An alternative fabrication of underoil superhydrophobic or underwater superoleophobic stainless steel meshes for oil-water separation: Originating from one-step vapor deposition of polydimethylsiloxane

Ni Wen, Xinrui Miao*, Xiaojun Yang, Mengying Long, Wanshun Deng, Qiannan Zhou, Wenli Deng*

College of Materials Science and Engineering, South China University of Technology, Wushan Road, Tianhe District, Guangzhou 510640, China

ABSTRACT

Considerable interest has been motivated in the study of oil-water separation by developing new materials and technologies. Here, we demonstrated a simple and effective method to separate oil-water mixtures using the prepared stainless steel meshes by vapor deposition of liquid state polydimethylsiloxane (PDMS). By changing the heating temperature, underoil superhydrophobic stainless steel meshes and underwater superoleophobic stainless steel meshes can be alternatively achieved. The former is used for heavy oil-water mixtures separation after oil prewetting, while the latter is utilized to separate light oil-water mixtures after water prewetting. As a result, a variety of light or heavy oil-water mixtures could be separated with the efficiency above 99.0%. The separation efficiency maintains high even after 60 separation cycles. In addition, these two types of meshes still take effects under severe environmental situation when they are employed to separate oils from strong acidic, alkaline, salt aqueous solutions, and hot or ice water.

1. Introduction

In the past decades, the expanding water pollution has seriously threatened the human health and ecological environment due to the frequent oil spill accidents, as well as ever-increasing industrial oily wastewater enrichment [1–3]. Therefore, an effective treatment of oily wastewater is highly desired. Conventional techniques for oil-water separation such as chemical oxidation [4], in situ burning [5], biological treatment [6], adsorption [7], floating [8], and degradation with chemical dispersants [9] are widely used. However, all of these methods cannot meet the increasingly strict demands for large amounts of wastewater treatment because of high cost, low separation efficiency, and secondary pollutant production. What's more, in order to recycle the precious oil resources, it is highly expected to selectively remove oil from water. Therefore, it is meaningful to develop advanced materials to separate oil-water mixtures in a selective, highly-efficient, and green manner.

Oil-water separation is an interfacial phenomenon, which allows us to design novel materials by using special wettability in an effective and facile manner [10–12]. On the one hand, inspired by lotus leaf, superhydrophobic and superoleophilic materials render an alternative route to separate oil-water mixtures, such as stearoyl chloride-modified

polymer [13], superhydrophobic mild steel mesh [14], superhydrophobic fabric [15,16], and carbon fiber aerogel [17]. In comparison to the superhydrophobicity in air, underoil superhydrophobicity is acquired in oil/water/solid three-phase system by introducing the oil into micro/nano-scale binary structure surface. The underoil superhydrophobic properties are commonly utilized to prepare stable "oil-removing" type materials [18]. However, they are not suitable for separating light oil-water mixture ($\rho_{water} > \rho_{oil}$) because water accumulated on the surface of material by gravity makes oil failing to contact and transit. On the other hand, inspired by fish scale, superhydrophilic and underwater superoleophobic materials such as palygorskite [19], hydrogel [20], copper hydroxide [21], attapulgite [22], and chitosan [23], will allow water to pass through and block the oil penetration. Similarly, as a "water-removing" type material, it is yet not appropriate for separating heavy oil-water mixture ($\rho_{water} < \rho_{oil}$).

To the best of our knowledge, most of the reports have shown various methods working efficiently either in "water-removing" [24,25] type or "oil-removing" [26,27] type. In contrast, there are some studies [28–32] overcome the drawbacks of single-property meshes for oil-water separation by combining underoil superhydrophobic and underwater superoleophobic properties. For example, Li et al. have fabricated waste potato residue coated mesh [28] and diatomite coated mesh [29]

---

* Corresponding authors.
 E-mail addresses: msxrmiao@scut.edu.cn (X. Miao), wldeng@scut.edu.cn (W. Deng).

for selective oil-water separation. In prior to separation, the mesh should be prewetted using ethanol to change the wettability. Raturi et al. [30] have provided ZnO-nanowires-coated mesh with reversible wettability by annealing in hydrogen or oxygen atmosphere. Cheng et al. [31] have designed a pH-responsive mesh as a separating medium. Liu et al. [32] have developed a superhydrophobic-superhydrophilic integrated system for continuous oil-water separation. However, these methods are complex, and some involved fluorosilane-modification are expensive and environmentally harmful.

Polydimethylsiloxane (PDMS) is a low-cost, nontoxic, and versatile material to modify diverse surface. It is documented that thermal evaporation of PDMS on a solid surface can generate a thin and uniform coating [33,34]. Few studies have reported vapor deposition of PDMS to prepare superhydrophobic and superoleophilic mesh for oil-water separation [35,36], while underwater superoleophobic mesh fabricated through the similar method has not been revealed. In our previous study [37], we have demonstrated the wettability change of the PDMS-soot-deposited glass surface dependent on the time and temperature of vapor deposition of PDMS. Therefore, it is reasonable to develop meshes with controllable wettability prepared by one-step vapor deposition of PDMS for selective oil-water separation.

Herein, we fabricate two types of stainless steel meshes with different wettability through one-step vapor deposition of PDMS in air for 2 h at 350 °C and 500 °C, respectively. The as-prepared meshes exhibit high separation efficiency larger than 99.0% both in "oil-removing" mode and in "water-removing" mode. Even after 60 cycles, the separation efficiency maintains high, 98.9% for the "oil-removing" type mesh and 99.5% for the "water-removing" type mesh. Furthermore, these meshes are of excellently chemical stability, which can be utilized to separate oils from extreme environmental conditions such as 1 M HCl, 1 M NaOH, 1 M NaCl aqueous solutions, and hot or ice water.

2. Experimental section

2.1. Materials

Stainless steel mesh (500 mesh size) was purchased from Dakun Sieve Co., Guangzhou, P. R. China. Liquid state PDMS (Sylgard 184) was purchased from Dow Corning, USA. Other chemicals (analytical grade) from Guangzhou Qianhui Materials Co. were used as received.

2.2. Sample preparation

Stainless steel mesh was cut into many pieces ($3 \times 3 \, cm^2$), and subsequent ultrasonically cleaned with acetone, absolute ethanol, and deionized water to remove the surface dirt and then dried at 50 °C. Cylindrical crucible (5-cm-height) containing 0.5 g liquid state PDMS was put into the muffle furnace, and then the cleaned stainless steel mesh was placed on the top of the crucible. The heating temperature was set from 100 °C to 550 °C with the interval of 50 °C. The heating rate was 10 °C/min, and the heating time was 2 h. The acquired stainless steel meshes were stored in a drying cabinet for the later study.

2.3. Oil-water separation

The as-prepared mesh was fixed between two glass tubes, reinforced by a stainless steel clip. A variety of oils, including chloroform, dichloromethane, hexane, petroleum ether, kerosene, and hexadecane, were used in this study. The selected oil (stained with Sudan III) was mixed with deionized water (stained with methylene blue), 1 M HCl, 1 M NaOH, 1 M NaCl, hot water (90 °C), and ice water, respectively. The isometric oil-water mixtures were poured into a test tube after the mesh prewetted by water or oil. The separation process was recorded by a digital camera (Sony, Japan). The oil-water separation efficiency (η) was defined to be the mass ratio of the selected oil after and before separation.

2.4. Characterization

The surface morphologies of as-prepared samples were observed by a field-emission scanning microscope (FE-SEM, NOVA NANO-SEM 430). The static contact angles (CAs) and sliding angles (SAs) were measured at ambient temperature by a contact angle measurement instrument (OCA35, Germany) equipped with a high speed video camera. For the static CAs measurement in air, water or oil droplets were directly placed on the sample surfaces in air using a micro-syringe. For the static oil contact angles measurement under water, the samples were first fixed in a transparent container filled with water. Then oil droplets were dropped carefully onto the sample surfaces using a micro-syringe. The measurements of the underoil water contact angles (WCAs) are similar to that of the underwater oil contact angles (OCAs). The final values of static contact angle (CA) and sliding angle (SA) were the mean of five measurements at different locations of each sample by employing 4 μL droplets. Fourier transform infrared (FT-IR) spectra were obtained by a FT-IR spectrometer (Vector 33, Germany). The X-ray diffraction (XRD) analysis was conducted using an X-ray diffractometer (X'pert Pro MPD, Netherlands) with Cu Kα radiation.

3. Results and discussion

Fig. 1a illustrates the fabrication process of samples, in which the liquid state PDMS serves as the only raw material. The different samples were harvested through altering the heating temperature. The relationship between the surface wettability (water CAs/SAs) and the heating temperature was investigated as shown in Fig. 1b. The CA of original stainless steel mesh is approximate 107°, revealing its weak
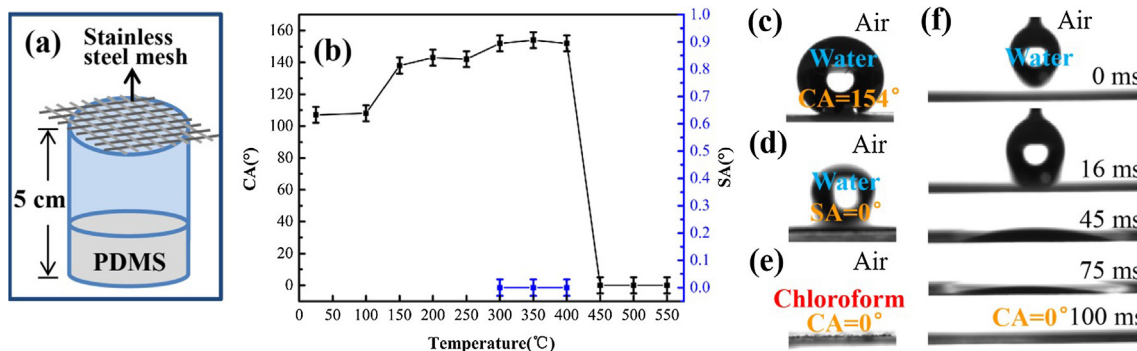

Fig. 1. (a) Schematic illustration of samples preparation. (b) Relationship between CAs/SAs and the heating temperature for water. (c–e) Surface wetting behavior of the mesh prepared at 350 °C (M-350): water CA in air (c); water SA in air (d); oil (chloroform) CA in air (e). (f) Surface wetting behavior of the mesh prepared at 500 °C (M-500). Note that a 4 μL water droplet spreads quickly over the mesh.