water, indicating the excellent water repellence of the meshes.
The separation processes of oil/water mixtures are shown in figure 4(a) and 4(b). The separation method was an oil-removal process, thus the separation method was suitable for heavy oil/water mixture. However, this separation method could also be used for floating oil/water mixture. The device was tilted about 20° to help the oil touch the surface of the SOO cement-coated mesh, thus the SOO cement-coated meshes could separate floating oil/water mixture without water-bridge[36]. Hexane, diesel, peanut oil and lubricating oil were used as floating oils. The mixture of floating oil and water was poured onto the SOO cement-coated mesh. The floating oil touched the surface of the mesh firstly, and passed quickly. Although the mesh was wetted by the oil, it showed good water repellence. The following water could not pass through the mesh, and occupied some area of the mesh. Thus, the oil came lastly passed through the remaining area. The separation efficiencies of the oil/water mixtures were all above 90% and even reached up to 96% for hexane/water mixture as shown in figure 4(c). Moreover, it should be noted that the separation efficiencies we gotten are slightly smaller than their true values because some oil adhered to the acrylic tubes and some oil was absorbed by the SOO cement-coated mesh. The FTIR spectra of the separated oils are shown in figure 4(d). All the absorption bands were corresponded to the characteristic vibrations of alkanes and ester groups. The band corresponded to hydroxy was not observed, indicating the high purity of the separated oil. Moreover, the purity of the collected water was measured by FTIR as well, and the oil contents in the
collected water were shown in figure 4(e). The oils contented in the separated water were 12 ppm, 37 ppm, 54 ppm and 64 ppm.

The SOO cement-coated meshes had not only high separation efficiency for oil/water mixture but also superior durability. As shown in figure 5(a), the SOO cement-coated mesh could be used to separate hexane/water mixture at least for 20 cycles with high separation efficiencies. Figure 5(b) shows the SOO cement-coated meshes have great stability, the CAs of the water droplets on the mesh were all above 150° and even after stored for 120 h. The process of bending the SOO cement-coated mesh and water droplets on the bent SOO cement-coated mesh were shown in figure 5(c). The water droplets on
the mesh that was bent for 30 times were all almost spherical, indicating the respectable durability of the SOO cement-coated meshes.

Figure 5. The durability of the SOO cement-coated meshes: (a) the variation of the separation efficiencies of the SOO cement-coated meshes with the hexane/water separation cycles, (b) the variation of contact angles of water droplets on the SOO cement-coated meshes with storage time in air, (c) the process of bending the SOO cement-coated mesh and water droplets on the bent SOO cement-coated mesh.

4. Conclusion
In this work, we simply fabricated a superhydrophobic-superoleophilic (SOO) cement-coated mesh for oil/water separation by dipping copper mesh in the paste of cement and surface modification. The micro/nanostructure and low surface energy endowed the SOO cement-coated meshes with excellent superhydrophobicity and superoleophilicity in air. The meshes had great oil absorption ability and high separation efficiency for various oils, and showed admirable recyclability and durability. The SOO cement-coated meshes could be used to separate oil/water mixture at least for 20 times with high separation efficiency above 90%, and had great superhydrophobicity after being bent for 30 times. The mesh also had unexceptionable stability. The CAs of water droplets on the meshes were all above 150° after stored for 120 h. This easy fabricated, low cost and robust method will have great potential to be used in industrial wastewater treatment and oil spill.

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