

Fabrication of Superhydrophobic Copper via Chemical Etching and Modification

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Abstract

Biological superhydrophobic surfaces are relatively common in nature. Inspired by the superhydrophobic feature, plentiful materials with hydrophobic surfaces have been fabricated for various purposes such as anti-corrosion, anti-icing, self-cleaning, friction reduction, and oil-water separation. In the present work, we report a scalable, simple, and rapid method to fabricate superhydrophobic film on copper substrates via a simple route including a chemical etching step in sodium persulfate and sodium hydroxide solution and followed by a modification step in stearic acid solution. The effect of the etchants concentration as well as etching time was investigated exhaustively. From the obtained results it was found that when a copper plate was etched in an etching solution with low etchant concentration, the contact angle of copper was greatly influenced by etching time. In contrast, the etching time hardly affected the contact angle of the copper plate at the high concentration of the etchants. The superhydrophobic feature of the copper surface (with a contact angle larger than 150°) was only achieved in certain fabrication conditions. The superhydrophobic copper substrates demonstrated good anti-corrosion properties. The corrosion current density of superhydrophobic copper substrates was 85 times smaller than that of pristine ones when manufactured under optimal conditions. In addition, the as-prepared superhydrophobic copper mesh was used to successfully separate toluene from its aqueous mixture. The superhydrophobic copper has great potential for applications in oil-water separation and anti-corrosion in aqueous environments.

Keywords: Oil-water separation, wettability, superhydrophobic, copper.

1. Introduction

In past years, with the development of the various industry fields, the gas and oil demand has grown up. Following the increasing growth of oil trading and shipping along with the increase in oil spill accidents as well as industrial oily wastewater, oil-water separation has become a worldwide challenge. Currently, numerous approaches have been proposed to treat oil-water pollution issues, including centrifugation, precipitation tanks, flotation technologies, oil-absorbing materials, combustion, and so on [1]. Each treatment method shows its advantages and disadvantages. The collection of oil for the water surface is often preferred because of its proper disposal of the oil [2]. According to this approach, functionalized materials with novel wettability such as superhydrophobicity, superhydrophilicity, superoleophilicity, and superoleophobicity have been attractive due to their selective wetting behaviour to water and oil.

In general, materials used for oil-water separation can be classified into two types, viz. filtration materials and absorbent materials [1]. Compared with the filtration materials (meshes, membranes, and textiles), the absorbent materials enable instant usage of oily wastewater without pre-collection before treatment.

To date, diverse porous materials such as sponges, aerogels, and particles have been developed and showed certain noticeable achievements [3]. For example, the carbon aerogels offer a high oil absorption capacity of up to 900 times their weight [4] or a polyester-based sponge can separate a large amount of oil up to 35,000 times its weight [5]. Unfortunately, these materials reveal some disadvantages including (i) insufficiently high absorption capacity, which requires a large amount of the absorbent materials for the oil-removing process, and/or (ii) requirement of the subsequent complicated stages (mechanical handling and distilling) to recover oil from the used absorbent materials [3]. Thus, in very recent years, oil-skimmers with a configuration of a barrel mounted by a superhydrophobic mesh cap, which can be equipped with a commercial vessel, have been designed to collect oil effectively. In this case, the recovery of a large amount of oil probably proceeds easily. The oil collection capacity of the skimmers only depends on the volume of the containers. The oil obtained after permeating the superhydrophobic mesh flows into the barrel and is then collected favourably without any subsequent mechanical handling processes, for example, squeezing out oil like the absorbent materials.

Copper is regarded as the most important engineering metal because of its wide applications in daily life and industrial production. In addition, copper exhibits novel properties such as low price, earth abundance, good processability, high corrosion resistance, and high conductivity [6]. Thus, the development of copper-based functional materials, in specific, superhydrophobic materials, has gained great attention. Compared with other substrates, superhydrophobic copper surfaces can be easily fabricated by simple chemical etching in acids or bases [2,7], and electrodeposition [8]. In a previous report, Feng and co-workers fabricated a superhydrophobic copper mesh by etching the copper substrate into $K_2S_2O_8/NaOH$ and then modifying the surface with octadecyl phosphonic acid [9]. Besides, the other etching agents such as $(NH_4)_2S_2O_8/NaOH$, $K_2S_2O_8/KOH$, and $FeCl_3/HCl$ along with other modification agents such as lauric acid, myristic acid, 1-octadecanethiol were also used [7,10].

Herein, we report a simple, economical, efficient, and eco-friendly approach to fabricating superhydrophobic copper substrates (plates and meshes) by etching in the $Na_2S_2O_8/NaOH$ solution mixtures and surface modification in stearic acid. The effect of the concentration of the etching agents and the etching time on the wettability property of the copper has been examined. The prepared superhydrophobic copper samples show high diverse application potential in oil-water separation, anti-corrosion, and self-cleaning. In addition, this facile approach enables large scale production of the superhydrophobic copper samples of any size as desired.

2. Experimental Section

2.1. Chemicals and Materials

All chemicals including sodium persulphate ($Na_2S_2O_8$, $\geq 98\%$), sodium hydroxide ($NaOH$, $\geq 98\%$), toluene ($\geq 99.5\%$), methylene blue, absolute ethanol and stearic acid ($CH_3(CH_2)_{16}COOH$) were purchased from Sigma Aldrich and used as received without further purification. Commercial copper plates and meshes were provided by JD Hardware Wire Mesh Company.

2.2. Fabrication of Superhydrophobic Copper

Copper plates with $2\text{ mm} \times 20\text{ mm} \times 60\text{ mm}$ dimensions were polished with abrasive papers of the various grades from #800, #1200 to #2000, then degreased with absolute ethanol, rinsed in distilled water, and dried in a vacuum chamber at $70\text{ }^\circ\text{C}$. Subsequently, the samples were immersed in the dilute nitric acid and rinsed in distilled water before etching in the solution mixture of $NaOH$ and $Na_2S_2O_8$ with different concentrations. After that, the samples were rinsed thoroughly with distilled water and dried at

$80\text{ }^\circ\text{C}$. In the next step, the samples were immersed in 0.01 M stearic acid in absolute ethanol solvent for 24 h before being dried in a chamber at $100\text{ }^\circ\text{C}$ for 30 min . The surface area of the copper substrates etched and modified was fixed at 4 cm^2 . Similarly, the copper meshes with a wire diameter of about $125\text{ }\mu\text{m}$ were rinsed thoroughly, etched, and modified at the optimized conditions.

2.3. Characterizations

Contact angle measurements were performed using a digital camera with an aperture of $f/1.7$, a shutter speed of $1/60$ and a focal length of 3.92 mm along with ImageJ software. The volume of a water droplet in each measurement was $5\text{ }\mu\text{L}$. Contact angle measurements were conducted at three different positions of the sample surfaces. The morphology of the copper samples was examined using field-emission scanning electron microscopy (FESEM, HITACHI S-4800, Japan). The phase structure of materials was investigated using X-ray diffraction (XRD, EQUINOX 5000, France). Anti-corrosion properties of the superhydrophobic copper were examined by Tafel plot and electrochemical impedance spectroscopy techniques, which proceeded on an Autolab potentiostat. These measurements were conducted using a three-electrode configuration with a copper plate as a working electrode, a saturated calomel electrode (SCE) as a reference electrode and a platinum mesh as a counter electrode. The used electrolyte was $3.5\text{ wt.}\%$ $NaCl$ solution. All potential values mentioned in this study are versus the potential of the SCE.

Additionally, to demonstrate the oil/water separation ability of the superhydrophobic copper, 20 mL of toluene-distilled water mixture was separated using a superhydrophobic copper mesh (#80).

3. Results and Discussion

Fig. 1a shows the surface images of the copper plates etched in 0.1 M $Na_2S_2O_8$ solutions containing $NaOH$ with different solutions for various etching periods. From the colour of the insoluble reaction products left on the surface of the copper plates after etching, it is recognized that the high concentration of $NaOH$ and long etching period promoted the etching process of the copper substrate. The deep blue colour of etching products is observed most clearly for the sample immersed in the solution containing 2.5 M $NaOH$ for 5 min . The copper plates after the etching were immersed in the ethanol solution of 0.01 M stearic acid for 24 h . Like the samples after etching, the surface of the copper plates after the superficial modification exhibit changes in colour from deep blue to bright blue (Fig. 1b). The colour change revealed the presence of a new reaction product on the copper surface after the modifying step.

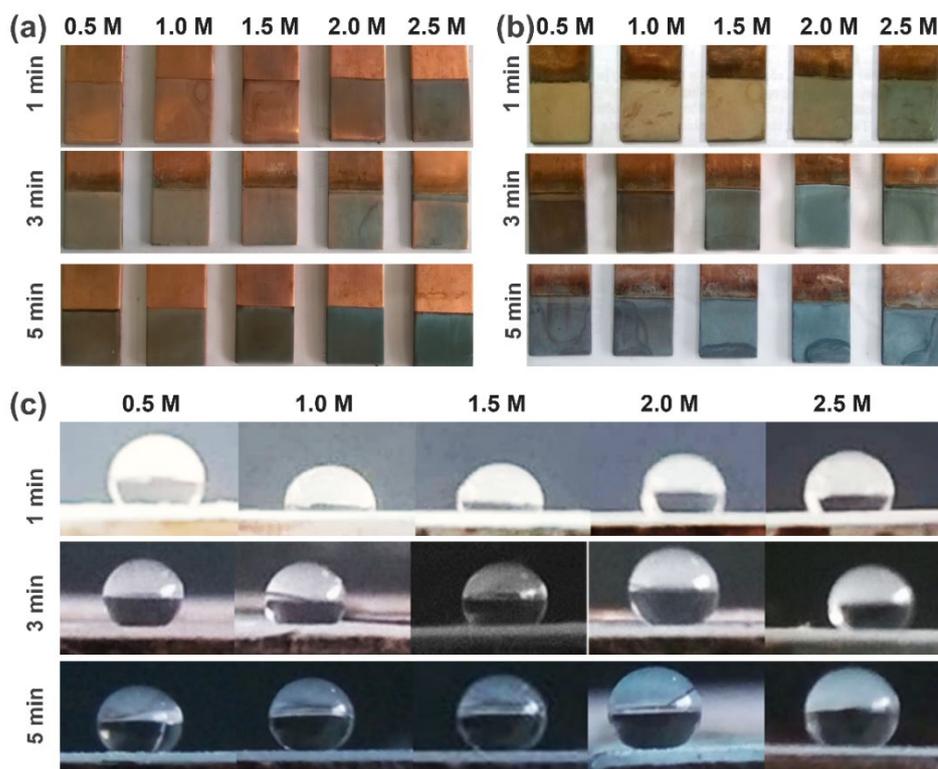


Fig. 1. Optical images of copper plates: (a) after etching in solution mixtures of 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$, and NaOH with different concentrations for various times, (b) after modifying in 0.01 M stearic acid. (c) Photographs of water droplets on the prepared copper plates

After the etching and surficial modification processes, the surface of all the copper samples exhibited obvious hydrophobicity, which is characterized by the typical spherical shape of the water droplets on the prepared copper samples (Fig. 1c). To evaluate exactly the contact angle of the water droplets, the ImageJ software was used to measure.

Fig. 2 shows the dependence of the contact angle on the concentration of NaOH corresponding to the different etching times. It is observable that, for the short etching duration of 1 min, the contact angle of the copper sample tends to increase with the increase in the concentration of NaOH. In particular, the contact angle increased from 115.8° for the sample etched in the NaOH concentration of 0.5 M to 132.3° for the sample etched in the NaOH concentration of 2.5 M. The increase in the contact angle of the copper substrate probably resulted from the increase in the surficial roughness of the copper substrate after etching. Probably, the etching period of 1 min is too short to create the essential roughness for the copper samples in these solutions of 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$. According to the Cassie - Baxter's theory [11], the superhydrophobicity of a surface is achieved only when the surface has a certain roughness and low surficial energy. When the etching time increased from 1 min to 2 min and 3 min, the contact angle increased significantly. For the samples etched in the low NaOH

concentrations such as 0.5 M, 1 M, and 1.5 M, the contact angle increased with the increase of NaOH concentration. However, the contact angle on the samples did not reach the value of 150° , the minimum criterion of the superhydrophobic surface. At the higher NaOH concentrations, viz. 2 M and 2.5 M, the contact angle of the copper samples achieved over 150° except for the sample etched in 1 min. In general, even at the high concentration of NaOH etching solution almost the copper surface only shows hydrophobicity but no superhydrophobicity for all investigated etching times.

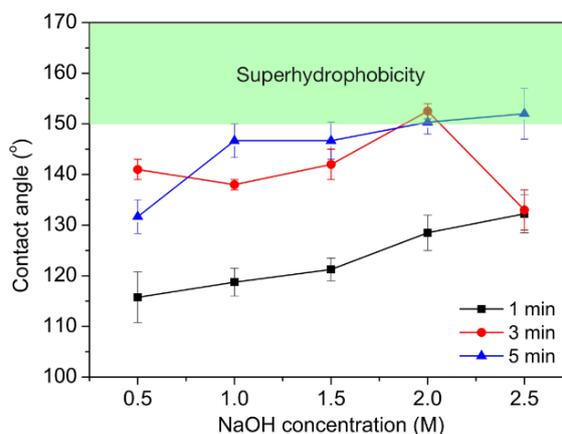


Fig. 2. Variation of contact angle of the copper plates etched in the 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$ solution containing 0.5 - 2.5 M NaOH for the periods of 1 - 5 min.

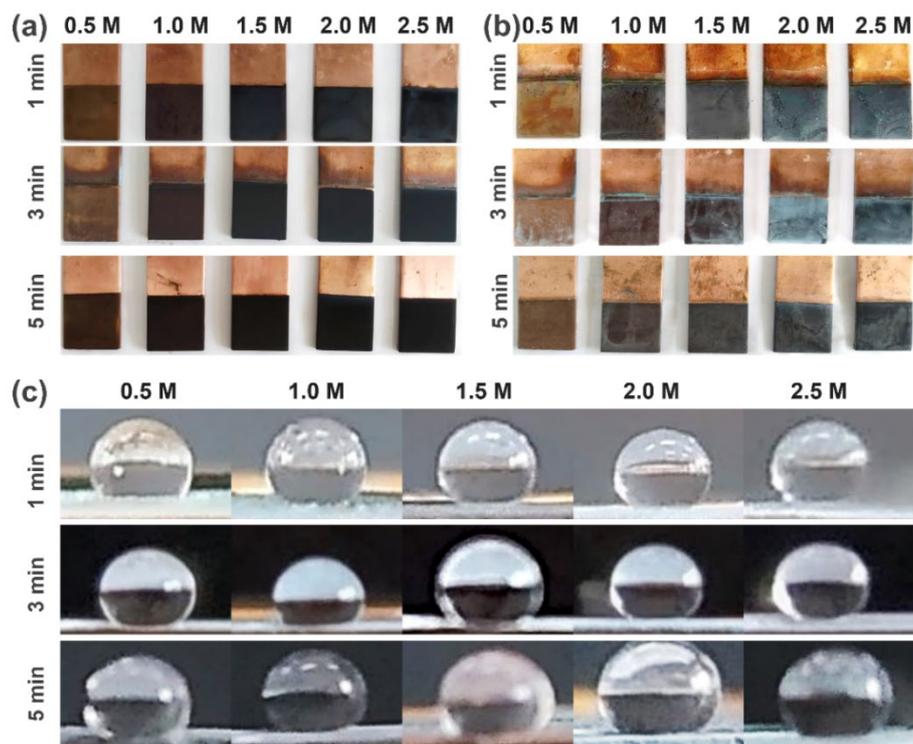


Fig. 3. Optical images of copper plates: (a) after etching in 0.5 M $\text{Na}_2\text{S}_2\text{O}_8$ and NaOH with different concentrations for various times, (b) after modifying in 0.1 M stearic acid. (c) Photographs of water drops on the surfaces of the prepared copper plates.

Next, the effect of the $\text{Na}_2\text{S}_2\text{O}_8$ concentration on the wettability property of the copper substrate was investigated. Fig. 3a shows the images of the copper plates after etching in the 0.5 M $\text{Na}_2\text{S}_2\text{O}_8$ solution with different NaOH concentrations and in the various etching times. It is easy to recognize that the colour of the surfaces of the copper samples is quite different from that of the copper samples etched in the etching solution with the lower $\text{Na}_2\text{S}_2\text{O}_8$ concentration, 0.1 M (Fig. 1a). The copper surface with dark brown colour was observed for the samples etched in the solutions of 0.5 M $\text{Na}_2\text{S}_2\text{O}_8$ while the blue colour was recorded for the samples etched in 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$. After modification in stearic acid, the surfaces of the copper samples seem to be covered by a blue product layer (Fig. 3b), which is analogous to the samples etched in the solutions of 0.1 M.

Fig. 3c shows the images of water drops on the surface of the copper plates after the etching and modifying processes. Compared with the images of the water drops in Fig. 1c, the water drops on the copper plates etched in the high $\text{Na}_2\text{S}_2\text{O}_8$ concentration of 0.5 M appear rounder and fuller. This indicates the hydrophobicity of the copper surface was improved. This is also verified quantitatively by the analysis results in Fig. 4. It is worth seeing that with the high $\text{Na}_2\text{S}_2\text{O}_8$ concentration of 0.5 M, the superhydrophobicity of the copper plate was achieved, corresponding to the NaOH concentration over 1.5 M within the etching periods of 1 - 5 min.

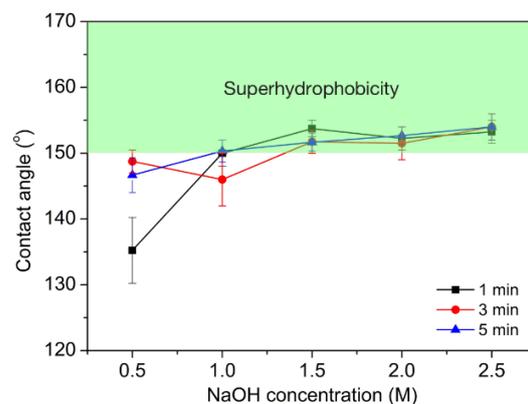


Fig. 4. Variation of the contact angle of the water drops on the surface of the copper plates prepared with the etching solution of 0.5 M $\text{Na}_2\text{S}_2\text{O}_8$ and 0.5-2.5 M NaOH for different etching periods.

In addition, with the etching solution containing 0.5 M $\text{Na}_2\text{S}_2\text{O}_8$ when the NaOH concentration increased over 1.5 M the contact angle of the water drops on the surface of the prepared copper plates was almost unchanged despite the increase in the etching time. In specific, the contact angle of the water drop was around $152^\circ - 154^\circ$ for the copper samples etched in the etching solution of 0.5 M $\text{Na}_2\text{S}_2\text{O}_8$ and 1.5 - 2.5 M NaOH for 1 - 5 min. Hence, it can be stated that the fabrication of the superhydrophobic copper surface is easily implemented in the etching solutions containing the high concentrations of the etchants, viz. 0.5 M $\text{Na}_2\text{S}_2\text{O}_8$ and 1.5 - 2.5 M NaOH for 1 - 5 min,

followed by the modifying process in the 0.01 M stearic acid. The highest contact angle that the copper sample achieved was 154.1°, corresponding to the etching in the solution of 0.5 M Na₂S₂O₈ and 2.5 M NaOH for 3 min, and subsequently modifying in the 0.01 M stearic acid.

To determine the composition of the superhydrophobic surface, the copper sample prepared in the etching solution of 0.5 M Na₂S₂O₈ and 2.5 M NaOH for 5 min, followed by the modifying and drying processes was analyzed by the XRD method.

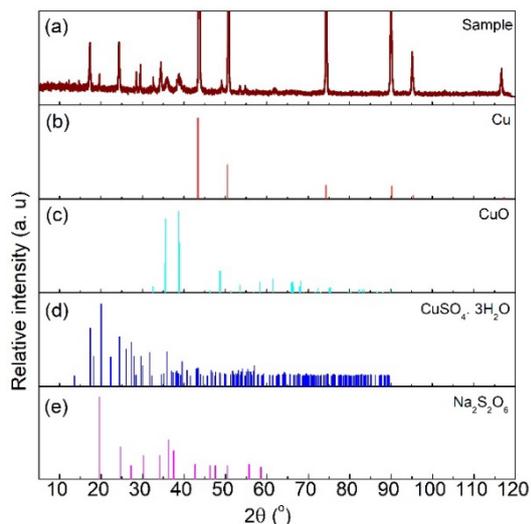
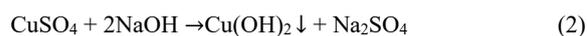


Fig. 5. XRD patterns of (a) a superhydrophobic copper plate and corresponding references: (b) Cu (#03-065-9743), (c) CuO (#01-089-5898), (d) CuSO₄·3H₂O (#01-072-1299), (e) Na₂S₂O₆ (#00-015-0172).

Fig. 5 presents the XRD pattern of the sample along with the standard diffraction lines of the compounds detected after using X'Pert high score software. It is observable that, after the etching and modifying processes, the typical diffraction peaks of the copper substrate at the 2θ angles of 43.2°, 50.4°, 74°, 89.9° and 94.4°, corresponding to the crystalline Cu phase with a cubic structure (JCPDS card 03-065-9743) was detected. In addition, other minor diffract peaks were also recorded. These peaks relatively match the diffraction lines of the crystalline phases of CuO (JCPDS card 01-089-5898), CuSO₄·3H₂O (JCPDS card 01-072-1299), and Na₂S₂O₆ (JCPDS card 00-015-0172). The XRD results in this study are also totally consistent with the previous report [12]. This proved the presence of the reaction products after the etching and modifying processes. Accordingly, the chemical reactions occurring in the fabrication process of the hydrophobic copper surface can be proposed as follows:

In the etching process:



In the modification process:

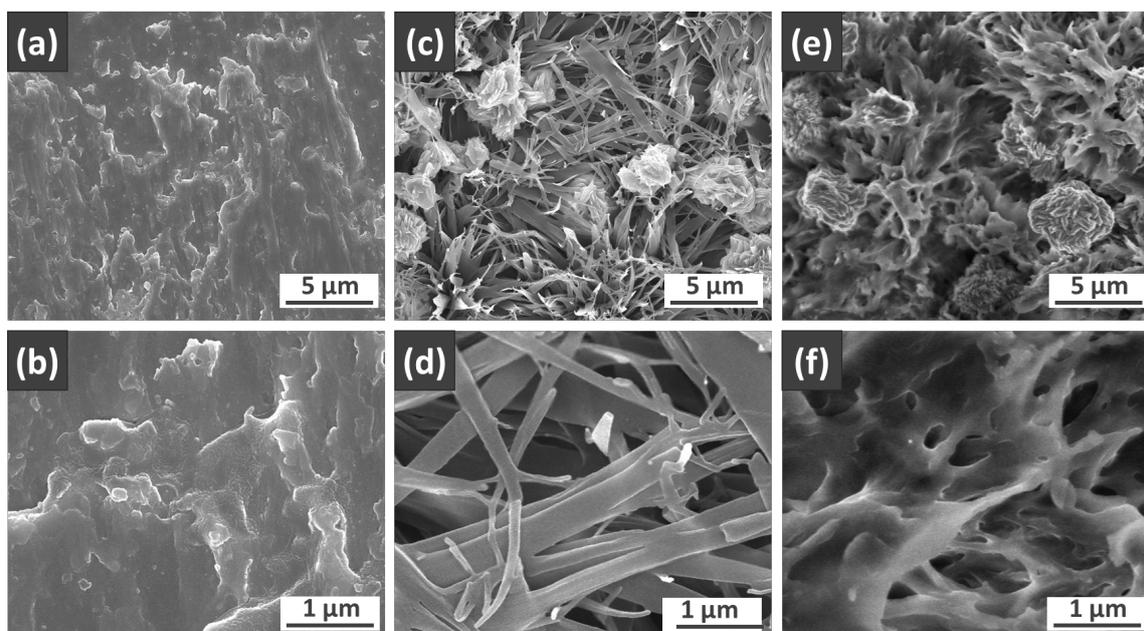
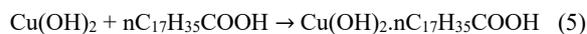
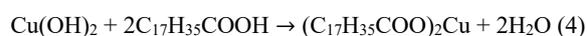


Fig. 6. Low and high resolution SEM images of a copper plate: (a,b) fresh, (c,d) after etching in 0.5 M Na₂S₂O₈ and 2.5 M NaOH in 5 min (e,f) after modifying in 0.01 M stearic acid

So, if based on the etching and modifying processes as described above, the optimal conditions for fabrication of superhydrophobic copper can be explained as follows: In fact, the NaOH etchant served as a supporting substance while $\text{Na}_2\text{S}_2\text{O}_8$ worked as a main etchant. Thus, the concentration of NaOH in the etching solution affected negligibly on the contact angle of the copper samples. The copper samples difficultly achieved superhydrophobic property even being etched in the solutions with the high concentration of NaOH for different etching times. In contrast, when the concentration of $\text{Na}_2\text{S}_2\text{O}_8$ increased from 0.1 M to 0.5 M, the superhydrophobicity of the copper easily attained for the high concentration of NaOH. With the high amount of the etchants, the amount of copper was etched much. Simultaneously, the insoluble etching products such as $\text{Cu}(\text{OH})_2$ and CuO were generated increasingly. This led to the high roughness of the copper surface, followed by the increasing contact angle (see Fig. 4). However, the highest contact angle of the copper was achieved at the etching time of 3 min instead of 1 min or 5 min. It is possible that, for the short etching time like 1 min, the amount of the formed etching products was insufficient, followed by the low surface roughness. Meanwhile, for the long etching time like 5 min, the amount of the generated etching products were large, leading to the insufficiently porous and thick product film on the surface of the copper samples. As a result, the surface roughness of the sample is not also high. Only with the sufficient etching time of 3 min, the the surface roughness of the sample was appropriate. Accordingly, the sample achieved the highest contact angle at this time.

To examine the morphological change of the copper plate during the fabrication of the superhydrophobic surface, the surfaces of the copper samples before and after etching and after modifying were analyzed by SEM. As observed from Fig. 6a, b, the surface of the copper plate is relatively smooth. However, after being immersed into the etching solution, the copper was dissolved to participate in the chemical reactions (1) and (3). As a result, the surface was etched and became rougher. The new etching products were formed and redeposited on the copper surface (Fig. 6c, d). It is easy to see that, the formed products exhibit the shape of the nanoneedle arrays. The nanoneedles have a diameter of about 300 nm and a length of $\sim 5 \mu\text{m}$. In addition, the nanoneedles are covered by some urchin-like microparticles. The morphology of the copper sample after etching in the solution of $\text{Na}_2\text{S}_2\text{O}_8$ and NaOH in the present work is totally analogous to that of the other copper samples as reported previously [2,12]. Following the modification process in the stearic acid, the copper surface changed from the sharp nanoneedle type to the rough dendrite type (Fig. 6e,f). This demonstrates the chemical attack

caused by stearic acid. Accordingly, the surface morphology integrity of the copper substrate no longer remained. Obviously, each step in the fabrication process of the superhydrophobic copper influences significantly the morphology of the sample surface, accompanied by tuning the contact angle of the sample.

One application of the superhydrophobic materials is established to be anticorrosion. Thus, to evaluate the application potential for this field, the superhydrophobic copper sample fabricated at the optimized conditions was measured Tafel polarization in 3.5 wt.% NaCl solution. For comparison, two copper samples including a pristine copper sample and an etched copper sample were also measured (Fig. 7). After Tafel analysis using the Nova 2.11 software, it was found that after etching the copper sample showed the almost same corrosion behaviour as the pristine. In particular, the pristine copper sample had a corrosion potential of -0.3 V and a corrosion current density of $7.11 \times 10^{-4} \text{ Acm}^{-2}$ (Table 1). Similarly, the etched copper offered a corrosion potential of -0.3 V and a corrosion current density of $8.86 \times 10^{-4} \text{ Acm}^{-2}$. So, even after etching the copper was more aggressive because of its high surface area (Fig. 6c, d).

Table 1. Tafel analysis result of the copper samples

Sample	E_{corr} (V)	I_{corr} (Acm^{-2})
Pristine	-0.30	7.11×10^{-4}
After etching	-0.31	8.86×10^{-4}
After modifying	-0.12	8.28×10^{-6}

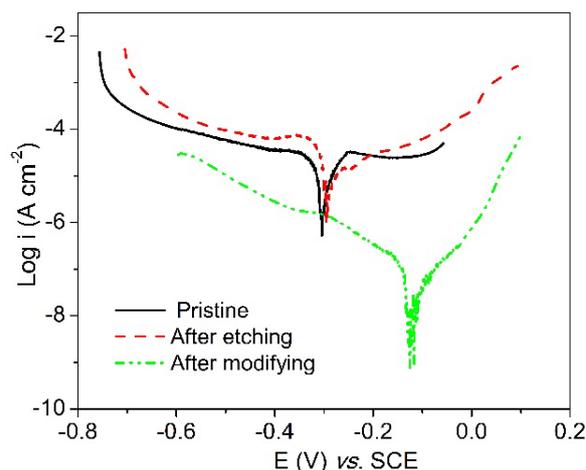


Fig. 7. Tafel polarization plots of the copper sample before and after treatment to achieve superhydrophobicity.

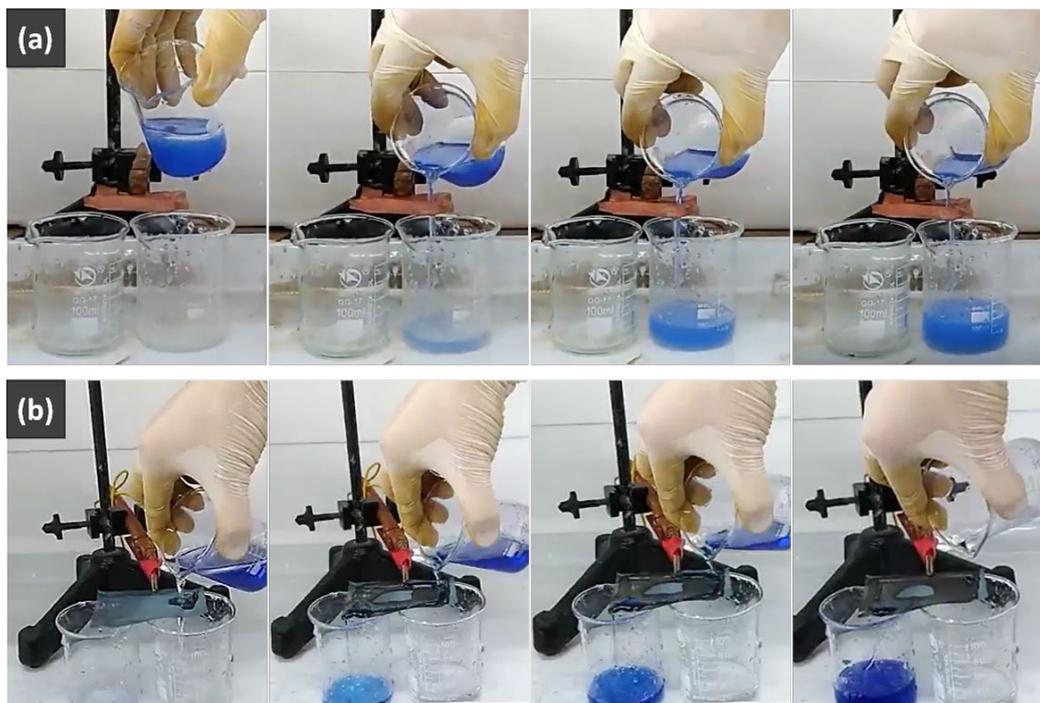


Fig. 8. Illustration of the oil-water separation ability of a hydrophobic copper mesh.

In contrast, after modifying with stearic acid, the surface of the copper plate became less rough. The presence of the stearate salt, as well as the absorbing stearic acid on the copper surface, induced its low surface energy. This led to the difficult accessibility of the aqueous solution to the surface of the copper plate. This results in effectively preventing the corrosive agents from attacking the copper substrate. As a result, the corrosion potential of the copper sample after modification shifted by 0.19 V to the positive potential direction. Furthermore, the corrosion current density of the superhydrophobic copper plate was $8.28 \times 10^{-6} \text{ Acm}^{-2}$, which is 85 and 107 times smaller than those of the pristine and etched copper plates, respectively. This implies that the superhydrophobic surface of the copper substrate offers high anticorrosion behaviour. Accordingly, the modification of the metal surface to become a superhydrophobic surface is an effective strategy for the protection of the metal from corrosion.

Besides, to show the oil/water separation application of the superhydrophobic copper fabricated in the present work, a superhydrophobic copper mesh was fabricated at the optimal condition. A water-oil mixture of distilled water and toluene oil was used as typical oily wastewater. The distilled water and toluene are transparent. For easy recognition of the water phase, methylene blue was dissolved into the mixture (methylene blue is only dissolved in water but not in toluene). As indicated in Fig. 8a, for the fresh copper mesh, the mixture of water and toluene both passed through the mesh into a beaker, suggesting the

good wettability of fresh copper mesh for both two liquids, methylene blue-containing water and toluene.

Water and toluene oil were not separated from each other. In contrast, for the superhydrophobic copper mesh (Fig. 8b), the oil-water mixture was separated into two liquid flows once being poured into the superhydrophobic mesh. The transparent liquid flow, toluene oil, passed through the mesh into the beaker on the right. Meanwhile, the remaining liquid flow with blue colour, which represented the aqueous phase, spread over the mesh and drained into the beaker on the left. So, it can be concluded that the separation of the oil-water mixture was performed successfully using the superhydrophobic copper mesh.

4. Conclusion

In this study, a superhydrophobic copper surface with a maximum contact angle of 154.1° was fabricated by the chemical etching technique in combination with modification in stearic acid. After etching in the alkaline solution of $\text{Na}_2\text{S}_2\text{O}_8$, the surface roughness of the copper substrate was enhanced remarkably. With the high concentration of NaOH and $\text{Na}_2\text{S}_2\text{O}_8$ as well as the long etching time, the contact angle of the copper substrate against the water drops increased. The optimal fabrication process to obtain a superhydrophobic copper plate is etching the copper plate in the solution of 0.5 M $\text{Na}_2\text{S}_2\text{O}_8$ and 2.5 M NaOH for 3 min, then modifying it in the 0.01 M stearic acid for 24 h. The obtained measurements demonstrated that the superhydrophobic copper had a good corrosion resistance and could separate the oil-water mixture effectively. The optimal

superhydrophobic copper demonstrated 85 times-higher anticorrosion ability than that of pristine one. The successful fabrication of superhydrophobic copper surfaces in this study demonstrates that using cheap etching agents such as $\text{Na}_2\text{S}_2\text{O}_8$, NaOH and stearic acid will firmly lower the manufacturing cost of superhydrophobic copper samples on the large scale.

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