Construction of super-hydrophobic copper alloy surface by one-step mixed solution immersion method

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Abstract. This paper presents a method for preparing a super hydrophobic surface with a fast, simple, low-cost, one-step reaction by immersing copper alloy in an ethanol solution containing silver nitrate and myristic acid. The effects of reaction time, reaction temperature, reactant concentration and reaction time on the wettability of the material were studied. The surface wettability, appearance, chemical composition, durability and chemical stability of the prepared samples was measured by water contact angle (CA), scanning electron microscopy (SEM), energy dispersive spectrometer (EDS), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The results show that when the reaction time is only 10min, the surface WCA of the prepared material can reach 154.9. This study provides an effective method for the rapid preparation of stable super hydrophobic surfaces.

1. Introduction
In the process of detecting soil oil pollution by resistivity method, metal copper is generally used as ground electrode. However, the corrosion resistance of copper electrode in complex soil is very poor, the corrosion of copper electrode has a great influence on the increase of material cost and measurement precision, the super-hydrophobic surface can effectively improve the corrosion resistance of the surface. The super hydrophobic surface refers to a special surface layer with an apparent contact angle (CA) greater than 150° and a rolling angle (SA) less than 5°. Typical examples are the natural leaves [1], rice leaves [2], butterflies Wings [3] and shark skin [4] and so on. Since the super hydrophobic material has excellent super water repellency, it has application potential in the self-cleaning [5], anti-corrosion [6], anti-icing [7] and drag reduction [8], microfluidic devices [9] 10] and other areas. In general, super hydrophobic surfaces can be prepared by coating surface energy substances on special micro-nano rough structures [11].

Due to copper and its alloys have excellent thermal conductivity, mechanical properties, etc., it is widely used in the construction, automotive, aviation and power transmission [12] and other fields. But the frozen frost problems of copper parts exposed in the low-temperature refrigeration and corrosive problems exposed during transport seriously affecting the use of copper and its alloy performance, to bring a greater harm to the equipment, so the application of copper alloy products have been limited [13]. If the super-hydrophobic coating is prepared on the surface of copper and its alloys, the corrosion can be slowed due to the self-cleaning and waterproofing properties of the coating. Therefore, it is necessary to prepare a super hydrophobic coating on the surface of copper and its alloys. In recent years, researchers have developed a super hydrophobic structure of copper and its
alloys through a variety of techniques, such as chemical etching [14], electrochemical deposition [15], laser etching [16], self-assembly [17] and sol-gel [18] and other methods [19]. Dai et al. [14] used a chemical etching method to soak the pure copper mesh in a mixture of NaOH and K$_2$S$_2$O$_7$ for 30 min to construct a Cu (OH)$_2$ roughened structure which was then modified with n-octadecyl phosphate and had a surface contact angle of 158.9°. He et al. [15] deposited a layer of tin film on the surface of the copper substrate by electrodeposition, and then annealed at 180 °C to prepare a super-hydrophobic tin film into a porous "fungus-like" micro-nano rough structure, the surface contact angle can up to 170°. B.S. Yilbas [16] using the laser etching method on the surface of phosphor bronze structure of its surface roughness through the carbon dioxide laser, prepared with super-hydrophobic, high hardness and low friction coefficient of super-hydrophobic surface. CDGu et al. [19] first equipped with a 1:2 mixtures of trichloromethane and ethylene glycol was stirred at 75 °C until a colorless liquid was formed, then AgCl was added as a eutectic solvent, and the copper alloy C194 was immersed in a eutectic solvent To obtain a suitable rough structure, and then immersed in the dodecyl alcohol ethanol solution for 20h, the contact angle of 160° super hydrophobic surface has been prepared. It can be seen that most of the preparation methods of copper and its super hydrophobic surfaces have the disadvantages of complicated process, high preparation requirements or long preparation period, greatly limit their application in industry.

Based on it, this paper studies a method for rapid preparation of super hydrophobic membrane: the copper alloy was immersed in a mixed ethanol solution of silver nitrate and myristic acid by simple chemical solution etching and self-assembly. The self-assembled layer of nutmeg was formed while the micro-nano geometry was formed on the surface, acidic monolayer self-assembly, super-hydrophobic surface has successfully prepared with a simple one-step reaction. In this paper, the effects of time, temperature and the concentration of myristic acid and silver nitrate on the surface wettability were studied and characterize the morphology, hydrophobic properties and stability of the super hydrophobic surface.

2. Experiment

2.1. Reagents and materials
BZn18-18 copper-nickel alloy (Cu> 53.5 wt%, Zn balance, Ni <19.5%), Yangzhou City in the stainless steel Limited; Silver nitrate (≧ 99.95%, Shanghai Pharmaceutical Factory); Myristic acid (≧ 98.0%, Sinopharm Group Chemical Reagent Co., Ltd.); Anhydrous ethanol (analytical grade), distilled water made by the laboratory.

2.2. White copper surface pretreatment
Using copper (made into 3cm × 6cm) as the substrate, with gold sandpaper polished for 20 minutes to remove the surface oxide, polished to light level, and then with anhydrous ethanol, acetone ultrasonic cleaning three times, each time for 5 minutes. And then use ultrasound cleaned it in anhydrous ethanol, acetone for three times respectively, each cleaning 5 minutes, and finally rinse with deionized water, nitrogen dry to be used.

2.3. Preparation of Super Hydrophobic Surfaces
Through the combination of chemical etching and self-assembly, the washed copper-nickel alloy was immersed in a mixed ethanol solution of silver nitrate and myristic acid. The self-assembled myristic acid monomolecular layer was constructed while the rough structure was constructed on the surface of copper. The concentration of silver nitrate (0 mM, 10 mM, 20 mM, 40 mM, 60 mM, 100 mM), myristic acid concentration (0 mM, 3.6 mM, 7 mM, 15 mM, 20 mM, 30 mM, 40 mM), reaction time (3min, 5min, 10min, 20min, 30min, 50min), the reaction temperature (30°C, 40°C, 50°C, 60°C) is regarded as the independent variable, the contact angle of the prepared sample is the dependent variable, to explore the optimal preparation conditions.
2.4. Instrumentation and characterization
The surface morphology of the super hydrophobic samples was observed by scanning electron microscopy (SEM, XFlash Detector 430-M). The wettability of the samples was characterized by contact angle measuring instrument (TBU 90E) at room temperature. The contact angle of six different locations on the sample surface was measured, and distilled water was used as the detection solution. The amount of water droplets used was 5 μL, and the average value of the 6-point contact angle was taken as the contact angle. The phase of the sample was analyzed by X-ray diffractometer (XRD, DX-2700). The surface elements of the sample were qualitatively analyzed by Energy Disperse Spectroscopy (EDS, XFlash Detector 430-M). The prepared sample was immersed in water and a conventional organic solution for a period of time to measure the contact angle to reflect its stability.

![Image of super hydrophobic surface preparation process diagram]

**Figure 1.** Super hydrophobic surface preparation process diagram

3. Results and discussion

3.1. Effect of silver nitrate etching on the concentration
Figure 2 shows the contact angle of the copper-clad surface under different concentrations of silver nitrate (0 mM, 5 mM, 10 mM, 20 mM, 40 mM, 60 mM and 100 mM). The corresponding surface contact angles were 92.5°, 140°, 148.3°, 150°, 149.5°, 147.5° and 148.0°, respectively. It is obvious that the contact angle gradually rises to the peak and then flatten out with the increase of the etching concentration, the reason is the solubility of silver nitrate in ethanol is fixed, when the concentration of silver nitrate reaches 20 mM, saturated solution has been formed, so the concentration does not affect the formation of copper surface roughness. When the etching concentration is 20 mM, the contact angle is 150°, and the concentration is the most economical concentration, so that the etching concentration is preferably 20 mM.
Figure 2. The contact angle of white copper at different concentrations of silver nitrate (0 mM, 5 mM, 10 mM, 20 mM, 40 mM, 60 mM and 100 mM), myristic acid 15 mM ethanol solution, reaction temperature 50°C, reaction time 10 min

3.2. The effect of reaction time

Figure 3 shows the contact angle of the copper-clad surface after silver nitrate (20 mM) etching and myristic acid (15 mM) self-assembly reaction at different reaction times (0 min, 3 min, 5 min, 10 min, 20 min, 30 min, 50 min) is 106°, 142°, 145.2°, 152.2°, 148.2°, 147.3°, 145°. It can be seen that as the reaction time increases, the contact angle increases first and then decreases, because the etching of the surface of the copper base is not complete before the reaction time is less than 10 min, and the surface of the copper-nickel alloy fails to form a suitable rough structure, at the same time, silver film on the myristic acid adsorption is not sufficient, leading to changes in contact angle gradually increased. When the reaction time exceeds the optimum reaction time (10 min), the rough structure of the surface of the material is crosslinked and collapsed, resulting in an increase in the contact area between the water droplets and the material matrix, and thus the contact angle decreases. In the reaction 10 min, the contact angle reached a peak of 152.2°. In summary, 10 min is the best reaction time.
3.3. The effect of reaction temperature

Figure 3 shows the effect of the reaction temperature on the contact angle of the copper-clad surface in a mixed ethanol solution of silver nitrate and myristic acid. The contact angles were 131, 140, 153.2 and 144 at 40°C, 50°C and 60°C, respectively. It can be seen that as the reaction temperature increases, the contact angle increases first and then decreases. The reason is that when the temperature does not reach 50°C, the reaction is accelerating with the reaction temperature increases, silver nitrate on the surface of the material to accelerate the etching rate, while the reaction speed of myristic acid hydrophobic long chain assembly on the silver film surface is accelerating. When the temperature is higher than 50°C, the appearance of the surface of the sample is observed at 70°C, and found that the surface of the material cracking. At 50°C, the contact angle of the material reaches a peak of 153.2°, so it is determined that the optimum reaction temperature is 50°C.

3.3. The effect of reaction temperature

Figure 4 shows the effect of the reaction temperature on the contact angle of the copper-clad surface in a mixed ethanol solution of silver nitrate and myristic acid. The contact angles were 131, 140, 153.2 and 144 at 40°C, 50°C and 60°C, respectively. It can be seen that as the reaction temperature increases, the contact angle increases first and then decreases. The reason is that when the temperature does not reach 50°C, the reaction is accelerating with the reaction temperature increases, silver nitrate on the surface of the material to accelerate the etching rate, while the reaction speed of myristic acid hydrophobic long chain assembly on the silver film surface is accelerating. When the temperature is higher than 50°C, the appearance of the surface of the sample is observed at 70°C, and found that the surface of the material cracking. At 50°C, the contact angle of the material reaches a peak of 153.2°, so it is determined that the optimum reaction temperature is 50°C.

**Figure 3.** The contact angle of copper-copper surface after silver nitrate and myristic acid mixed at different times (3min, 5min, 10min, 20min, 30min and 50min), reaction temperature 50°C, silver nitrate (20 mM) and myristic acid (15 mM) in a mixed ethanol solution.

**Figure 4.** Contact angle of copper surface in different concentrations of silver nitrate and myristic acid at different reaction temperatures (30°C, 40°C, 50°C and 60°C), reaction time 10 min.
3.4. The effect of myristic acid concentration

Figure 5 shows the contact angle of self-assembly of myristic acid at different concentrations (0 mM, 3.6 mM, 7 mM, 15 mM, 20 mM, 30 mM, 40 mM) on the surface of copper-nickel. The results were 63°, 140.2°, 146.5°, 147.5°, 152.7°, 145.3° and 118.9°, respectively. It can be seen that with the increase in myristic acid concentration, the contact angle instantaneously increases and tends to be flat after the lower, it may be due to the concentration of myristic acid is low, the formation of self-assembled film layer coverage is not enough, but the concentration is too high, myristic acid and easy polymerization in the solution is not conducive to self-assembly on the surface of copper. When the myristic concentration was 20 mM, the contact angle reached a peak of 152.7°. Therefore, the self-assembly concentration of myristic acid is preferably 20 mM.

![Graph](image)

**Figure 5.** The effects of different concentrations of myristic acid (0mM, 3.6 mM, 7 mM, 15 mM, 20 mM, 30 mM and 40 mM) on the surface of copper-nickel alloy.

Silver nitrate concentration of 20mM, reaction time 10min, reaction temperature 50 °C

In one word, the optimum reaction conditions were as follows: silver nitrate 20mM, myristic acid 20mM, reaction time 10min, reaction temperature 50 °C

3.5. Surface morphology and wetting properties of copper before and after the reaction

The surface morphology of the sample at different reaction times was observed by SEM, and Fig. 6 were SEM images observed at magnification of 2000 and 5000 magnifications. From Fig. 6 (a1, a2), it can be seen that there is no other topography other than the stress scratches generated during the process before the reaction, at this point the CA is 103.1° (Figure 7a), the sample surface showing a weak hydrophobicity. It can be seen from Fig. 6 (b1, b2) that the small and sparse submicron spherical stacking structure appears when the copper-nickel matrix is reacted in solution for 3 min, at this point the CA is 144.7° (Figure 7b), the sample surface near the super-hydrophobic properties. It can be seen from Figure 6 (c1, c2), when the white copper matrix in the solution for 10min, the sample surface similar to the coral-like, spherical particles further accumulation, closely arranged, layer stacked layer, there are obvious hierarchical structure and self-similarity, and the pellets are formed into spherical micro clusters with diameters between 4 and 7 μm, at this point the CA is 154.7° (Fig. 7c), and on the surface, the water droplets are extremely unstable and drops rapidly on the slightly tilted surface (<5°) to reach the super hydrophobic level. It can be shown that the appropriate microstructure plays a crucial role in the hydrophobicity of the material surface, and a large amount of air can be captured in
the gap formed by the micro-nanostructures, thus making the surface of the material super hydrophobic. This can be explained by the Cassie-Baxter equation [20].

\[
\cos \theta = f \cos \theta_c + f - 1
\]  

(1)

In the formula, \( \theta_c \) is the intrinsic contact angle (the contact angle of the copper-coated surface after cleaning), \( \theta = 154.7^\circ \), \( \theta_c = 103.1^\circ \), can get \( f = 0.124 \). This data shows that only about 12.4% of the material surface is in contact with water droplets. The reason is that the microstructures formed by the formation of spherical micro clusters contain a large amount of air, which effectively prevents the water droplets from penetrating into the surface of the copper.

It can be seen from Fig. 6 (d1, d2) that when the reaction time is increased to 20 min, the spherical micro clusters are collapsed, and the contact angle is reduced to 147.2° in Fig. 7 (d). This is due to the decrease of the roughness of the structure, the liquid-gas interface ratio is decreasing, and the ratio of the liquid-solid interface is increasing, leading to the decrease of the contact angle. To sum up: building a suitable rough surface is the key to the preparation of super-hydrophobic surface [21].
Figure 6. SEM images (a1, a2) represent the surface morphology of the cleaned copper-copper surface at 2000 and 5000 magnifications.

(b1, b2) represents the surface morphology of the copper surface at 2000 and 5000 magnification, which reacted in a mixed ethanol solution of silver nitrate and myristic acid for 3 min. (c1, c2) shows the surface morphology of the copper-copper surface at 2000 and 5000 magnification, which reacted in a mixed ethanol solution of silver nitrate and myristic acid for 10 min. (d1, d2) shows the surface morphology of the copper-copper surface after 2000 and 5000 magnification, which reacted in the mixed ethanol solution of silver nitrate and myristic acid for 20 min.
Figure 7. The contact angle of the material surface at different reaction times

(a) represents the cleaned copper-nickel surface; (b) the surface of the copper-nickel alloy after 3 minutes of reaction in a mixed ethanol solution of silver nitrate and myristic acid; (c) the surface of the copper-nickel alloy after 10 minutes of reaction in a mixed ethanol solution of silver nitrate and myristic acid; (d) the surface of the copper-nickel alloy after 20 minutes of reaction in a mixed ethanol solution of silver nitrate and myristic acid.

3.6. Chemical composition
Figure 8. (a) XRD spectrum after cleaning the surface of the copper (curve 1) and prepared in the mixed solution of super-hydrophobic surface (curve 2, 0.1 g silver nitrate / 0.15 g myristic acid).

(b) Pure myristic acid (curve 1) in the FT-IR spectrum and a super hydrophobic surface (curve 2, 0.1 g silver nitrate / 0.15 g myristic acid) prepared in a mixed solution; (c) Coordination modes between metal ions and carboxyl groups: monatomic chelate ligands (mode 1), bidentate chelate complexes (mode 2), bidentate bridge complexes (mode 3).

XRD can analyse the crystal structure of copper and surface coatings. From the graph a (1), it can be seen that characteristic diffraction peak of Cu0.7Zn0.3 (111), Cu0.7Zn0.3 (200), Cu0.7Zn0.3 (200) were found at 2θ = 42.46°, 49.43°, 72.51°. Ag (111) corresponding to the characteristic diffraction peaks of standard pdf97-004-4387 appear at 2θ = 38.1° after simultaneous treatment with silver nitrate and myristic acid, indicating that silver film was successfully constructed on the surface of copper substrate. Since the electrode potential of Zn is -0.7628V, the electrode potential of Ni is -0.23V, the electrode potential of Cu is +0.3402V, and it can be seen that the electrode potential of Zn is the lowest, therefore, in the oxidized silver nitrate solution, zinc is preferentially reduced with silver nitrate. The preferential dissolution mechanism [22] also argues that in the process of corrosion, the zinc will first dissolve and then continue to dissolve through the vacancy, and the copper element has left behind because of its positive electric potential, this also explains why the rough structure constructed in the SEM is not dense. The reaction process of copper in silver nitrate solution:

\[ \text{Zn} + 2\text{Ag} \rightarrow \text{Zn}^2+ + 2\text{Ag} \]  \hspace{1cm} (2)

\[ \text{Cu} + 2\text{Ag} \rightarrow \text{Cu}^2+ + 2\text{Ag} \]  \hspace{1cm} (3)
FT-IR IR spectroscopy can explain the combination of silver surface and myristic acid. It can be seen from the figure that pure myristic acid has a strong peak at 1702 cm\(^{-1}\), corresponding to the tensile peak \(-C = O\) in the COOH group. After the white copper was immersed in a mixed ethanol solution of silver nitrate and myristic acid, the strong peaks were divided into two peaks and transferred to 1580 cm\(^{-1}\) and 1447 cm\(^{-1}\), corresponding to the anti-symmetric telescopic peak \(-COO-\) (vas) and the symmetric expansion joints \(-COO-\) (vs)[23]. Compared with the standard peaks of myristic acid, the infrared peaks on the surface of super hydrophobic copper have an absorption peak at 2920 cm\(^{-1}\) and 2850 cm\(^{-1}\) due to symmetrical and antisymmetric stretching vibration peaks -CH2-[24]. It can be seen, by silver nitrate and myristic acid mixed ethanol solution soaked, myristic acid hydrophobic long chain is indeed assembled to the silver film surface. It is speculated from the reaction mechanism of 4-dimethylaminobenzoic acid with silver film [25] that the myristic acid molecule is also bonded to the substrate by two symmetrical oxygen atoms of the carboxyl group, in the form of carboxylate through the chemical adsorption and silver film surface to form self-assembled monolayer, effectively reducing the surface free energy, thereby greatly improving the hydrophobic surface of the material the reaction process is as follows:

\[
\text{Ag-OH+ CH3(CH2)12COOH} \rightarrow \text{CH3(CH2)12COO-Ag+H2O} \quad (4)
\]

The coordination pattern in Figure c can be pushed out from the separation frequency (\(\Delta \nu = \text{vas}-\text{vs}\)) of the FT-IR spectrum. In general, a high \(\Delta \nu\) value (> 200 cm\(^{-1}\)) corresponds to a single atom chelate ligand (Mode 1) and the value of \(\Delta \nu\) in the bidentate chelate complex (mode 2) is much smaller <100 cm\(^{-1}\), the value of \(\Delta \nu\) in the double-tooth bridge complex (mode 3) is close to 150 cm\(^{-1}\)[26,27]. The \(\rho = 133 \text{ cm}^{-1}\) on the surface of the copper-copper in the mixed solution was found, indicating that myristic acid and silver were present in a double-tooth bridge composite mode.

In order to confirm the chemical composition of the surface of the copper-nickel alloy before and after the reaction, EDS analysis was performed, and the results are shown in Fig. 9 and Table 1. In Figure a, Cu, Zn, Ni and C elements can be clearly observed, the corresponding atomic percentage was 60.89%, 30.26%, 7.04% and 1.42%, corresponds to the distribution of elements on the surface of the copper-copper. The atomic percentage of Cu, Zn, Ni, C was 52.81%, 18.52% ,6.92%,1.48%, respectively. The presence of Ag is due to the substitution reaction between silver nitrate and Zn and Cu, corresponding to an increase in the percentage of Ag atoms, a decrease in the percentage of Zn and Cu atoms. Glycurium was soaked in a mixed solution of silver nitrate and myristic acid. The Ag element was also observed in the graph c, but the atomic percentage was reduced from 33.2% to 17.9%. This also further illustrates the reaction of myristic acid and silver film, which is also consistent with the results of XRD (Fig. 8a) and IR (Fig. 8b).
Figure 9. EDS spectra and element mapping images under different processes before and after the reaction: a1, a2 is a copper-clad surface; b1, b2 silver nitrate solution; c1, c2 mixed solution of silver nitrate and myristic acid.

Table 1. Atomic percentage of each element before and after the reaction

| Reaction conditions                                    | Element (at%) |
|--------------------------------------------------------|---------------|
|                                                        | Cu  | Zn  | Ni  | Ag  | C  |
| Cleaning                                               | 60.89| 30.26| 7.04| 1.42|    |
| Silver nitrate solution                                | 52.81| 18.52| 6.97| 33.2| 1.48|
| Silver nitrate and myristic acid mixed solution        | 50.09| 17.74| 6.86| 17.9| 3.29|

4. durability and chemical stability

In the practical application of super-hydrophobic surfaces, durability and chemical stability are very important. In order to test the performance of the prepared super hydrophobic surface, the stability of the sample was tested differently. The measurement of the contact angle was obtained by taking the average value of three points on the sample.
Figure 10. Effect of exposure time on contact angle

It can be seen from the figure that the contact angle decreases from 154.7 to 152.7 after exposure in the air for one month, the sample surface is still in a super hydrophobic state, the contact angle is only slightly changed. The experimental results show that the prepared samples still have good hydrophobic properties and excellent durability even exposed to moist air.

Figure 11. Effect of immersion time on the contact angle of the sample in 3.5 wt% NaCl solution

Figure 11 shows the effect of the immersion time on the contact angle of the metal super hydrophobic surface in 3.5 wt% NaCl solution. After 48 h, the contact angle of super hydrophobic surface decreased from 154.7 to 149.7, and the contact angle fluctuated little, which indicated that simulated sea water had little effect on the super hydrophobic performance of the prepared material.

To evaluate the durability and chemical stability of the prepared super hydrophobic surface, the sample was immersed in an acidic or alkaline solution of different pH values (1-14) for 24 h [28]. Figure 12 shows the effect of the pH of the solution on the super hydrophobic properties of the prepared material. The pH of the solution is adjusted by hydrochloric acid and sodium hydroxide. Strong acid or alkali solution (pH 1, 2, 3 and 13, 14) will destroy the prepared material of the super-
hydrophobic membrane layer, resulting in reduced super hydrophobic properties, except these solutions all the other solutions will not affect the super hydrophobic properties of this material, and the contact angle is all above 150°. The results show that the super hydrophobic material not only has super hydrophobic properties in pure water but also in corrosive alkaline solution. However, in the strong acid or strong alkaline environment, the super hydrophobic surface loses its super hydrophobic properties, this may be a new direction for our future research.

Figure 12. The contact angle of the sample which was immersed in a solution of different pH values for 24 h

5. Summary
In summary, we have studied a simple and efficient method for preparing super hydrophobic materials. The super hydrophobic surface was prepared quickly in one step by immersing the copper alloy in a mixed ethanol solution of silver nitrate and myristic acid. In this work, we optimized the reactant concentration, reaction time, reaction temperature, and so on. The results show that the surface of the super hydrophobic copper alloy is prepared by soaking the copper alloy in a mixed ethanol solution of 20mM silver nitrate and 20mM myristic acid at 50°C for 10 min, and the corresponding surface CA can reach 154.9°. The surface has long-term durability and chemical stability. This simple and efficient method can be used to prepare super-hydrophobic surface to open up a new shortcut, super-hydrophobic material is expected to large-scale preparation.

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References
[1] Marmur A. The Lotus Effect: Superhydrophobicity and Metastability [J]. Langmuir the Acs Journal of Surfaces & Colloids, 2004, 20 (9):3517.
[2] K. Liu, X. Yao, L. Jiang, Recent developments in bio-inspired special.
[3] Y. Zheng, X. Gao, L. Jiang, Directional adhesion of superhydrophobic butterfly wings, Soft Matter 3 (2007) 178–182.
[4] G.D. Bixler, B. Bhushan, Fluid drag reduction with shark-skin riblet inspired.
[5] [6] [7] [8] [9] [10] [11] [12] [13] [14] [15] [16] [17] [18]
[21] Seifzadeh D, Golmoghani-Ebrahimi E. Formation of novel and crack free nanocomposites based on sol gel process for corrosion protection of copper [J]. Surface & Coatings Technology, 2012, 210 (8): 103-112.

[22] Gu C D, Xu X J, Tu J P. Fabrication and Wettability of Nanoporous Silver Film on Copper from Choline Chloride-Based Deep Eutectic Solvents [J]. Journal of Physical Chemistry C, 2010, 114 (32): 13614-13619.

[23] A.B.D. Cassie, S. Baxter, Wettability of porous surfaces, Trans. Faraday Soc. 40 (1944) 546–551.

[24] Ishizaki T, Hieda J, Saito N, et al. Corrosion resistance and chemical stability of super-hydrophobic film deposited on magnesium alloy AZ31 by microwave plasma-enhanced chemical vapor deposition [J]. Electrochimica Acta, 2010, 55 (23):7094-7101.

[25] Langeneffer E E, Robinson F P A. Investigation of tensile stress induced by induced by dezincification layer during corrosion of brass [J]. Corrosion, 1969, 25 (3):137.

[26] W. Xu, A. Song, S. Dong, J. Chen, J. Hao, A systematic investigation and insight into the formation mechanism of bilayers of fatty acid/soap mixtures in aqueous solutions, Langmuir 29 (2013) 12380-12388.

[27] S. Gunasekaran, R.K. Natarajan, A. Kala, Spectrochim. Acta A 68 (2007) 323e-330.

[28] Lee S J, Han S W, Yoon M, et al. Adsorption characteristics of 4-dimethylamino- benzoic acid on silver and titania: diffuse reflectance infrared Fourier transform spectroscopy study [J]. Vib Spectrosc, 2000,24 (2): 265-275.

[29] Y. Qiao, Y. Lin, Y. Wang, Z. Yang, J. Liu, J. Zhou, Y. Yan, J. Huang, Metal-driven hierarchical self-assembled one-dimensional nanohelices, Nano Lett. 9 (2009) 4500-4504.

[30] G. B. Deacon, R. J. Phillips, Relationships between the carbon-oxygen stretching frequencies of carboxylate complexes and the type of carboxylate coordination, Coord. Chem. Rev. 33 (1980) 227-250.

[31] Liu Y, Liu J, Li S, et al. Biomimetic Superhydrophobic Surface of High Adhesion Fabricated with Micronano Binary Structure on Aluminum Alloy [J]. Acs Applied Materials & Interfaces, 2013, 5 (18):8907.