A Facile Electrodeposition Process for the Fabrication of Superhydrophobic and Superoleophilic Copper Mesh for Efficient Oil–Water Separation

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ABSTRACT: A superhydrophobic and superoleophilic copper mesh with excellent oil–water separation efficiency was successfully fabricated via electrodeposition and then surface modification with lauric acid. The surface morphologies, chemical composition, and wettability were characterized by means of scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FT-IR) spectroscopy, and water contact angle (WCA) measurements. It was found that the as-prepared surface is both superhydrophobic and superoleophilic, with static WCA values as high as 155.5° ± 3° and an oil contact angle (OCA) of 0°. Furthermore, the as-prepared surface exhibited excellent oil–water separation efficiency including petroleum, toluene, hexane, gasoline and diesel, even after being recycled 10 times. In addition, the as-prepared copper mesh shows self-cleaning character with water and chemical stability. This study provides a facile, inexpensive, and environmentally friendly route to fabricate large-scale and excellent oil–water separation surface with high separation efficiency for a great number of potential applications.

1. INTRODUCTION

In the past few years, with the increase of oil spill accidents and industrial oily wastewater, oil–water separation has become a worldwide challenge and has aroused much attention.1–4 To resolve these water pollution issues, many approaches have been used for the treatment of oil–water pollution, including filtration, oil skimmers, centrifugal machine, precipitation tanks, magnetic separations, flotation technologies, oil-absorbing materials, and combustion.5–11 However, most of the methods involve harsh conditions, such as expensive equipment, complex devices, complicated processing steps, high processing cost, long processing time, and so on. Taking all factors into account, separation treatment stands out from the rest as a simple, universal, scalable approach for valid removal of oil from water.

In addition, surfaces with superhydrophobic and superoleophilic wettability have triggered unprecedented research excitement in the field of filtration.12–15 Many plants and insects exhibit excellent superhydrophobicity, such as lotus leaves, rose petals, marigold petals, water striders, butterfly wings, rice leaves, mosquito eyes, and so on. Taking inspiration from nature, superhydrophobic surfaces are fabricated by simulating typical structures of plant surface and considering chemical composition simultaneously.16–20 Also, materials with special wettability and micro-nanoscale structures have attracted increasing attention for oil–water separation. This filtration process needs excellent wettability materials, which are both superhydrophobic (water contact angle (WCA) of >150°) and superoleophilic (oil contact angle (OCA) of <5°). Oil can selectively penetrate through the mesh while water is blocked. Designing and fabricating coatings with special wettability would be a facile and effective way to solve the problem of oil–water separation.21–23

In the past several years, numerous methods have been reported for the manufacture of the superhydrophobic surface for oil–water separation on metal meshes such as chemical etching24, electro-spinning25,26, layer by layer,27,28 self-assembly,29,30 sol–gel method,31–36 ARGET-ATRP,37 zeolite-coated method,38 self-assembly of block co-polymers,39 chemical vapor deposition (CVD) method,40–42 electrodeposition, and so on.43,44 Meanwhile, many scholars have focused on the research of underwater superoleophobic surface. Dudchenko et al.45 have demonstrated a membrane-based and fouling-free oil/water separation method that couples carbon nanotube poly(vinyl alcohol) underwater superoleophobic ultrafiltration membranes with magnetic Pickering emulsions. Dunderdale et al.36 highlighted the pH-responsive superoleophobicity of pDMAEMA brush surfaces, which gives excellent oil drop mobility and low adhesion underwater. However, to better resolve oil–water separation in industry, the method of facile and large-scale preparation must be developed.

Copper mesh is widely used for the separation of oil and water, because of its porous structure, which is composed of microfibers. Based on the above-mentioned discussions, we reported a simple, highly efficient, and low-cost route to preparing superhydrophobic copper meshes. In this research, copper meshes with superhydrophobic and superoleophilic surfaces were fabricated by electrodeposition and then modified with lauric acid. The electrodeposition process takes place at atmospheric pressure, using a solution of 0.2 M sulfuric acid and 0.15 M copper sulfate that were cured under ambient conditions.
conditions. The superhydrophobic copper meshes can be easily combined with an independent device, which acts as a filter, forming a barrier that allows oils to pass through while repelling water.

2. EXPERIMENTAL METHODS

2.1. Materials. The 40 mm × 10 mm × 2 mm copper plate and copper mesh (120, 150, and 180 mesh woven from 0.08, 0.07, and 0.05 mm diameter wire, respectively) were obtained from Hebei Shijiazhuang Yuanpeng Metal Manufacturing Works. The meshes had pore diameters of 124, 100, and 80 μm, respectively. Lauric acid (C₁₂H₂₄O₂, 97.5%, Tianjin Guangfu Fine Chemical Research Reagent Institute), copper sulfate (CuSO₄, 99%, Tianjin Zhiyuan Chemical Reagent Institute). All other chemicals were purchased from Beijing Chemical Works, were of the highest commercially available grade, and were used without further purification. This includes hydrochloric acid, anhydrous ethanol, chloroform, Methylene Blue, toluene, petroleum ether, and hexane.

2.2. Sample Preparation. Copper plate and meshes were ultrasonically rinsed for 5 min in a solution of diluted hydrochloric acid, anhydrous ethanol, and distilled water to remove the oxide film and organic matter on the surface of the copper mesh, respectively. The obtained mesh then was used as the cathode and a copper plate was used as the anode. The reaction solution was contained 0.2 M sulfuric acid and 0.15 M copper sulfate. Finally a direct current (DC) voltage of 4.0 V was applied to the two electrodes for different times (100, 150, 200, 250, 300, 350, and 400 s) with a distance of 3 cm. At the end of the experiment, the sample was washed with a sufficient amount of distilled water. The resulting copper meshes then were dried in a vacuum oven at 60 °C for 20 min.

2.3. Surface Modification. The prepared copper meshes were immersed in a 1.5 × 10⁻³ M ethanol solution of lauric acid and for 12 h under ambient conditions. The –COOH groups can be chemically adsorbed onto the native oxide surface of copper clusters and the surface-active molecules form a self-assembled monolayer. The resulting copper meshes then were dried in a vacuum oven at 60 °C for 10 min.

2.4. Sample Characterization. The water/oil contact angle (WCA/OCA) values were measured by using a contact angle meter (Model OCA 20, Dataphysics, Germany) at room temperature. Water droplets (3 μL) were carefully dropped onto the surfaces, and the average static contact angle (CA)
value was obtained by measuring five different positions of each surface. The surface morphologies of as-prepared samples were examined via field-emission scanning electron microscopy (SEM) (Model EVO 18, Zeiss) and atomic force microscopy (AFM) (Model Dimension Icom, Bruker). The chemical composition of the samples was characterized using an X-ray photoelectron spectroscopy (XPS) system (Model XR50, SPECS, Japan) and Fourier transform infrared (FT-IR) spectrophotometer (JASCO, Japan). Oil concentrations were measured by an automatic infrared oil analyzer (Model JLBG-158, Xi’an Yima Opto-Electrical Technology Co., Ltd., China).

2.5. Oil–Water Separation Apparatus. The device consists of two quartz tubes, which are 100 mm and 150 mm in length, respectively, and 30 mm in diameter. The as-prepared copper mesh was fastened between the quartz flange fixtures by four screws, and the device was positioned at a tilt angle of ~20°. The oil/water mixture was poured onto the mesh. The separation was achieved driven by gravity.

3. RESULTS AND DISCUSSION

3.1. Surface Morphology. The wettability of solid surfaces is strongly dependent on both the geometrical structure and the chemical composition. Figures 1a–e show SEM images of the woven copper mesh formed using ~100-μm-diameter wires as substrates. The typical image of a copper mesh substrate that has been knitted by copper wires with a pore diameter of ~100 μm is shown in Figure 1a, which indicates that the pristine mesh has a smooth surface. The morphology of the copper mesh was greatly influenced by the electrodeposition time. Figure 1b shows the SEM image of the copper mesh with an electrodeposition time at 100 s. It can be clearly seen that the surface was relatively smooth, with only some small spherical particles. No obvious submicrometer and nanoscale particles are observed in the magnified images. As shown in Figure 1c, as the electrodeposition time increased to 150 s, the microscale particles on the surface of the copper mesh became rougher, and the spherical particles were increased. Figure 1d shows the SEM image of the copper mesh after an electrodeposition time at 250 s, spherical particles several hundred nanometers in size were uniformly dispersed on the surface of the wires. It can be seen that the pristine mesh wires has been completely covered by circular particles. There is a large amount of micro-nanoscale circular particles, which can capture a large amount of air. Therefore, it provides the geometric conditions for the formation of hydrophobicity. However, as the time increases to 300 s (Figure 1e), the size of the particles was much larger than that observed at 250 s, and the rough micro-nanoscale structure, which was slightly damaged because of spherical submicrometer structure, is replaced by a larger crystal structure with diameters of 5–10 μm. Longer electrodeposition times encouraged the formation of larger surface features that, in some locations, resembled broccoli structures. It can be seen from Figure 1f that these broccoli structures grew orthogonally out of the mesh wire walls. These findings show that an increase in electrodeposition time leads to a change in morphology, resulting in a transition of the wetting state from hydrophobic to superhydrophobic. The microsized spherical particles, in combination with the nanoscale granular protuberance, endowed a hierarchical composite structure to the mesh that possessed superhydrophobic behaviors. Such micro-nanoscale hierarchical structures can help support water droplets and are necessary for superhydrophobic surfaces. From the surface morphology of the copper meshes, we deduce that the ideal electrodeposition time is 250 s.

Furthermore, the three-dimensional (3-D) morphology of the as-prepared copper mesh has been characterized by AFM. Figure 2 shows the AFM images and surface roughness values of the copper-coated mesh. Taking into account the fact that the copper wire is a curved surface, we can only roughly calculate the root-mean-square surface roughness (RMS). The height of the micro-nanoparticles is concentrated in the range of 0–1.1 μm. The surface roughness of the coating is 993 nm (RMS value).

3.2. Chemical Characterization. XPS is used to test the chemical composition of the thin film of the as-prepared surfaces modified after electrodeposition. Figure 3 shows the XPS spectrum of the as-prepared superhydrophobic surface after modification with lauric acid. It reveals the presence of carbon, oxygen, and copper on the as-prepared surfaces. One can see the strong peak of C 1s at 284.78 eV and O 1s at 531.2 eV. Figure 3c presents the Cu 2p XPS spectrum of the as-prepared copper mesh surface. This region includes one highlight peak at 933.5 eV; therefore, elemental copper is expected to exist on the as-prepared mesh surface after electrodeposition. Figures 3b and 3d reveal the presence of carbon and oxygen on the as-prepared surfaces. One can see the strong peak of C 1s at 284.78 eV and O 1s at 531.2 eV. Compared to the untreated copper mesh, the contents of elemental carbon and oxygen were obviously increased on the as-prepared surfaces, which were treated with lauric acid, which indicated that the as-prepared coating on the as-prepared copper mesh surface was copper, and the surface was successfully modified with lauric acid.

The sample was modified to reduce the surface energy after the electrodeposition of copper. In order to confirm the presence of lauric acid on the coated surface of the copper mesh, FT-IR spectra was used. Figure 4 shows FT-IR spectra of the electrodeposition mesh before and after being modified by lauric acid. Compared to the sample before modification, many absorption bands are detected on modified sample surface, which indicates that the copper mesh surface has been
successfully modified. The FT-IR spectrum exhibits typical absorption features of the coupled −COO− stretching vibrations at 1701 cm\(^{-1}\), CH\(_3\)− stretching vibrations at 2920 cm\(^{-1}\), and CH\(_2\) stretching vibrations at 2855 cm\(^{-1}\). It is known that the CH\(_3\) group had a surface energy of 24 mJ/m\(^2\) and the CH\(_2\) group had a surface energy of 31 mJ/m\(^2\), both of which were widely used to reduce the free energy. The FT-IR spectra indicated that the lauric acid was bound to the copper mesh surfaces.

### 3.3. Surface Wettability

#### 3.3.1. Formation of Superhydrophobicity

A combination of SEM, XPS, and FT-IR characterizations shows that the micro-nanoscale hierarchical structures were created and that low-surface-energy materials were successfully prepared on the surface of copper mesh through this method. It was expected that the micro-nanoscale hierarchical composite structure and chemical component made the as-prepared mesh possess superhydrophobicity, and the surface wettability was evaluated by CA measurement.

Figure 5a shows that the water contact angle (WCA) of the pristine copper mesh was 79°. For the copper mesh after an electrodeposition time of 250 s only and the sample modified by lauric acid only, the WCAs were measured to be 118° and 120°, respectively, as shown in Figures 5b and 5c. In contrast, an oil droplet (toluene) with a low surface tension quickly spreads on the surface and permeates through it, exhibiting a highly oleophilic property. Figure 5d shows the image of a water droplet (3 μL) on the as-prepared copper mesh. Its WCA approaches 155.5° ± 3°, indicating that the surface has superhydrophobicity.

The resulting meshes transitioned to a dull red color from their pristine purplish-red color and showed superhydrophobicity, as shown in Figure 6a. When the as-prepared superhydrophobic copper mesh and original hydrophilic copper mesh were immersed in water, a plastron (air pockets) that was indicative of a robust Cassie–Baxter state was formed on the as-prepared mesh surface only. The submerged as-prepared copper mesh looked like a silver mirror when viewed at a glancing angle, as shown in Figure 6b. To further illustrate that the as-prepared mesh has better reflectance, two samples were immersed in water again. The reflectance of these two samples was measured in the visible light range. As shown in Figure 6c, the as-prepared sample had a reflectance of ∼40%. However, the original sample had a reflectance of ∼8%, because of the reflectance of light at the air layer trapped on the surface. This trapped air can effectively prevent wetting on the as-prepared copper mesh surface under water. After several minutes of
Figure 5. Surface wettability of the pristine and as-prepared mesh: (a) the photograph of water droplet on the surface of pristine copper mesh; (b) the photograph of water droplet on the surface of copper mesh after 250 s of deposition only; (c) the photograph of water droplet on the surface of copper mesh modified by lauric acid only; and (d) the photograph of water droplet on the surface of as-prepared copper mesh.

immersion testing, the material surfaces were completely dry and still displayed a large CA (>150°) with water droplets.

3.3.2. Effect of the Electrodeposition Time on Wettability. The fabrication of nanostructures on a copper mesh by electrodeposition is an inexpensive and facile technique; however, this method always needs to accurately control the deposition time and solution concentration, which play important roles in crystal growth. Because the roughness and crystallinity are positively related. Thus, we explored the effect of different electrodeposition times on wettability. The samples were prepared under 100, 150, 200, 250, 300, 350, and 400 s of deposition time. Figure 7a shows the relationship between electrodeposition times and static CAs on the as-prepared surface. The CA value reached 134° after a deposition time of 100 s. With the time was extended to 250 s, the CA value reached 155.5° ± 3° and the sliding angle reached 13° ± 4°. Meanwhile, the advancing and receding angles shown in Figure 7b were measured, still showing very good hydrophobic property. Thus, the as-prepared copper mesh possessed superhydrophobic with low adhesion character. According to the test results, we deduce that the ideal electrodeposition time is 250 s.

In addition, we find that the pore size is also important, because different pore sizes can result in different wetting performances. Therefore, we chose the above-mentioned 150 mesh as a contrast test and carried out another two groups of experiments to investigate the relationship between pore size and wetting performance. Figure 7 displays the WCAs as a function of the electrodeposition time of the electrochemical deposition (all of three copper meshes were obtained with the same immersion time and were modified with the same concentration solution of the lauric acid)1. As shown in Figure 8, for the maximum pore size (120 mesh) of copper mesh, an increase in plating time results in a gradual increase in CA values. However, the hydrophilic state remained (WCA < 65°) after an electroplating time of 400 s. The resulting electrodeposition is deposited on the copper wire—the larger the pore size, the smaller the effective deposition area will be—so large pore size is not conducive to building superhydrophobic micro-nanostructures. To get the superhydrophobic state, a longer plating time may be required. In contrast, for the copper mesh (180 mesh) with a minimum pore size, an opposite trend in CA is observed: an increase in plating time results in a gradual decrease in CA values. This is because a smaller aperture will provide better microscale roughness for the copper mesh, which is an essential necessity to obtain the superhydrophobicity. Compared with copper mesh (180 mesh) with a pore size of 80 μm, the copper mesh (150 mesh) with a pore size of 100 μm had a larger pore size. Thus, copper mesh with a larger pore size is more favorable for the permeation of water. Taking into account the properties of velocity, plating time, and wetting, we can determine that the optimal pore size is ∼100 μm.

3.4. Self-Cleaning Effect. As a comparison, self-cleaning tests were carried out with two types of copper mesh, including pristine and as-prepared, as shown in Figure 9. Here, the graphite is used to represent the conventional pollutant. Removal of fine graphite powder on the superhydrophobic surface is documented in the above images (see Figures 9a−c). For graphite particles, excellent self-cleaning properties were observed. The graphite particles are wetted by the water and imbibed into the droplet as it rolls off the surface. Superhydrophobicity is essential for such self-cleaning particles. When the pristine copper mesh was used, water droplets adhered to the surface and could neither imbibe the particles nor roll off the surface, as shown in Figure 9b. Thus, no self-
cleaning properties were observed on the pristine copper mesh surface.

3.5. Chemical Stability. It is well-known that Cassie-like wetting is temporary under water. We have explored temporal changes to the CA value over extended periods. We put the as-prepared sample into the water for different time periods and then removed it and immediately measured the CA. Figure 10 shows the relationship between the soaking time and static CA. After 2 h of soaking, the sample can keep a CA value of $140^\circ \pm 3^\circ$ and has good hydrophobicity. However, after the sample was dried after a certain period of time, its original superhydrophobicity was again restored. Therefore, the as-prepared sample could exist stably in the water and lauric acid does not dissolve into the water phase.

In order to further illustrate the stability of samples prepared under corrosive environment, the sample was estimated by measuring the static WCA values for samples that were immersed in aqueous solutions for 10 min at various pH values (ranging from 1 to 14). Figure 11 shows the relationship between the pH values and the static CA; the measured static CA ranged from $143^\circ \pm 3^\circ$ to $152^\circ \pm 2^\circ$. After immersion in the corrosive solution, the samples still have excellent hydrophobic proprieties. The results indicate that the as-prepared surface has good chemical stability in aqueous solutions of most acidic, alkali, and some aqueous salts.

4. SEPARATION OF OIL AND WATER

Because of a combination of superhydrophobicity and superoleophilicity, the as-prepared mesh has great potential to be applied to oil–water separations. The oil–water separation experiment was performed as shown in Figure 12. The as-prepared copper mesh was fixed between two quartz tubes. In order to ensure the sealing performance, there are two sealing rings in the junction of the two quartz tubes. Compared to water, oil has a lower density. Therefore, the measured oil floats on the water, with no contact with the copper mesh.

The short glass tube was replaced by a longer bent one, and the device was placed at a tilt angle of $\sim 30^\circ$. In this experiment,
25 mL of petroleum ether (dyed with oil red) was poured into 25 mL of water (dyed with Methylene Blue) contained in a beaker, and the petroleum ether floated on top of the aqueous phase, because of its lower density. When the mixture of petroleum ether and water with a total volume of 50 mL was poured into the quartz tube, the petroleum ether penetrated the mesh and flowed down the beaker underneath, while the water was retained in the upper glass tube. During the oil−water separation process, no artificial external force was employed, indicating its easy operation and low energy costs. Note that the ubiquitous water loss induced by the water adhesion on the surface of glass vessels during the oil−water separation process was not considered in the efficiency calculations.

Oil−water separation efficiency was used to quantitatively describe the oil−water separation ability of the as-prepared copper mesh. Because the superhydrophobic layer is robust, the as-prepared mesh can be reused. Therefore, we investigated the suitability of a copper mesh for the separation of other oils from water. The recycling ability was also investigated by taking the petroleum ether/water mixture as an example. We measured the separation efficiency of the as-prepared copper mesh with different types of oil, such as petroleum, toluene, hexane, gasoline, and diesel. The oil separation efficiency ($R$, expressed as a percentage) was then calculated based on the following equation:

$$R (%) = \left(1 - \frac{C_p}{C_O}\right) \times 100$$

Herein, $C_O$ and $C_p$ are the oil concentrations in the pristine oil−water mixture and after the separation of water, respectively. The oil concentration were measured using an automatic infrared oil analyzer. As shown in Figure 13, different types of oils such as gasoline, diesel oil, petroleum, toluene, and hexane, can be separated using the above apparatus at an efficiency of more than 93%. The stability of the as-prepared mesh differs only slightly, even after 10 cycles, indicating its general suitability for various oil−water separations. After 10 separate experiments, the sample was rinsed with sufficient alcohol and distilled water to remove the surface of the oil, and then it was dried under atmospheric conditions for 10 min. Measuring the CA again shows that the CA approached 148° ±
3°, which indicates that the organic solvent will not damage the structure and chemical composition of the hydrophobic surface. There is a good combination of the laurel acid and the rough surface; therefore, the lauric acid does not dissolve into the oil phase.

5. CONCLUSIONS

A facile method to fabricate a copper mesh with selective wettability has been demonstrated. Superhydrophobic and superoleophilic meshes were fabricated by an electrodeposition method and then modified on lauric acid coatings. The as-prepared copper mesh surface not only exhibits superhydrophobicity, with a water contact angle (WCA) of 155.5° ± 3°, but also superoleophilicity with an oil contact angle (OCA) of 0°. In addition, a series of oil/water mixtures, such as petroleum ether/water, hexane/water, toluene/water, gasoline/water, and diesel/water, were observed to be separated by the mesh, with a separation efficiency of >93%; it remained high even after 10 cycles. Furthermore, the as-prepared superhydrophobic copper mesh shows self-cleaning character and chemical stability. The fabrication process is facile, inexpensive, and environmentally friendly, and suited to large-scale applications. Because of the excellent oil/water performance, the as-prepared copper meshes have potential applications in treating industrial oil–water mixtures and environmental oil spills.

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