Facile Approach in Fabricating Superhydrophobic and Superoleophilic Surface for Water and Oil Mixture Separation

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ABSTRACT Metal copper mesh with superhydrophobic and superoleophilic surface had been successfully fabricated via a facile solution−immersion process. The hierarchical structure was prepared on the commercial copper mesh surface by etching with the nitric acid. After being modified by 1-hexadecanethiol (HDT), the as-prepared mesh indicated both superhydrophobic and superoleophilic property simultaneously. This as-prepared metal mesh could then be applied for oil and water mixture separation. The unusual wettability of the as-prepared mesh was stable in corrosive conditions, such as acidic, basic, and salt solutions. The solution−immersion method was simple, time-saving, and inexpensive and therefore exhibited great potential application.

KEYWORDS: separation • superhydrophobic • superoleophilic • copper mesh • corrosive condition

INTRODUCTION

Recently, the solid surface with the unusual wettability possessing not only superhydrophobic property (water contact angle higher than 150° and sliding angle less than 10°) but also superoleophilic property (oil contact angle less than 5°) (1, 2), had attracted great interest of research because of its enriched practical applications, including as a self-cleaning surface (3), as marine coatings (4, 5), as separation films for water and oil (6), and as functional microfluidic devices (7). The superhydrophobic surfaces are self-cleanable, which therefore indicated little adhesion to water droplets, similar to the case of the famous lotus leaf, on which the water droplet could roll off freely (8). As known from previous literature, the wettability of the lotus leaf was governed by both its surface chemical composition and micro−nano hierarchical structures (papillae-shape structures) on its surface (9–13). Hence, according to previous reported studies, the hierarchical structure surface modified by low surface energy materials could enhance the wettability of the surface and produce superhydrophobic surface (14). On the basis of this principle, several methods had been reported for constructing superhydrophobic surface, including chemical vapor deposition (15), sol−gel process (16), and solution−immersion process (17). Among these approaches, solution−immersion is one particularly good method because of its high efficiency and simplicity. However, very few works have been reported regarding fabrication of metal mesh in obtaining superhydrophobic and superoleophilic surface simultaneously for water and oil separation with this approach (18, 19).

Separation of water and oil mixture is considered as one difficult task due to some challenges associated with current systems, including low separation efficiency and involvement of complex separation instrument. To overcome these problems, the wettability of the surface was demanded to show both superhydrophobic and superoleophilic property simultaneously. With appropriate design, the surface that simultaneously displayed superhydrophobic and superoleophilic property could be obtained (20). Recently, many superhydrophobic and superoleophilic films applied in oil and water mixture separation had been successfully prepared, such as the polymer composite film of polyurethane film combined with polystyrene microspheres (21), the metal meshes made by the spray and dry process (18), the electrochemical deposition method (22), and the wet chemical approach (19). However, among these approaches and materials, the fabrication process usually was time-consuming and the surface wettability did not keep stable in corrosive liquids. These drawbacks dramatically limited their applications and practicability for mass production. Therefore, new preparation strategies for film that exhibits stable unusual wettability through simple, practical approaches are highly desirable.

Herein, we reported a new strategy in the preparation of superhydrophobic and superoleophilic copper mesh surface through solution−immersion in nitric acid solution and sequential modification with HDT. The as-prepared copper mesh could be used for the separation of water and oil through simple, time-saving, and inexpensive process. The morphology and the composite of the resulting mesh surface were characterized by scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS). The wettability

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was investigated by drop shape analysis system. The effect of pore size on the wettability and the stability of the surface wettability of the as-prepared mesh in acidic, basic, and salty solutions were also studied in detail.

EXPERIMENTAL SECTION

2.1. Materials. The copper meshes with pore sizes ranging from 44 to 490 μm were purchased from Daoxu Company in China. Nitric acid (HNO_3, 68 wt % in water), sodium chloride (NaCl), hydrochloric acid (HCl, 37 wt %), and sodium hydroxide (NaOH) were analytical grade. 1-Hexadecanethiol (HDT) was obtained from Aldrich. All the chemical reagents were used as received without any purification. In all process, absolute ethanol and deionized water were used.

2.2. Preparation of Metal Meshes with Superhydrophobic and Superoleophilic Property. The commercial copper meshes with different pore sizes were dipped into 4.0 M HNO_3 solution for 4 min. The surface of copper meshes was etched by the HNO_3 because of the reaction between Cu and HNO_3. The resulting copper meshes were washed by deionized water and absolute ethanol, and then were immersed into 1.0 mM HDT ethanol solution for 1 h to graft HDT. After the surfaces were rinsed with absolute ethanol and dried by nitrogen, the wettability of the as-prepared copper mesh surfaces was determined through contact angle measurements.

2.3. Stability of the Wettability of the As-Prepared Metal Mesh. To investigate the stability of the surface wettability of the as-prepared metal meshes in acidic and basic solutions, the as-prepared metal meshes were dipped into the solutions with pH values ranging from 1 to 14 for 1 h. Moreover, to determine their stability in salt solution, the as-prepared metal meshes were dipped into 0.1 M NaCl solution for 24 h. After being washed by absolute ethanol and dried by nitrogen, the wettability of the as-prepared copper meshes was characterized by contact angle measurements.

2.4. Characterization. Scanning electron microscope (SEM) images to investigate the morphology of the meshes were collected on a JEOL JEM-6700F at 3 KV. The samples were sputtered with a layer of platinum (~2 nm thick) prior to imaging to improve conductivity. Oil and water contact angles were measured by the drop shape analysis system (DSA 10 MK2, KRUSS) at ambient temperature. Three microliters of deionized water or 10.0 μL of diesel oil was dropped onto the samples and the static contact angle was determined by the average of at least five measurements taken at different positions on each sample. The sliding angle was defined as the critical angle where a water droplet with a certain weight begins to slide down the inclined as-prepared metal meshes. X-ray photoelectron spectroscopy (XPS) using Mg Kα excitation (1253.6 eV) was collected in a VG ESCALAB MKII spectrometer. Binding energy calibration was based on C 1s at 284.6 eV.

RESULTS AND DISCUSSION

The wettability of the original copper with the pore size of 125 μm and the as-prepared copper mesh with the pore size 135 μm was investigated through water contact angle measurements (Figure 1). The original copper mesh had a water contact angle of less than 90° (Figure 1a), which indicated hydrophilic properties because of the native oxidized layer on the surface. However, after grafting HDT, which could be self-assemble on the metal mesh surface to reduce the surface energy (23), the water contact angle of the copper mesh increased up to 125° ± 1° (Figure 1b), which showed hydrophobic property. To construct the superhydrophobic surface, the dilute HNO_3 solution was first applied to etch copper mesh for a short time and then HDT was grafted. As a result, the water contact angle of the as-prepared mesh sufficiently increased up to 153° ± 1° (Figure 1c), and the water sliding angle on the as-prepared mesh was found to be less than 5° (Figure 1d), indicating the formation of superhydrophobic surface. This result clearly indicated the successful preparation of the superhydrophobic surface on the copper mesh surface through the solution−immersion process.

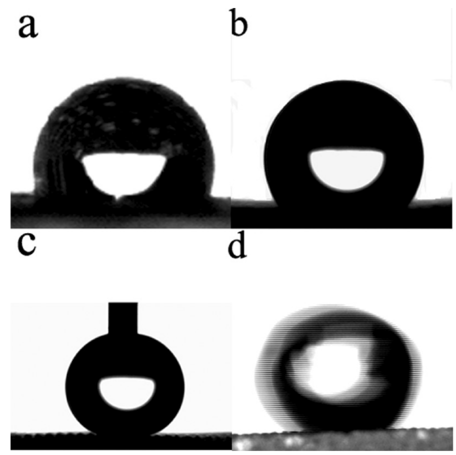

FIGURE 1. Water contact angles (WCA) investigation: (a) WCA of the original copper mesh was about 78° ± 1°. (b) WCA of the original mesh modified by HDT was about 125° ± 1°.(c) WCA of the as-prepared mesh was about 153° ± 1°.(d) The sliding angle of water on the as-prepared mesh.

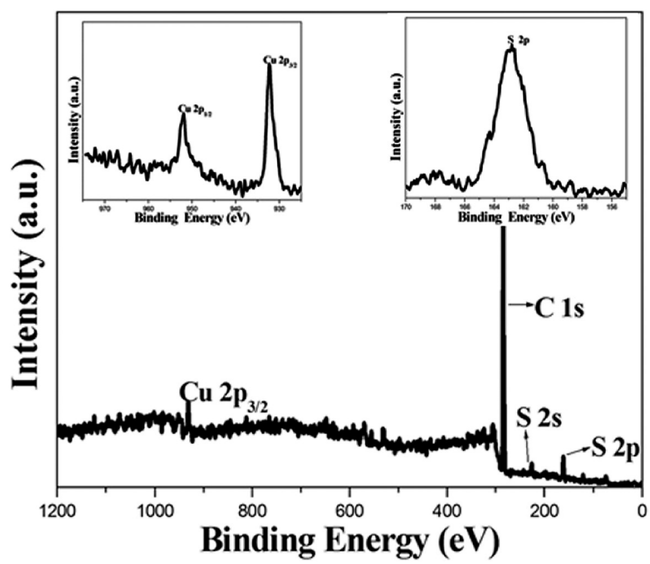

FIGURE 2. XPS spectra of the as-prepared mesh after being grafted by HDT.

X-ray photoelectron spectroscopy (XPS) is a sensitive tool in determining the surface chemical compositions. Hence, the XPS spectra of the as-prepared metal mesh were shown in Figure 2. The peak at 284.6 eV corresponded to the binding energy of C 1s. The peak at 932.4 eV corresponded to the binding energy of Cu $2p_{3/2}$, and in the left inset image, we could see the peak of Cu $2p_{1/2}$ appeared at 951.9 eV. The peak at 161.9 eV was the characteristic signals of S 2p (right inset image), which suggested that HDT had been successfully grafted on the surface of the etched mesh.

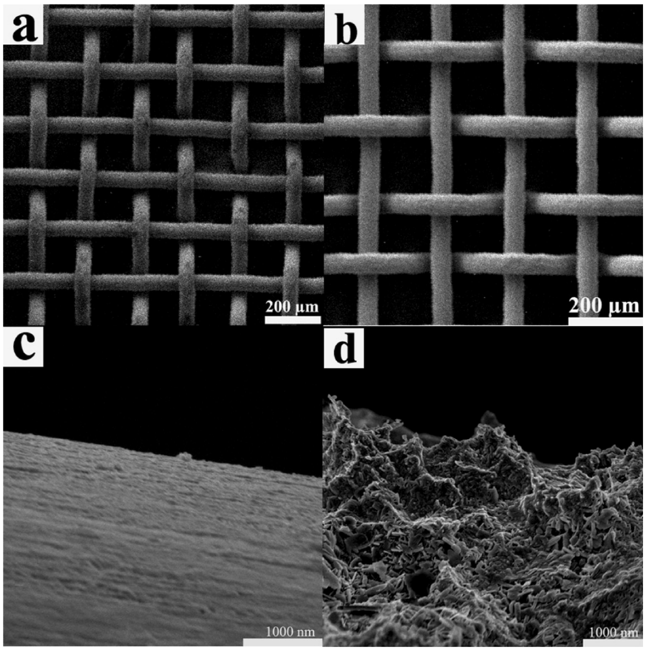

FIGURE 3. SEM images of the initial copper mesh (a, c) with pore size of 125 μm and the as-prepared mesh (b, d) with pore size of 135 μm.

It was well-known that surface geometrical structure played an important role in construction of the superhydrophobic surface, similar to the lotus leaf's self-cleaning property resulting from its micro- and nanostructure (24). The surface morphology of our copper mesh was also investigated. As shown in Figure 3, significant differences were observed between the initial metal mesh and the as-prepared metal mesh. The low magnified SEM image (Figure 3a) showed that the initial mesh was knitted by copper wire and the average pore size was about 125 μm. After it was etched (Figure 3b), the average pore size was increased to 135 μm. And the structure of the copper mesh kept the original shape without decomposition. Moreover, the high magnified image (Figure 3c) showed the initial mesh surface structure was smooth. The etched copper wire substrates (Figure 3d), on the other hand, indicated the formation of many nano-hill-like structures on the surface because of the reaction (1).

$$Cu + H^{+} + NO_3^{-} \rightarrow Cu^{2+} + NO + H_2O \qquad (1)$$

The Cassie–Baxter eq 2 (25) and Wenzel eq 3 (26)

$$\cos\theta_{\mathrm{r}} = f_1 \cos\theta - f_2 \qquad (2)$$

$$\cos\theta_r = r\cos\theta \qquad (3)$$

could be applied in explaining the relationship between the surface structure and the surface contact angle, where θ_r and θ represented the contact angles of a rough surface and a native flat surface while the f_1 and f_2 were the fraction areas of a liquid droplet in contact with surface and air on the surface, respectively (i.e., $f_1 + f_2 = 1$), and r was the roughness factor. According to the eq 2, the water contact angle increased with larger surface coverage and roughness of the micronanostructure with higher f_2 value. It had been demonstrated in literature that the hierarchical structures could effectively increase the roughness of the surface and hence increase the water contact angles on these surfaces (27–31). Thus, according to the eq 2, the f_2 value of the rough surface mesh was rapidly increased to 0.78, which explained the observed superhydrophobicity of the etched copper mesh, which is possible attributed to the surface roughness of as-prepared mesh as shown in Figure 3d. This rougher surface was favorable to trapping a large amount of air in voids and thus induced the superhydrophobic surface.

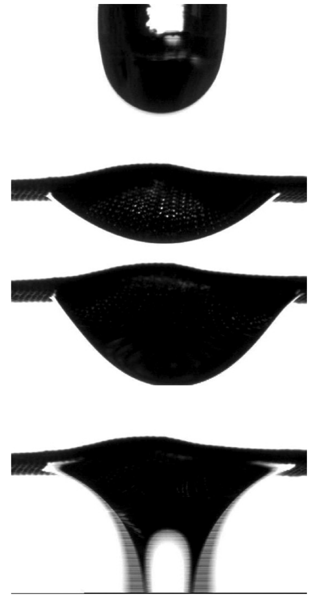

FIGURE 4. Permeating behavior of diesel oil droplet on the as-prepared mesh.

According to the eq 3, the surface oleophilicity can be enhanced by increasing the surface roughness because of the original copper mesh was oleophilic materials. Here the as-prepared mesh showed superoleophilicity. As shown in Figure 4, when diesel oil droplet was dropped on the as-prepared mesh surface, it penetrated through the mesh freely. In addition, the water sliding angle on the as-prepared mesh was less than 5° (Figure 1d), suggesting that the water droplet on the surface was not stable and could roll off freely. Thus, the as-prepared mesh, with the exhibited superhydrophobic and superoleophilic property, could be applied to separate water and oil mixture. This experiment was performed as shown in Figure 5. When the mixture of water and diesel oil was poured onto the as-prepared mesh, the oil quickly permeated through the mesh and dropped into the tube. Meanwhile, all of the water flowed along the outside of the test tube into the beaker below: highly effective separation of water and oil mixture was achieved using the as-prepared mesh.

It has been reported by Jiang and co-workers (18) that the wettability of the mesh depended on the pore size. The pore size of the metal mesh from 80 to 200 μm had been applied to separate water and oil mixture (22). In this study,

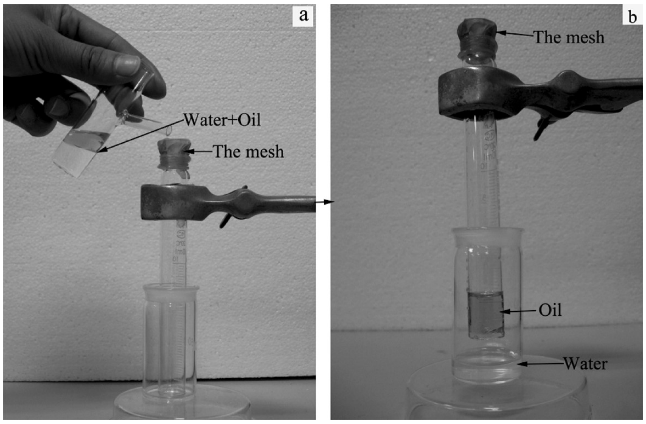

FIGURE 5. Simple instrument fabricated by ourselves was used to separate the mixture of diesel oil and water.

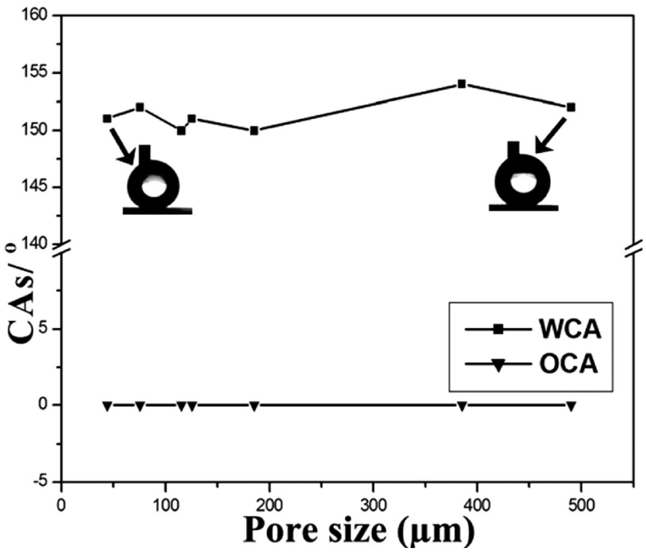

FIGURE 6. Relationship between pore size and contact angles of water and oil of the as-prepared meshes.

the meshes with the pore sizes ranging from 44 to 490 μm before being etched were selected to be investigated. Figure 6 illustrated the relationship between the pore diameter and the contact angles of water and oil of the as-prepared meshes. The experiment results showed that all the water contact angles were above 150°, while the oil contact angles were close to 0°, which indicated that these meshes displayed superhydrophobicity and superoleophilicity simultaneously. When the mixture of water and diesel oil was poured onto these the as-prepared meshes, the water droplets could easily roll off and the diesel oil droplets could penetrate through all the meshes freely. The results revealed that the meshes with the pore sizes from 44 to 490 μm could be used for separation of oil and water mixture.

Although some similar separation films had been successfully prepared previously (19), the unusual wettability was often sensitive to environment, which limited their applications. Particularly, in corrosive liquids, the unusual wettability surface could be destroyed in a short time. To investigate the stability of the as-prepared mesh, the material with pore size of 135 μm was dipped into the corrosive solutions, including the acidic or basic solutions for 1 h or

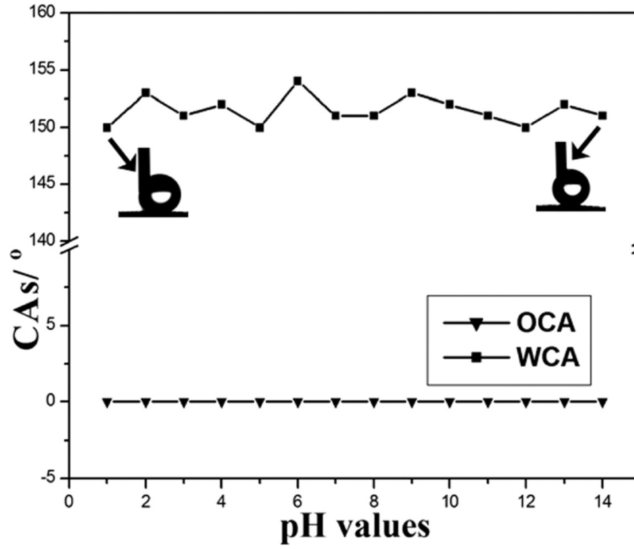

FIGURE 7. Relationship between pH values and contact angles of water and oil of the as-prepared meshes.

FIGURE 8. Water contact angle of the as-prepared mesh after being dipped in NaCl solution.

salt solutions for 24 h. After the meshes were rinsed by ethanol and dried over nitrogen, the color of all the as-prepared metal meshes did not change. In comparison, the initial metal mesh changed from amaranth to brown because of the corrosion of metal copper in the air and water interface. The stable wettability was tested through oil contact angles and water contact angles as shown in Figure 7 (indication of the correlation between the pH values and the contact angles). This diagram indicated that all the water contact angles were larger than 150°, and oil contact angles were close to 0° in a wide pH range (from 1 to 14), which suggested good stability of the wettability. Furthermore, the as-prepared mesh was also treated with NaCl solution for 24 h; the superhydrophobic property of the as-prepared metal mesh could also remain stable (Figure 8), and the diesel oil droplets could permeate through freely. These results revealed the good stability of the superhydrophobic and superoleophilic property of the as-prepared copper meshes, which made them attractive materials for oil–water separation.

CONCLUSIONS

In summary, the superhydrophobic and superoleophilic surface on common industrial copper mesh was achieved using nitric acid solution as etchant and grafting with HDT on the surface. The as-prepared mesh can be applied as effective materials for the separation of water and diesel oil mixture. Compared to other materials for separation of water and oil, the reported process was simple, time-saving and inexpensive. Moreover, the process is effective for a large range of materials with pore sizes from 44 to 490 μm with great stability under acidic, basic and salt conditions. Therefore, this reported process exhibits the strong potential for industrial production.

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