One-step electrodeposition to fabricate superhydrophobic coating and its reversible wettability transformation

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Abstract

A one-step electrodeposition method was utilized to fabricate coatings with switchable wettability on stainless steel meshes to extend the application of materials in the intelligent material industry. This method did not involve low surface energy materials and had advantages of simple and good repeatability. Through changing pH value, deposition temperature and voltage, the relationship between morphology and wettability of the as-prepared coatings were studied. The SEM results show numbers of particles on the coatings under the optimum condition and some of them aggregated into micro-pine hierarchical structures. The coatings achieved superhydrophobicity with a contact angle of 155.5°. After being placed at 450 °C for 3 h, the superhydrophobic film turned into superhydrophilic. The film regained superhydrophobicity after hydrothermal treatment in glucose aqueous solution, which exhibited a reversible transition between superhydrophobicity and superhydrophilicity. In addition, the superhydrophilic coatings could be used to separate light oil, such as diesel, gasoline, toluene, benzene and lubricants, excellent oil-water separation ability of 95%.

1. Introduction

Special wettability includes superhydrophobic, superhydrophilic, superoleophobic and superoleophilic, which can be applied to anti-corrosion, anti-icing, self-cleaning, oil/water separation, drug delivery, and targeted release, to develop the controllable intelligent materials [1–7]. Coatings with switchable wettability display different wettability when the environment changes, such as temperature, light, pH, solvent, electricity, which could be used to develop smart material versatilely. [8–13] Generally, common superhydrophobic coatings are liable to gather electrostatic charges in practical application [14], lead to fire or explosion. If the coating is conductive, then charges could be transferred and concentration would be eliminated. Coatings displaying different wettability to temperature can be used in oil–water separation, microfluid device, functional textiles, filters and controlled drug release [10, 15, 16]. Furthermore, this kind of special coatings also can be utilized for anti-corrosion, anti-fog, anti-icing, drag reduction, pharmaceutical, self-cleaning, water recycling, shielding, solar cells and sensors [17, 18].

Copper oxide (CuO) and cuprous oxide (Cu$_2$O) both are the important inorganic chemical raw material [19, 20]. Cu$_2$O has good thermal stability, which is stable in the dry air condition [21]. CuO, with monoclinic structure and excellent stability, is an ideal solar cell material [22]. Although Cu$_2$O/CuO is well-known, Cu$_2$O as a naturally hydrophobic material and its further oxide CuO as a hydrophilic material are seldom studied. According to the Wenzel model [23], roughness can enlarge the wettability of the material, namely, from hydrophobicity to superhydrophobicity or hydrophilicity to super-hydrophilicity. Therefore, if the Cu$_2$O/CuO coatings have proper roughness, they may exhibit superhydrophobicity/superhydrophilicity. Based on their own chemical property, Cu$_2$O in the humid air or under the higher temperature will change into CuO [24].
Simultaneously, CuO can also be decomposed or deoxidized into Cu2O. The switchable wettability is acquired without chemical modification through raising the temperature and deoxidization [25, 26].

In this paper, a one-step electrodeposition method was utilized to fabricate corrosion-resistant coatings with switchable wettability on stainless steel meshes, which could be used in oil-water separation. The transition process of wettability and oil-water separation characteristics were studied. This kind of method did not involve low surface energy materials and had advantages of simple and good repeatable. Through changing pH value, deposition temperature and voltage, the relationship between morphology and wettability of the as-prepared coatings was analyzed. Heat and hydrothermal treatments were applied to study the reversible transition between superhydrophobicity and superhydrophilicity. In addition, the superhydrophilic coatings could be used to separate light oil, such as diesel, gasoline, toluene, benzene, and lubricants.

2. Experimental section

2.1. Materials and reagents

Stainless steel 304 meshes, acetone (AR), ethanol (AR), HCl (36%), lactic acid (AR), sodium hydroxide (AR), copper sulfate (AR) and glucose (AR) were used in the experiments. All reagents were bought from Sinopharm Chemical Reagent Corp without further purification. The resistivity of deionized water used in all of the experiments was larger than 18 MΩ cm. The meshes were cut into 5 cm × 3 cm × 0.1 cm slices. To remove the oxide layer, the substrates were immersed into a 0.1 M HCl solution for 5 min. Then, they were cleaned through degreasing in acetone for 5 min. Finally, those substrates were rinsed with deionized water and ethanol for 5 min successively. All cleaning processes were conducted in an ultrasonic cleaner.

2.2. Electrodeposition process

The electrodeposition process was carried out by a direct-current power supply (Zhaoxin RXN-605D) at normal temperature in an aqueous solution containing copper sulfate (0.025 mol l⁻¹) and lactic acid (0.4 mol l⁻¹). To investigate the effect of solution pH on the performance of coatings, various aqueous solutions with different pH values were prepared through NaOH. The cleaned mesh substrate was set as a cathode, a Pt plate (5 cm × 3 cm × 0.2 cm) as anode with a distance of 4 cm. Moreover, in order to explore the influence of the electrodeposition voltage on the wettability of resulted coatings, different voltages and time were applied to the device. After deposition, the meshes were removed, and then rinsed with ethanol and deionized water thoroughly and dried with a hairdryer immediately.

2.3. Switchable wettability processes

After the electrodeposition process, the as-prepared meshes were placed into the oven in the air at 60 °C for 3 h. Then, the samples were transferred into an oven at 120 °C for 12 h to achieve superhydrophobicity. Some of the superhydrophobic meshes were heated at 450 °C for 3 h, as a result, they turned into black and acquired superhydrophilicity. In order to realize switchable wettability, a reductive aqueous solution composed of glucose (0.25 mol l⁻¹) and NaOH (1.0 mol l⁻¹) was poured into a 50 ml autoclave. The black and superhydrophilic mesh was placed in the autoclave that is maintained at 120 °C for 3 h. After this hydrothermal process, the mesh achieved superhydrophobicity and turned into brick red again. The whole process of fabricating coatings with switchable wettability on meshes was displayed in figure 1.

2.4. Characterization and tests

An optical contact angle meter (OCA35, Dataphysics) was used to measure water/oil (olive oil, benzene, methylbenzene, and dichloromethane) contact angle (CA)/slide angle (SA) with 5 μl drops. The average value was determined by measuring five different positions. The surface morphologies were investigated by scanning electron microscopy (SEM) with a scanning electron microscope (Quanta 200) equipped with an X-act electron microprobe for energy-dispersive x-ray spectroscopy (EDS). X-ray diffraction (XRD) spectroscopy (D8ADVANCE, Bruker) and x-ray photoelectron spectroscopy (XPS, PHI Quantera, ULVAC-PHI Inc., Japan) with Al K x-ray source using the C 1s peak energy (284.8 eV) as a calibrated energy standard were performed to investigate the chemical composition of the coatings. The superhydrophobic and superhydrophilic meshes were fixed in the middle of the oil-water separation device. Then, the oil-water mixture was poured into the device, and the oil phase or the water phase could be automatically separated.
3. Results and discussion

3.1. Effect of pH value on surface morphology and wettability

The morphology of the reaction product can be affected by the pH value of the electrodeposition solution, which influences the transfer of ions. In order to investigate the effect on the morphology of the steel mesh surfaces, different pH value was used. Importantly, the temperature and voltage maintain at 50 °C and 5 V for 20 min. Figure 2 illustrates SEM images obtained at different pH from 2.0 to 13.0 in the electrodeposition process. Figure 2(a) shows the surface topography obtained at pH 2.0, which is relatively smooth, only little dendritic structure gathering around knots. Figure 1(f), the high-magnification SEM image of figure 2(a) demonstrates that the mesh surfaces are composed of plate-like structures, without obvious micro/nanoscale structures. As shown in figure 2(b), as pH increased to 7.0, micro-pine hierarchical structures have emerged. It can be seen from figure 2(g) that the pine structures consist of countless micro/nanoparticles. Figure 2(c) presents an SEM image at pH 9.0, in which the distribution of pine structures turns into more uniform (figure 2(h)) adjoined by microparticles. There are a large number of micro/nanostructures composing hierarchical structures, which
can trap plenty of air. However, when pH is increased to 11.0, shown in figure 2(d), the pine structures grow too fast to fracture and some of the hierarchical structures are dissolved (figure 2(i)). Finally, when the solution becomes strong basic (pH 13.0), the topography of micro/nanoparticles is disappeared and the number of the particles decreases (figure 2(h)).

The surface wettability of the prepared steel meshes is evaluated by water CA/SAs, which is shown in figure 3. All the tested samples were placed into the oven at 60 °C for 3 h and at 120 °C for 12 h. As displayed in figure 3, the CA of the mesh obtained at pH 2.0 is 150.6 ± 1.3° with a SA 5.0, which is superhydrophobic. As the pH increased to 7.0, the CA reaches 152.2 ± 0.1° and SA is 4°. When pH rises to 9.0, the largest CA value of 155.5 ± 0.2° is obtained and the SA is reduced to 1°, displaying the high superhydrophobicity. However, as the solution alkalinity increases, the pine structures fracture and some of the hierarchical structures are disappeared. The CA is decreased to 152.3 ± 1.7° with a SA of 2° when the pH of the solution is 11.0. Finally, as pH reaches 13.0, the CA is decreased to 150.6 ± 0.5° and SA increases to 8°. In all, when pH is 9.0, the meshes consist of uniformly pine structures and possess the best superhydrophobicity. Therefore, pH 9.0 is defined as the optimal pH in fabricating samples.

### 3.2. Effect of temperature on surface morphology and wettability

To study the effect of temperature on the morphology and wettability, the pH and voltage maintain at 9.0 and 5 V for 20 min. The temperature ranges from 5 °C~75 °C and the results are shown in figure 4.

After electrodeposition for 20 min under the temperature of 5 °C, the surface of the mesh is almost smooth as seen in figure 4(a). The activity of Cu²⁺ is limited under the low temperature, which results in the reaction product with less quantity. From the magnified image figure 4(f), it can be seen that the mesh is covered by particles in the micron size range. As the temperature increased to 15 °C, there are more particles produced on the mesh surfaces (figure 4(b)) and those particles agglomerate into microspheres, as shown in figure 4(g). As the
As illustrated, the temperature has a great effect on the morphology of mesh surfaces. In addition, the wettability of a surface depends on the chemical composition and microstructures. It can be deduced that the CA/SAs will vary with temperature. The results are shown in figure 5. When the temperature is as low as 5 °C, the CA is 151.9 ± 1.3° with a SA of 6°. In sequence, the CA at a temperature of 15 °C is 152.2 ± 1.7° and the SA is about 5°. As the temperature reaches 30 °C, the CA rises to 152.3 ± 1.5° and SA decreases to 4°. With the improvement of temperature, more and more particles are emerged on the mesh surfaces and gather into pine structures. The as-prepared meshes acquire the largest CA value 155.5 ± 0.4° and SA rises to 75 °C, which display distinguished superhydrophobicity. Nevertheless, as the temperature is increased to 75 °C, the CA becomes 154.6 ± 0.4° and SA rises to 2°. Consequently, the morphology and wettability are intensely affected by temperature. To obtain the most excellent superhydrophobicity, 50 °C is selected as the optimal parameter.

3.3. Effect of voltage on surface morphology and wettability
The electrodeposition method possesses many advantages such as easy to conduct, fast, controllable morphology and thickness, which has been widely used in preparing coatings on various substrates. Different electrodeposition voltages were applied under constant 20 min, pH 9.0 and 50 °C to investigate its effect on the morphology and wettability. Figure 6 illustrates SEM images under the voltage of 1 V, 3 V, 5 V, 7 V, and 9 V. Figure 6(a) shows the surface topography at a voltage of 1 V, which is almost smooth. From the magnified image figure 6(f), the mesh surface is covered by numberless micro/nanoparticles and discreet ‘dimples’. As shown in figure 6(b), as the electrodeposition potential increased to 3 V, more products have emerged on the mesh. Those micro/nanoparticles aggregate into micro–pine hierarchical structures, as shown in figure 6(g). As the voltage continuously rises, the dimension of the pine structure can be larger and larger. When the voltage reaches 5 V, it can be seen from figure 6(c) that the pine structures consist of countless micro/nanoparticles. From the magnified image figure 6(h), the size of ‘pine’ is increased surrounded by micro/nanoparticles and structures become relatively uniform, composing hierarchical structures, which can trap plenty of air and results in the formation of a superhydrophobic surface. Figure 6(d) presents an SEM image with a deposition voltage at 7 V, in which the pine structures obviously grow up in size adjoined by micro–pine structures. It can be seen from figure 6(i), those structures are uniformly distributed on the mesh surface. However, when the potential is increased to 9 V, the number of micro–pine structures is reduced (figure 6(e)) and those structures randomly distribute on the mesh surfaces (figure7(j)). The former uniform hierarchical structures disappear under such high-level voltage, on account of the high speed of dissolution.

The surface wettability of the prepared is evaluated by water CA/SAs, which are shown in figure 7. The CA of the mesh under a potential of 1 V is 143.9 ± 0.2°, displaying high adhesive hydrophobicity. As the
electrodeposition potential increased to 3 V, the chemical reaction in the solution becomes more active. Therefore, the CA reaches 148.0 ± 2.6° with a SA of 5°, which shows the mesh possesses low adhesive hydrophobic property. When the voltage approaches 5 V, as seen in figures 6(c) and (h), hierarchical structures appear on the mesh, which can trap plenty of air and result in superhydrophobicity. Meantime, the largest CA value of 155.5 ± 0.2° is acquired and the SA is about 1°, displaying the high superhydrophobicity. When the potential reaches 7 V, the hierarchical structures still exist on the mesh, of which the CA is maintained 153.7 ± 1.7° and SA is as low as 2°. However, as the voltage reaches to 9 V, partly the hierarchical structures are disappeared, the CA is decreased to 152.3 ± 1.5° with a SA 4°. In conclude, the mesh surfaces acquire the most excellent morphology and superhydrophobicity under the condition of pH 9.0, 50 °C and 5 V, which are selected as the optimal parameter to prepare samples.

3.4. Reversible wettability transformation
Cu2O is naturally hydrophobic and CuO is hydrophilic, which can obtain superhydrophobicity and superhydrophilicity without modifying the low surface energy according to the Wenzel model that rough structures will magnify the wettability. The meshes under the optimal parameters were used to investigate wettability transformation and mechanism. After the electrodeposition process, they were removed from the device and flushed with water. Then those samples were placed at 60 °C for 3 h at 120 °C for 12 h. As a result, the superhydrophobicity was acquired and the mesh surface turned in brick red. Some of the superhydrophobic meshes were heated at 450 °C for 3 h. Under such a high temperature, they turned into black and superhydrophilicity. The switchable wettability is realized through a hydrothermal reduction reaction. A reductive aqueous solution composed of glucose and NaOH was poured into a 50ml autoclave. The black and superhydrophilic mesh was placed in the autoclave that is maintained at 120 °C for 3 h. Finally, the mesh retrieves superhydrophobicity and turned into brick red again.
The surface morphology of those samples is displayed in figure 8. The mesh surface after electrodeposition and certain heat treatment consists of pine structures and micro/nanoparticles, which uniformly distributes on the surface, as shown in figures 8(a) and (d). The CA reaches 155.5 ± 0.2° and SA decreased to 1°, displaying in the inserted figure of figures 8(a) and (d). Meantime, the mesh turns from metal color into brick red. After heating at 450 °C for 3 h, the pine structures grow up and form micro-papillae (figure 8(b)), which are adjoined by countless micro/nanoparticles (figure 8(e)). The superhydrophobic meshes become superhydrophilic with a CA of 0° and turn into black. In order to realize the switchable wettability, the black meshes were put into an autoclave suffered a hydrothermal reduction reaction. Due to the high temperature and reduction effect of glucose, from figures 8(c) and (f), the original micro-papillae change into smaller papilla and the surrounded particles become finer. Therefore, the superhydrophilic meshes transform into superhydrophobic and brick red again with the CA 154.8 ± 0.6° and SA of 1° (the inserted figure of figures 8(c) and (f)). Through high-temperature oxidation and hydrothermal reduction, the meshes acquire switchable wettability and color. Moreover, after 5 cycles, the brick red meshes still maintain good superhydrophobic, as shown in Table 1.

Table 1. Contact angles and sliding angles of the meshes by different cycles.

| Cycles | 0      | 1st    | 2nd    | 3rd    | 4th    | 5th    |
|--------|--------|--------|--------|--------|--------|--------|
| Contact angles | 155.5 ± 0.2° | 154.8 ± 0.6° | 154.5 ± 0.5° | 153.7 ± 0.7° | 153.2 ± 0.8° | 152.6 ± 0.6° |
| Sliding angles  | 1°      | 1°      | 1°      | 1°      | 1°      | 1°      |

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3.5. Special wettability

In the inserted figures of figure 8, the surface wettability of the prepared meshes is evaluated by distilled water CA/SAs. The CA of the stainless mesh under the optimal parameters is 155.5 ± 0.2°, which shows the mesh possesses superhydrophobic properties. As illustrated, the CA of the black mesh is 0°, displaying superhydrophilic. Nevertheless, the superhydrophilic meshes transform into superhydrophobic and brick red again with the CA 154.8 ± 0.6° and SA 1°, which indicates that all the as-prepared surfaces possess low adhesive hydrophobicity. Based on the equation of Cassie and Baxter [27], we can get the idea that the air content trapped in the surface give rise to superhydrophobicity:

\[ \cos \theta = f_1 \cos \theta_0 - f_2 \]  

(1)

According to previous literature [28], the CA of Cu2O on a smooth surface is only about 110° and the CAs of the original and reduced superhydrophobic meshes are 155.5° and 154.8° severally. Herein we calculate that the \( f_1 \) of the original mesh is only 0.14. The excellent superhydrophobic property of the stainless meshes has directly related to the large contact area between water and air.
3.6. Chemical composition characterization

EDS, XRD and XPS spectra were used to inspect the chemical composition of the reversible meshes. Figure 9 displays the EDS analysis of the superhydrophobic and superhydrophilic meshes, which demonstrates that both of the coatings are mainly composed of Cu and O. The atomic ratio of the original superhydrophobic mesh Cu:O = 67.8%: 32.2% = 2.1 : 1. After high thermal oxidation, the atomic ratio Cu:O is 59.69%: 40.31% = 1.5 : 1. Finally, the atomic ratio Cu:O turning into 65.3%: 34.7% = 1.9 : 1 ≈ 2:1.

The XRD spectrum is exhibited in figure 10(a), which demonstrates that the original brick-red superhydrophobic mesh is composed of Cu2O. After high-temperature oxidization, the black superhydrophilic mesh consists of CuO. This kind of black superhydrophilic mesh regains superhydrophobic after hydrothermal reduction reaction, which is composed of Cu2O and CuO. In addition, figure 10(b) presents the XPS survey spectrum, on which C, O, Cu can be observed. Figures 10(c) and (d) show the Cu 1s and O 1s decomposition-fitted curves of the XPS spectrum. Presumably, the Cu 1s spectrum consists of three peaks: the peaks at 952.0 eV, 934.6 eV, and 932.3 eV are attributed to Cu2O. Moreover, the O 1s spectrum of the original superhydrophobic mesh one peak located at a binding energy of 532.0 eV is owing to the Cu2O bond. In summary, it can be deduced that Cu2O with low surface energy is generated on the original. The surface after high thermal oxidation is composed of CuO, which regained Cu2O under the hydrothermal reduction.

3.7. Reversible wettability mechanism

SEM images combined with EDS, XRD and XPS characterizations demonstrate that hierarchical micro/nanonodules structures are generated and Cu2O with low surface energy is prepared on the stainless meshes. When the DC voltage is applied to the two electrodes, Cu2+ around the cathode will react with electrons, generating Cu+, which will react with OH− and generates CuO. Therefore, the concentration of H+ in the solution rises and part of H+ acquiring electrons generates H2. Moreover, the released H2 around the cathode during the electrodeposition process may lead to the formation of micro/nanostructures [29], which can be observed in SEM images. Based on the Cassie-Baxter state, plenty of air can be trapped into the micro/nanostructures easily. Cu2O can be oxidized into CuO under high thermal conditions. Moreover, due to the high temperature and reduction effect of glucose, CuO will react with C6H12O6 and generate Cu2O in the basic environment. The reaction processes can be formulated as follows [30]:

\[
\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+ \quad (2)
\]

\[
2\text{Cu}^{2+} + 2e^- + 2\text{OH}^- \rightarrow \text{Cu}_2\text{O} \downarrow + \text{H}_2\text{O} \quad (3)
\]

\[
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 \uparrow + 2\text{OH}^- \quad (4)
\]

\[
2\text{Cu}_2\text{O} + \text{O}_2 \rightarrow 4\text{CuO} \quad (5)
\]

\[
2\text{CuO} + \text{C}_6\text{H}_12\text{O}_6 + \text{NaOH} \rightarrow \text{Cu}_2\text{O} \downarrow + \text{C}_6\text{H}_11\text{O}_7\text{Na} + \text{H}_2\text{O} \quad (6)
\]
3.8. Oil/water separation

Since the as-prepared meshes are superhydrophobic or superoleophilic that can be a practical property for oil spill clean [31–34]. We investigate the oil absorption ability of the brick red superhydrophobic and black superhydrophilic meshes. A mixture of 25 ml deionized water and 25 ml oil (dichloromethane, carbon tetrachloride, diesel, gasoline, toluene, benzene, and lubricants) was used in this test. In our case, the oil was colored with oil red, and the water was dyed with methylene blue. The superhydrophobic coatings could be applied to separate heavy oil or organic solvent, such as dichloromethane and carbon tetrachloride, etc. In addition, the superhydrophilic coatings could be used to separate light oil, such as diesel, gasoline, toluene, benzene, and lubricants, etc. When the superhydrophobic meshes contacted with the mixture, water was repelled from the surface while the oil was quickly penetrated through as soon as it touched the surfaces. As a result, in figure 11, the heavy oil can be separated from the mixture successfully. In the figure 11(b), the oil was separated by superhydrophobic meshes and saved in the bottles below the separator, resulting water in the separator. In addition, the superhydrophilic meshes exhibit opposite performance to oil and water. In the beginning, the mesh was prewet and could repel oil from the surface while water was quickly penetrated through as soon as it touched the surfaces. As shown in figure 11(c), the water was removed by the superhydrophilic meshes and then retaining oil in the separator. Furthermore, this superhydrophobic and superhydrophilic meshes could be reused for absorbing oil, which are significant features for practical application. All the meshes with special wettability display excellent oil-water separation ability, of which the oil/water separation ratio is above 95%, even after reused 5 times.

4. Conclusions

In this study, the one-step electrodeposition method was used to fabricate coatings with switchable wettability on stainless steel meshes to extend the application of a one-step electrodeposition method and materials with special wettability in intelligent material industry. This kind of method did not involve low surface energy materials and had advantages of simple and good repeatable. Through changing pH value, deposition temperature and voltage analyzed the relationship between morphology and wettability of the as-prepared
coatings. The SEM results show particles on the film under the optimum condition and some of them aggregated into micro-pine hierarchical structures. The coatings achieved superhydrophobicity after certain heat treatment, and the water contact angle reached 155.5° and became brick red. After being placed at 450 °C for 3 h, the superhydrophobic film turned into superhydrophilic and became black. The coatings regained superhydrophobicity after hydrothermal treatment in glucose aqueous solution, which exhibited a reversible transition between superhydrophobicity and superhydrophilicity. Investigating the chemical components of samples under different treatments was used to analyze the transition mechanism. The results demonstrated that the sample under certain heat treatment after electrodeposition was Cu2O. After high-temperature treatment, the film was CuO and turned into Cu2O after hydrothermal treatment. The superhydrophobic coatings remained superhydrophobicity after being stored at room temperature for 40 weeks. Moreover, the oil-water separation capability was studied by the separation appliance. The superhydrophobic coatings could be applied to separate heavy oil or organic solvent, such as dichloromethane and carbon tetrachloride, etc. In addition, the superhydrophilic coatings could be used to separate light oil, such as diesel, gasoline, toluene, benzene, and lubricants, etc. All the coatings with special wettability exhibited excellent oil-water separation ability, which was above 95%.

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Figure 11. Photograph of separation process: (a) oil-water separation device, (b) superhydrophobic mesh, (c) superhydrophilic mesh.
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