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Facile fabrication of superhydrophobic copper mesh for oil/water separation and theoretical principle for separation design

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ABSTRACT

A facile fabrication method was developed to obtain the superhydrophobic copper mesh for oil/water separation. The fabrication process involves the oxidation of the copper mesh followed by low pressure annealing at low temperature. The latter treatment enhances the hydrophobicity of the mesh by the formation of the Cu_2O surface layer. This superhydrophobic mesh demonstrates high mechanical flexibility and the chemical stability. Moreover, the superhydrophobicity remains even for hot water drops (>90 °C), indicating its thermal stability. Because of high oil affinity and water repellency of this superhydrophobic mesh, the mixture of various organic solvents with water can be easily separated into individual components. The separation efficiencies for the oil/water mixture were above 99% even after 40 separation cycles. Also, it was successful for the separation of hexadecane/hot water (>90 °C) mixture. The separation performance is practically competent according to the water intrusion pressure and oil flux. Our superhydrophobic meshes are robust in harsh water conditions and can be employed as an efficient filtration membrane. Based upon the experimental results and capillarity model, the design principle for oil/water separation membranes was proposed as well.

1. Introduction

Environmental protection from oil spillage and chemical leakage caused by the industrial activities is highly desirable in the present world. The oil-spill can occur during oil exploration, transport and storage. Owing to these frequent oil-spill accidents and disposal of industrial oily waste-water, a simple, effective, and durable separation process is required to mitigate associated accidents and the oil/water separation thus becomes a global challenge [1–5]. To tackle the problems of oil-water pollution, several methodologies have been used, including filtration, biological treatment, air flotation, coagulation, oil-absorbing materials, oil skimmers and combustion [4,6–9]. However, they generally suffer from limitations such as low selectivity, generation of a secondary pollutant, and complicated and expensive processing steps. These limitations have encouraged the scientific community to develop more effective oil/water separation technologies [5,8–10].

One of the ways to separate oil from water is to employ such a material that interacts preferably with one of the components in the oil/water mixture [4,10]. Organic materials such as hydrophobic aerogels, carbonaceous materials, and cross-liked polymers were often employed for separation. However, they lack high separation efficiency and good recyclability, and can produce secondary pollutant [11–14]. Recently, low energy surfaces disfavoring water have been employed for oil/water separation. Inspired from the water-repellency lotus leafs, these superhydrophobic/superoleophilic surfaces can selectively repel water and interact favorably with oil [4,5,15]. Surfaces having static water contact angle (CA) above 150° are superhydrophobic [16–18]. These extreme water repellency surfaces have found widespread applications such as self-cleaning, anti-icing, and drag reduction in microfluidics [19–22].

The surface wettability is generally controlled by chemical composition and surface roughness. The influence of the latter can be described by two mechanisms: Wenzel and Cassie-Baxter. In the Wenzel model, the grooves on the surface are completely filled by the liquid drop. In the Cassie-Baxter model, however, the drop remains atop the air trapped in the grooves (air pockets). According to the base of the liquid drop, the former case has a homogeneous wetting surface, while the latter case involves a heterogeneous surface [19,21,23]. On the basis of the Cassie-Baxter scenario, superhydrophobic surfaces can be fabricated either by modification of rough surfaces via a thin coating of low interfacial energy materials or by generating surface roughness on a low energy substrate. Note

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that large surface roughness suffers the weakness of low resistance to mechanical stresses, though it induces superhydrophobicity. Typically, fluorinated alkyl radicals ($-CF_3$,$-CF_2H$, $-CF_2-$) were used as low surface energy materials [21–25]. Among these, polytetrafluoroethylene (PTFE) containing $-CF_2-$ groups is the most attractive material [21,26,27]. Recently, PTFE has been coated on the steel wires to fabricate superhydrophobic meshes for oil/water separation [27].

Superhydrophobic metallic meshes have been fabricated by application of surface modifiers, electrospinning, chemical vapor deposition, spray drying, electrodeposition, and seed growth [27–32]. However, those fabrication methods involve high temperature synthesis and long processing time and they lack chemical stability, which can hinder their economic viability and large scale production [5,32]. Moreover, the superhydrophobic structures lose the superhydrophobicity upon exposure to chemicals and even to hot water with temperature $\geq$55 °C. Thus, their applications such as oil/water separation were limited under harsh conditions [33–35]. The loss of the superhydrophobicity against hot water drops is attributed to the condensation of liquid vapors in the grooves, leading to the loss of air pockets and the crossover from the Cassie-Baxter to Wenzel scenario [33–35]. The condensation can be minimized by incorporating structural material (nanowires or nanotubes), which provides grooves with small radii of curvature, [34–36] or its combination with low surface energy material to the substrate

In this work, facile and inexpensive fabrication of superhydrophobic copper meshes has been reported without using low surface energy material. In addition to strong affinity toward oil and repulsion to water, the resultant mesh exhibited the mechanical flexibility and stability. Moreover, it can resist various chemicals and hot water (chemical and thermal stability). The fabricated mesh was employed for separation of the oil/water mixture. The separation efficiency was very high and the good recycle ability was demonstrated as well. The mixture of hexadecane/hot water has been successfully separated by using this superhydrophobic mesh. Furthermore, the separation performance regarding the intrusion pressure and oil flux has been examined. Finally, the theoretical principle for designing efficient oil/water separation has been proposed based on our experimental outcomes and the capillarity model.

2. Experimental

2.1. Materials

Sodium n-dodecyl sulfate (SDS, 99%), n-hexadecane (99%), polystyrene (M.W. 100k) and polyvinyl acetate (PVA, M.W. 50k) were procured from Alfa Aesar (United Kingdom); hydrogen peroxide (30%, w/w) from Sigma-Aldrich (Germany); anhydrous ethanol (99.5%) from Echo Chemical Co. (Taiwan); n-hexane (95%) from Seedchem Co. Pvt. Ltd. (Australia); n-octane (97%) from TEDIA (USA); n-decane (99%) from Acros Organics (USA); liquid paraffin (extrapure) from Nihon Shiyaku Industries Ltd. (Taiwan); sodium hydroxide (96%) and hydrochloric acid (35%) from SHOWA chemical Co. Ltd. (Japan); polytetrafluoroethylene (PTFE) beads (2–3 µm) from Polysciences Ltd. (USA); dodecyltrimethylammonium bromide (DTAB, 99%) from TCI (Japan). The copper mesh (200) was bought from May-Chun Company Ltd. (Taiwan). All the analytical grade chemicals were used as such without further purification.

2.2. Methods

2.2.1. Fabrication of superhydrophobic copper mesh

The commercially available copper mesh (200) was cut into the desired size and washed with deionized water. The mesh was immersed in 1 M aqueous HCl solution at 50 °C for 30 min to remove the impurity and native oxide and then was washed with deionized water again. The mesh was then subsequently soaked in 30% (w/w) H_2O_2 solution for another 30 min at 50 °C. This treatment with H_2O_2 solution brings about the partial oxidation of the Cu mesh. The oxidized mesh was washed thoroughly with anhydrous ethanol and annealed at 100 °C in vacuum for 3 h. Note that the mesh was immersed in anhydrous ethanol during low pressure annealing. The resultant mesh becomes superhydrophobic.

2.2.2. PTFE coated mesh

Polystyrene (0.2 g) was dissolved in 9 ml toluene and the mixture was kept in ultrasonic bath at 70 °C for 1 h. To the mixture was added 0.30 g PTFE powder and then stirred well to obtain the temporarily stable dispersion. About 0.05 g of PVA was dissolved in 2 ml of acetone. The PTFE dispersion was then mixed with the PVA solution. The resultant mixture was casted onto the superhydrophobic Cu mesh with the help of the flat side of a spatula so as to form a thin uniform layer. The mesh was then dried at room temperature. Both polystyrene and PVA were added to improve the adhesion of PTFE powder to the mesh. The prepared PTFE coated Cu mesh was also used to evaluate the intrusion pressure and oil flux.

2.2.3. Characterization

The surface morphology of the untreated and the fabricated meshes were observed by using scanning electron microscopy (SEM) from Hitachi (S-3000H, Japan) and optical microscope (OM) from OLYMPUS (BX-51, Japan). The X-ray photoelectron spectrometer (XPS, Sigma Probe spectrometer, Thermo VG Scientific Co. Ltd) equipped with monochromatic aluminum anode X-ray source (Al K_α 1486.6 eV) was employed for XPS analysis.

2.2.4. Wettability characterization

The wetting behavior of pristine and treated Cu meshes has been characterized by Dataphysics DSA10-MK2 (Kruss, Germany) contact angle measurement system. The automated micro-syringe system releases water droplets having volume of 5 µL on the substrate surface. A charged coupled device camera was used for recording the shape of the droplets. These measurements were performed under ambient condition and finished within few seconds to eradicate the effect of water evaporation on the contact angle (CA) measurements. For hot water drop, the CA was measured within 5 s of placing boiling water drop on superhydrophobic mesh. The tilted plate method was used to determine the contact angle hysteresis (CAH). For the drop to move on a tilted surface, the drop should advance downhill and recede from the uphill side [20–23]. The difference between the advancing (θ_a) and receding (θ_r) angles is termed contact angle hysteresis[23], which is defined as $\Delta\theta = \theta_a - \theta_r$.

3. Results and discussions

Special wettability surfaces which have opposite affinities toward oil and water are promising materials for oil/water separation [4,20]. In this work, a straightforward fabrication method was developed to obtain the superhydrophobic copper mesh. Then, the effective oil/water separation has been achieved by this water repellent mesh. In order to elevate the maximum intrusion pressure that the oil/water separating mesh can sustain, a design principle has been suggested. Based on this idea, the copper mesh filled with PTFE powder has been made and it can withstand high water pressure.

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