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A Facile Solvent-Manipulated Mesh for Reversible Oil/Water Separation

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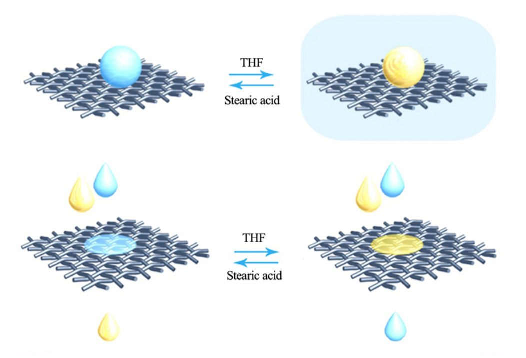
S *Supporting Information*

ABSTRACT: A controllable oil/water separation mesh has been successfully developed and easily manipulated by immersion in a stearic acid ethanol solution and tetrahydrofuran with a very short period of time. The superhydrophilic and underwater superoleophobic mesh is first obtained via a one-step chemical oxidation and subsequently converts to superhydrophobic after it is immersed in an ethanol solution of stearic acid for 5 min. The surface wettability is regained to superhydrophilic quickly by immersion in tetrahydrofuran for 5 min. More importantly, the reversible superhydrophobic-and-superhydrophilic switching can be repeated multiple times with almost no visible morphology variation. Therefore, this approach provides potential application in controllable oil/water separation and opens up new perspectives in manipulation of various metallic oxide substrates.



KEYWORDS: *solvent-manipulated, superhydrophobic-and-superhydrophilic switching, stearic acid, tetrahydrofuran, controllable oil/water separation, reversible oil/water separation*

1. INTRODUCTION

Oil/water separation has been an urgent worldwide challenge due to global water pollution caused by frequent oil spills and chemical leakage.[1−3] Basically, wettability of solid surfaces is controlled by the chemical composition and geometrical structures and can be enhanced by surface roughness.[4] Plenty of superwetting interfacial materials fabricated by designing superhydrophobic or superoleophobic surfaces have aroused great attention and have been efficiently applied for industrial oily wastewater treatment.[5−9] Therein, "oil-removing" type materials with superhydrophobicity and superoleophilicity can separate or absorb oils from water,[10−18] whereas the "water-removing" type materials with superhydrophilicity as well as underwater superoleophobicity can permit water passing through and block oils.[19−22] Among several forceful methods, the self-assembled monolayer (SAM) technique can effectively fabricate the superwetting surfaces by molecule-level variation of the architecture and proves potential utilizations in areas of anticorrosion, lubrication, biosensors, electrowetting chemistry, etc.[23−25] However, considering the demands of the economy and environment, it is of significance to prepare controllable functional materials that can selectively separate oil and water.[26]

Currently, the research of "smart" surfaces with reversible wettability has aroused great interest, especially the wettability switching between superhydrophobicity and superhydrophilicity achieved by external stimuli, such as light,[27,28] temperature,[29,30] electricity,[31] pH,[32,33] solvent,[34] etc. However, the surface wettability transitions triggered by the aforementioned approaches require a long period of time, even several weeks,[35] which are restricted to their large-scaled uses. Additionally, these approaches need either complex steps to fabricate[33] or special equipment to work.[6] Hence, it would be greatly acceptable to manipulate the wettability transition with a time-saving and convenient method.

Herein, a controllably reversible oil/water separation mesh has been developed, which can be easily manipulated by immersion in a stearic acid ethanol solution and tetrahydrofuran with a very short period of time. The superhydrophilic and underwater superoleophobic mesh was first obtained via a one-step chemical oxidation. The film was converted to superhydrophobic after being immersed in an ethanol solution of stearic acid for 5 min; however, it was regained to superhydrophilic quickly on immersion in tetrahydrofuran for 5 min (Figure 1a). The surface wettability switching between superhydrophobicity and superhydrophilicity could be manipulated repeatedly many times with almost no visible morphology variation. The advantages of the present approach include the facile steps, the cheap raw materials, the rapid transition, and reusability. Therefore, it provides potential applications in controllable oil/water separation, microfluidic tools, self-cleaning surfaces, etc.

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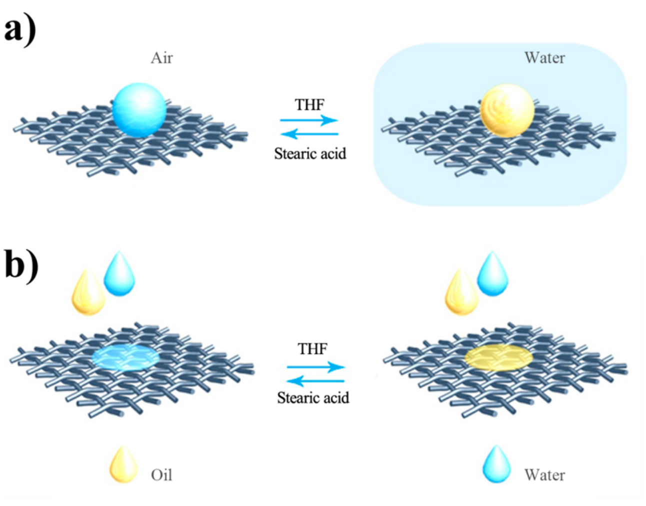

Figure 1. Schematic diagrams of the as-prepared mesh with reversible wettability switching for controllable oil/water separation: (a) When dipped into a stearic acid ethanol solution for 5 min, the mesh is superhydrophobic, whereas it converts to superhydrophilic and underwater to superoleophobic by immersion in tetrahydrofuran for 5 min. (b) After it was modified with stearic acid, oil can penetrate through the mesh, but water cannot, whereas, when desorbed by THF, water can pass through the mesh quickly, but oil cannot.

As shown in Figure 1b, the stearic acid modified mesh is superhydrophobic that can selectively permit oil passing through the mesh. In the meantime, water was blocked. When some tetrahydrofuran (THF) is added, the mixture of water and THF penetrates through the mesh subsequently because of the high solubility of stearic acid in THF. Interestingly, the THF desorbed mesh acts as superhydrophilic and underwater superoleophobic, which only allows water to permeate through the mesh. Owing to the fast wettability transition in combination with almost no visible morphology variation, this approach has created a new field for controllably reversible oil/water separation.

2. EXPERIMENTAL SECTION

2.1. Materials. Ethanol and acetone (Dongfanglongshun Co. Ltd., Beijing, China), potassium peroxydisulfate ($K_2S_2O_8$, Alfa Aesar, Tianjin, China), and stearic acid (J&K Co. Ltd., Beijing, China) were used as purchased. Other reagents from Sinopharm Chemical Reagents are of analytical grade and were used without further purification.

2.2. Preparation of Solvent-Manipulated Mesh. $Cu(OH)_2$ nanoneedle arrays were grown at ambient conditions, as described previously.[36,40] The commercial copper mesh was cut into 4 × 4 cm^2 pieces and ultrasonically cleaned in deionized water, acetone, and 1.0 M hydrochloric acid aqueous solution, respectively, so as to remove the surface dirt and oxide layers. The mesh was subsequently immersed in an aqueous solution of 0.05 M $K_2S_2O_8$ and 1.0 M sodium hydroxide (NaOH) for 30 min. After being washed with water carefully, the superhydrophilic mesh was obtained. Self-assembled monolayer (SAM) surface modification was performed by dipping the prepared mesh into an ethanol solution of 0.05 M stearic acid for 5 min, followed by drying, and the surface wettability switched into superhydrophobicity. Similarly, the wettability was reverted to superhydrophilicity by immersion in tetrahydrofuran (THF) for 5 min.

2.3. Instrumentation and Characterization. The SEM images were obtained by an environmental scanning electron microscope Quanta200. The X-ray photoelectron spectra (XPS) were taken by a Thermo Escalab 250Xi spectrometer using an Al Kα X-ray source (1486.6 eV). Contact angles were measured on an OCA20 machine (Data-Physics, Germany) at ambient temperature. The average value of five measurements acquired at different positions on the same sample was adopted as the contact angle.

2.4. Oil/Water Separation Experiments. Separation of oil/water mixtures with the solvent-manipulated mesh was performed as follows. The as-prepared mesh was fixed between two Teflon fixtures, which were both attached with a glass tube. The diameter of the glass tube was 25 mm. The oil/water mixtures (50 v/v%) were poured onto the mesh, and then the separation was proceeded by the force of gravity. Subsequently, 5 mL of THF was added into water in the upper glass; the THF mixed with water automatically and contacted the SAM modified mesh. The THF/water mixture permeated through the mesh, and the THF desorbed mesh was in situ obtained by the high solubility of stearic acid in THF.

3. RESULTS AND DISCUSSION

3.1. Mesh Morphology. A low-magnification SEM image exhibited a smooth surface of the untreated mesh (Figure 2a), which was made of copper wires with an average diameter of about 40 μm that were woven around each other to form square pores of approximately 50 μm. Chemical oxidation is an acceptable method to roughen the copper for its natural reduction property. Figure 2b shows the rough and uniform wires twisted regularly after straightforward oxidation of the copper substrate,[36] and the further-magnified image in the inset reveals that the mesh was covered with well-distributed copper hydroxide ($Cu(OH)_2$) nanoneedle arrays.[37] The microsized pores in combination with nanoscale roughness endowed a hierarchical composite structure to the mesh that possessed superwetting behaviors. It is known that OH^- groups on the $Cu(OH)_2$ surface can graft with molecules containing carboxyl groups via acid−base reaction. Figure 2c presents SEM images of $Cu(OH)_2$ covered mesh soaked in a stearic acid ethanol solution for 5 min. It was found that it was almost identical to the unmodified mesh, which signified the SAM of stearic acid with a thickness of less than a few nanometers. Afterward, the surface wettability could be easily manipulated with THF desorption for 5 min and almost no visible morphology varied at the surfaces of nanoneedle arrays, as shown in Figure 2d.

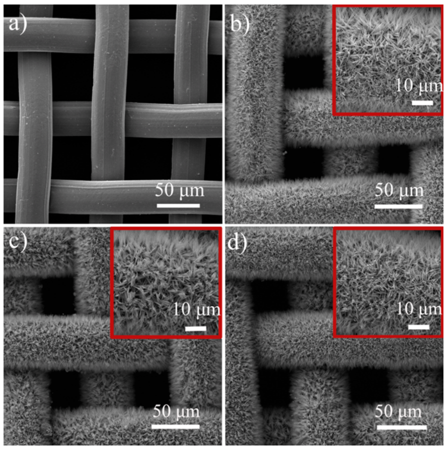

Figure 2. SEM images of the as-prepared mesh: (a) the untreated copper mesh with a smooth surface; (b) the oxidized mesh covered with $Cu(OH)_2$ nanoneedle arrays; the inset is the high-magnification view of nanoneedle arrays; (c) the SAM modified mesh with the high-magnification view in the inset; (d) the THF desorbed mesh with the high-magnification view in the inset.

3.2. Chemical Constitution of the Mesh. Constituent elements of the SAM modified film and THF desorbed film

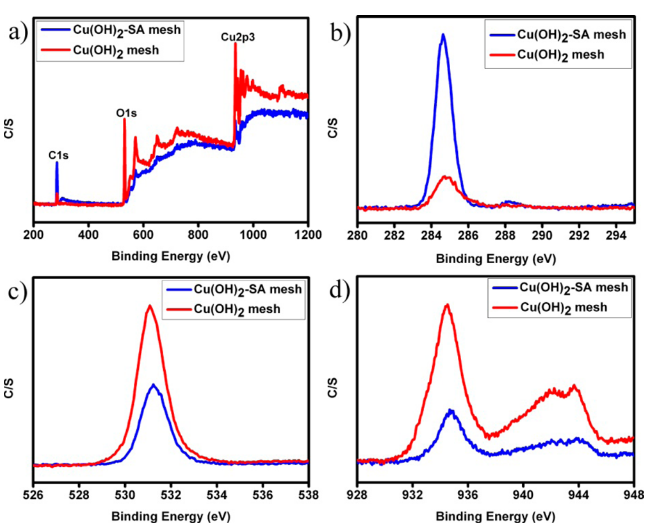

Figure 3. XPS spectra of the as-prepared mesh: (a) survey scans binding energy region from 0 to 1200 eV; (b−d) high-resolution XPS spectra of C 1s, O 1s, and Cu 2p^3 narrow scans as a function of electron binding energy. The blue peak was assigned to the stearic acid modified sample, and the red peak was ascribed to the THF desorbed mesh.

were probed by XPS to confirm the successful solvent manipulation. Figure 3a shows two spectra of three basic elements including carbon (C), oxygen (O), and copper (Cu) surveyed by scanning the binding energy from 0 to 1200 eV. The three main peaks at 284.8, 531.2, and 934.9 eV are marked with C 1s, O 1s, and Cu 2p^3, respectively. The strong C 1s peak observed at the binding energy of 284.8 eV in Figure 3b was assigned to the alkane chain and carboxyl group of the stearic acid molecule as well as oxidized carbon species of ethanol or carboxyl compounds absorbed from the ambient atmosphere. These carbon contaminants were also trapped in the THF desorbed mesh with the weak peak. Furthermore, the intensities of O 1s and Cu 2p^3 peaks (Figure 3c,d) increased considerably in the THF desorbed mesh due to the probability of Cu(OH)$_2$ predominating again after removal of SAM.

3.3. Mesh Wettability. It was expected that the micro- and nanoscale hierarchical composite structure made the as-prepared mesh possess superwetting behaviors, and the surface wettability was evaluated by contact angle measurement. Figure 4a displays that the water contact angle (WCA) of the oxidized copper mesh tended to 0°, whereas the oil contact angle (OCA) on the mesh surface underwater was about 158.5 ± 0.8° (Figure 4b), resulting from a water layer forming at the interface of the Cu(OH)$_2$-covered film that resisted oil droplets. The oxidized mesh was dipped in an ethanol solution of stearic acid for 5 min, surface active molecules absorbed onto the native oxide surfaces of Cu(OH)$_2$ arrays, and a SAM was formed via acid−base reaction between stearic acid and copper hydroxide on the mesh surface.[38] Interestingly, the SAM modified film showed superhydrophobicity with a WCA of about 155.4 ± 1.3° (Figure 4c), whereas the OCA on the mesh was close to 0° (Figure 4d), indicating the opposite wettability to the oxidized mesh. The SAM was easily released after the mesh soaked in THF for 5 min, and the wettability was reverted to superhydrophilicity and underwater superoleophobicity (Figure 4e,f). More importantly, the as-prepared meshes were stable at high temperature and possessed excellent antifouling property as well as low adhesion forces to water/oil droplets (see details in the Supporting Information, Figures S1−S3). These robust properties endowed the as-prepared mesh with the capacity of efficiently reversible oil/water separation.

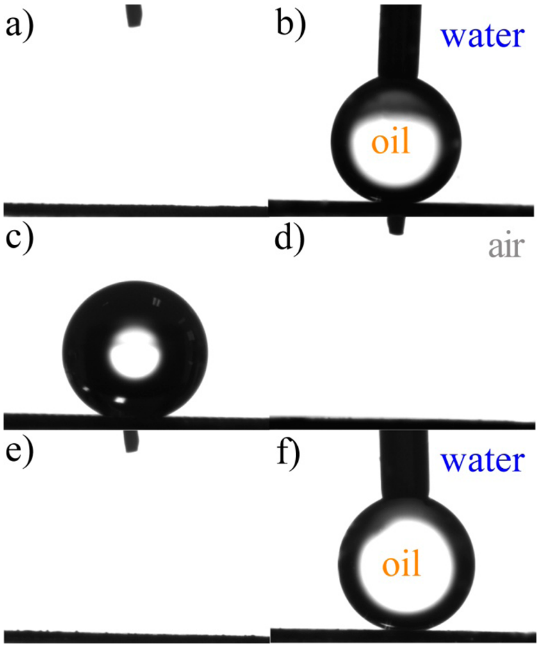

Figure 4. Surface wettability of the as-prepared mesh: (a, b) the photographs of water and underwater−oil droplets on the surface of the oxidized mesh; (c, d) the photographs of water and oil droplets on the surface of SAM modified mesh; (e, f) the photographs of water and underwater−oil droplets on the surface of THF desorbed mesh.

3.4. Solvent Selectivity. The results above illustrated that the superhydrophobic-and-superhydrophilic wettability switching could be realized by forming a SAM of a low surface energy molecule just like stearic acid and subsequent removal of the layer by solvent. However, it was important to select an appropriate solvent because the SAM of stearic acid on the Cu(OH)$_2$ nanoneedle arrays' surface could not be altered when immersing in other solvents, such as methanol, ethanol, acetone, toluene, or chloroform, for more than 30 min, respectively. As shown in Figure 5, the mesh retained superhydrophobicity with all WCAs on the SAM modified surface larger than 150°, whereas it became superhydrophilic

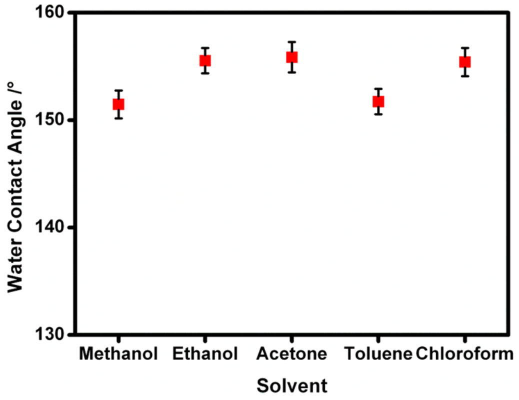

Figure 5. Solvent selectivity of the SAM modified mesh, the superhydrophobic behavior could not be altered by immersion of these solvents for more than 30 min.

after dipping into tetrahydrofuran for 5 min, which was due to the high solubility of stearic acid in THF (Supporting Information, Figure S4).

3.5. Reversible Oil/Water Separation. The reversible wettability switching manipulated with solvent was supposed to be applied for controllable oil/water separation. A series of proof-of-concept studies were operated to test the oil/water separation capacities of the as-prepared mesh. It was shown that the oxidized mesh possessed superhydrophilicity and underwater superoleophobicity to various oil droplets containing toluene, *n*-octane, chloroform, diesel, etc. (Supporting Information, Figure S5). Additionally, the mesh was confirmed to be suitable for separating diversified oil/water mixtures with high stability and separation efficiency (see details in the Supporting Information, Figure S6 and video S1). After it was rinsed with water thoroughly, the oxidized mesh was immersed in an ethanol solution of stearic acid for 5 min, followed by being dried and fixed into the fixtures. The short glass tube was replaced by a longer bent one, and the device was placed with a tilt angle of 15°. Based on the superhydrophobicity and superoleophilicity of the SAM modified mesh, the mixtures of diesel and water were separated quickly with diesel penetrating the mesh while the water along with almost no visible oil existing was blocked at the upper glass tube (Figure 6a,b). Subsequently, some THF was added into the water (Figure 6c), and the mixtures began to pass through the mesh after a few seconds (Figure 6d) depending on the good compatibility of THF and water in combination with the high solubility of stearic acid in THF. To verify the recovery of superhydrophilicity manipulated with THF, the diesel and water mixtures were poured onto the mesh once more. The phenomenon appears in Figure 6e,f, and the result that the corresponding XPS spectrum (Supporting Information, Figure S7) was almost the same with that obtained by dipping in THF for 5 min confirmed that the SAM had been removed successfully by THF. Therefore, a hydrogen-bond network film was formed throughout the oxide surface of $Cu(OH)_2$ nanoneedle arrays that permitted water passing through and blocked diesel simultaneously (see details in the Supporting Information, video S2). Subsequently, intruding pressure tests of the as-prepared mesh were evaluated, and the experiment intruding pressure values of water/diesel were calculated as follows

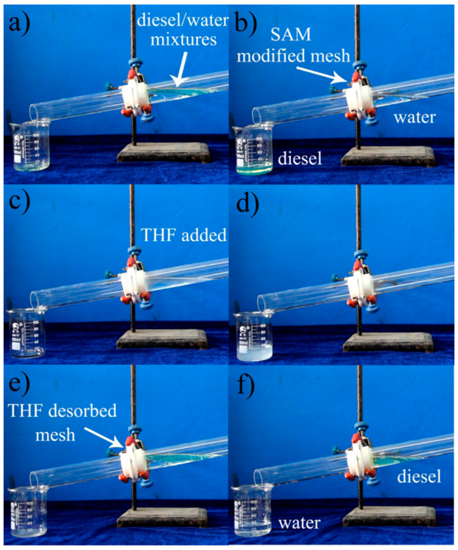

Figure 6. Oil/water separation studies of the SAM modified mesh, followed by being desorbed with THF: (a) The SAM modified mesh was fixed as above, and the device was placed with a tilt angle of 15°. The mixtures of diesel and water were poured into the upper tube; (b) diesel penetrated the mesh while water was blocked at the upper tube; (c) some THF was added into and mixed well with water; (d) the mixtures of THF and water passed through the mesh quickly; (e) the diesel and water mixtures were poured onto the mesh once more; and (f) water penetrated the mesh quickly while diesel was blocked in the upper tube.

$$P = \rho_l g h_{\max}$$

where ρ_l is the density of water/diesel, g is acceleration of gravity, and $h_{\max}$ is the maximum height of water/diesel that the as-prepared mesh can support. As shown in the Supporting Information, Figure S8, the maximum water height achieved on the SAM modified mesh exceeds 20 cm, and the intruding pressure of water is more than 1.96 kPa. After the mesh was desorbed with THF, the maximum diesel height is 18.92 ± 0.25 cm, and the average intruding pressure of the diesel is 1.53 ± 0.02 kPa. The intruding pressures of water/oil are relatively high compared to those of the earlier reports.[19,39] Therefore, the as-prepared mesh is capable of separating a large amount of oil/water mixtures.

3.6. Wettability Transition. The reversibility of the superhydrophobic-and-superhydrophilic switching mesh was studied by water contact angle measurements. The superhydrophobic mesh modified with a SAM of stearic acid could be easily converted to superhydrophilic via tetrahydrofuran desorption of stearic acid depending on its high solubility. Then, the superhydrophobicity was regained conveniently by immersing in an ethanol solution of stearic acid for forming a SAM on the mesh surfaces. The integrated switching process was fulfilled in 10 min and had been repeated 10 times successfully. The excellent reversibility of surface wettability was observed and is presented in Figure 7, which is greatly improved compared to the earlier works that required either a long period of time or complex steps. Consequently, it is a preferable choice for the large-scale application in oily wastewater treatment.

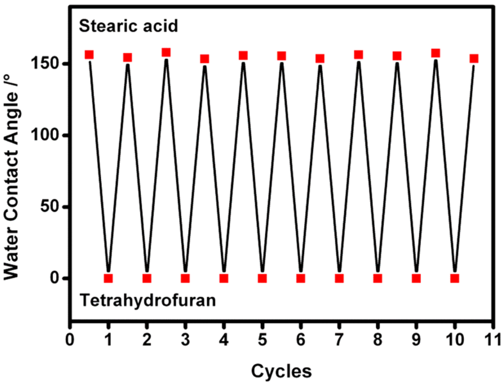

Figure 7. Reversibility of water contact angles on the as-prepared mesh by alternate immersion in THF and a stearic acid ethanol solution.

4. CONCLUSIONS

In conclusion, a controllably reversible oil/water separation mesh has been fabricated via a simple and scalable approach at ambient conditions. The film demonstrates superhydrophobicity and superoleophilicity after immersing in an ethanol solution of stearic acid for 5 min and then switches to the antifouling property for oils with underwater superoleophobicity by solvent manipulation of THF for 5 min. These reversible transitions can be manipulated repeatedly more than 10 times with almost no visible morphology variation. Importantly, this reversible mesh provides a candidate for controllably and efficiently separating a large amount of oil/water mixtures. Furthermore, this approach opens up new perspectives in manipulation of various metallic oxide substrates and applications in controllable oil/water separation, microfluidic devices, self-cleaning surfaces, and so on.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Robustness measurement, antifouling property test, sliding angle tests, solubility of stearic acid, underwater−oil contact angle measurement, diesel/water separation pictures, XPS spectrum of the THF desorbed mesh after diesel/water separation, intruding pressure tests, and separation videos of the as-prepared mesh, etc. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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