Preparation of superhydrophobic copper surface by a novel 
silk-screen printing aided electrochemical machining method

X Y Yan¹, G X Chen¹ and J W Liu²

1 State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China
2 College of mechanical and electrical engineering, Guangdong University of Technology, Guangzhou 510090, China
E-mail: fejliu@scut.edu.cn

Abstract: A kind of superhydrophobic copper surface with micro-nanocomposite structure has been successfully fabricated by employing a silk-screen printing aided electrochemical machining method. At first silk-screen printing technology has been used to form a column point array mask, and then the microcolumn array would be fabricated by electrochemical machining (ECM) effect. In this study, the drop contact angles have been studied and scanning electron microscopy (SEM) has been used to study the surface characteristic of the workpiece. The experiment results show that the micro-nanocomposite structure with cylindrical array can be successfully fabricated on the metal surface. And the maximum contact angle is 151° when the fluoroalkylsilane ethanol solution was used to modify the machined surface in this study.

1. Introduction
There had been no reported about why lotus leaf and other plants and insects have hydrophobic surface before 1992. Afterwards, Barthlott et al. introduce the ‘Lotus concept’ in 1992, which is also called “lotus effect”. Since then, Lotus leaves have widely attracted immense scientific attention due to their superior superhydrophobic properties. As for superhydrophobic surfaces, its water contact angle is higher than 150°, and roll angle is less than 10°. In fact, the double roughness structure is the origin of superhydrophobicity which is useful for floating ability on water surface. At the same time, epicuticular wax is also important, which is a typical low surface energy substance, so as to have superior superhydrophobic properties. Neinhuis et al. [1] demonstrated the super-water-repellent of the lotus leaf and attributed it to the double roughness surface structure with micro- and nanostructures, together with the hydrophobic properties of epicuticular wax.

Based on “lotus effect” theory, a series of fabrication methods (chemical substitution/deposition, electrochemical-etching, solution-immersion etc.) and hydrophobic agent (fluoroalkylsilane) have been...
reported for generating superhydrophobic surfaces. Cheng et al. [2] reported that the NiO/ZnO superhydrophobic surface on zinc was fabricated by chemical substitution/deposition and thermal annealing. Yang et al. [3] developed a simple and universal electrochemical-etching method to fabricate the superhydrophobic patterned surface on metal superhydrophobic substrates. Qu et al. [4] reported that superhydrophobic surfaces on engineering materials are prepared via a convenient solution-immersion method. And fluoroalkylsilane was used as a hydrophobic material to reduce the surface free energy. Up to now, more and more researchers have focused on their functions and applications in recent years, since there are many excellent properties besides superhydrophobicity. And it has been also considered for their practical applications in industry ultimately.

As we all know, metal is mostly corrosive, copper is no exception. To overcome this shortcoming, it is necessary to fabricate superhydrophobic copper surface with micro-nanocomposite structure to isolate with water, just because of the existence of water, causing copper corrosion. Zhang et al. [5] discovered that binary geometric structures at the micro- and nano-scale are fabricated on copper surfaces via simple sandblasting and surface oxidation process. He et al. [6] demonstrated that the micro/nano superhydrophobic surface on copper substrate has been successfully fabricated through a simple and effective electrodeposition method combined with annealing without low surface energy organics modification.

In this study, a silk screen printing technology was used to prepare the electrolytic mask on the copper surface, and a micro-nanocomposite structure of the copper surface can be obtained by electrochemical machining. The superhydrophobic copper surface was further modified by fluoroalkylsilane treatment. By analyzing the micro-nanocomposite structure topography, the mechanism of material erosion was studied during electrolytic machining. The formation conditions of superhydrophobic surface were analyzed by SEM and EDS. Meanwhile, the water contact angle of copper surface was measured by contact angle measurement.

2. Experimental and preparation
Copper substrates (99.9%) with a size of 4.0cm×4.0cm×0.02cm were obtained from Tianjin Kermel Chemical Reagent Co., Ltd., China, which was selected as experimental material; screen printing plate; Heptadecafluorodecyl trimethoxy-Silane (98%, HTS) was purchased from En Fujia Technology Co., Ltd., Shanghai, China, which served as low surface modification materials. The experimental device is home-made electrolytic power with voltage of 0-60V and current of 0-100A, the electrolyte is the solution of sodium nitrate (5 wt %) and ferric chloride (1 wt %).

Figure 1 shows home-made electrolytic processing machine and machining process, before electrochemical machining, the copper surface was printed a mask layer, and then the non-printed areas were electrolytic corrosion during electrochemical machining process. Subsequently, the mask layer was rinsed. Finally, low surface energy was enhanced by fluoroalkylsilane ethanol solution immersion. Therefore, the superhydrophobic copper surface with micro-nanocomposite structure was obtained.

Figure 1. Home-made electrolytic processing machine and machining process.
3. Results and discussion

3.1 Effect of different dot area rates on the micro-nanocomposite structure

The screen printing plate was made by the number of screens with 100 lines / inch. And the screen printing dot area rates of 30%, 35%, 40%, 45% and 50% were obtained. The electrolytic mask was formed by printing on the copper surface shown in Figure 2.

![Figure 2. Electrolytic mask printed out with different dot area rates.](image)

The electrolysis voltage was 5V. The interval between the cathode and the anode was 3 mm. The copper with the mask was electrolyzed for 50s. And the obtained morphology is shown in Figure 3. By the way, the shape of Figure 3 (a-e) corresponds to the shape of Figure 2 (a-e). It can be seen from Figure 3 that the area that protected by the electrolytic mask was not electrolyzed, indicating that the printed electrolytic mask can play a protective role in the electrolytic process. The edge of the mask has a sharp shape, while most of the obtained upper surface of the microcolumn is close to a circle after the electrolysis, suggesting that the sharp shape is wiped out during the electrolysis. Meanwhile, as the shape of the tip is too small, it fails to be well protected copper. The height of the microcolumn was measured at a height of about 8 μm. Since the purpose of this paper is to prepare a micro-nanocomposite structure, the smaller the column is, the smaller the better. Comparing with Figure 3a and b, the shape of Figure 3a is not as round as that of Figure 3b, while the size of the microcolumn of Figure 3c-e is larger than that of Figure 3b. In conclusion, the screen printing plate with 35% dot area rate was selected as a mask version.

![Figure 3. Different mask electrolysis obtained microcolumns.](image)

3.2 Effect of different time on the micro-nanocomposite structure

In order to make the higher microcolumn, the electrolysis time was extended during the experiment. Figure 4 shows that different shape was obtained by electrolysis for different times (30s, 50s, 60s, 70s, 90s) with corresponding height 5 μm, 8 μm, 9 μm, 10 μm, and 13 μm on the screen printing plate with 35% dot area rate. As can be seen from Figure 4, the shape of the microcolumn is good when the electrolysis is performed for 30s, and the size of the top and bottom of the microcolumn are similar, indicating that it is not obvious that stray corrosion during the electrolysis process, so the height of the microcolumn is only 5 μm. The height of the microcolumn reached to 9 μm, when the electrolysis was conducted for 60s, the side of the top and bottom of the microcolumn are not much difference. After the electrolysis for 70s, the height of the microcolumn reached to 10 μm, but the side of the top and bottom of the microcolumn are not the same, indicating stray corrosion is more obvious at this time. When the electrolysis carried out for 90s, although the height reached to 13 μm, the stray corrosion is too serious. At the same time, the top and bottom of the micro-column has much difference, and micro-column does not meet the requirements. Therefore, the choice of electrolysis 60s can get a higher degree of microcolumn.
Figure 4. different electrolysis time microcolumn.

Based on above investigation, the copper surface with the micro-nano composite structure was obtained. Following, the copper surface was treated as low surface energy surface by fluoroalkylsilane ethanol solution (configured by heptadecafluorodecyl trimethoxy-Silane and ethanol) immersion for 45 minutes. Then the surface was dried for 30 minutes. Finally, the surface of the superhydrophobic copper surface was obtained. The water contact angle of copper surface was measured by contact angle measurement. The results shown in Figure 5, the contact angle is 151°, and rolling angle is 7°, which was in line with the requirements of superhydrophobic.

Figure 5. The images of static contact angle on copper surface.

Figure 6 describes SEM magnified images of the copper surface. It can be clearly seen the edge of microcolumn, the side of microcolumn has a certain fine structure, because the electrolyte contained ferric chloride solution (1 wt%), and it was corroded the copper surface without mask protection during electrochemical machining process, resulting in the nano-scale structure was generated on the side of the microcolumn. And it is the condition to form a superhydrophobic surface. Therefore, superhydrophobicity can be achieved after fluorination.

Figure 6. SEM image of copper surface with micro-nanocomposite structure.

The superhydrophobic copper surface element was further analyzed, and the results shown in Figure 7. It can be seen that the F and Si elements appeared on copper surface, indicating that the copper surface was adhered by fluoroalkylsilane successfully.
Figure 7. The EDS spectra of superhydrophobic copper surface.

4. Conclusion
In this study, the screen printing and electrolytic processing method was skillfully combined to successfully prepare a micro-nanocomposite structure on the copper surface, and the superhydrophobic effect was achieved, the experiment can be concluded as follows:
1. The screen printing method was used to quickly prepare the controllable electrolytic mask for the size and pattern. The microcolumn with the size of about 150μm and the height of about 9μm can be obtained by electrochemical machining.
2. The ferric chloride was added to the electrolyte. The electrolyzed side of microcolumns corroded by the ferric chloride, so as to the nano-structure formed.
3. The copper with a micro-nanocomposite structure has superior superhydrophobicity with the contact angle of 151° and rolling angle of 7° after fluoroalkylsilane treatment.

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