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# Simple fabrication of superamphiphobic copper surfaces with multilevel structures

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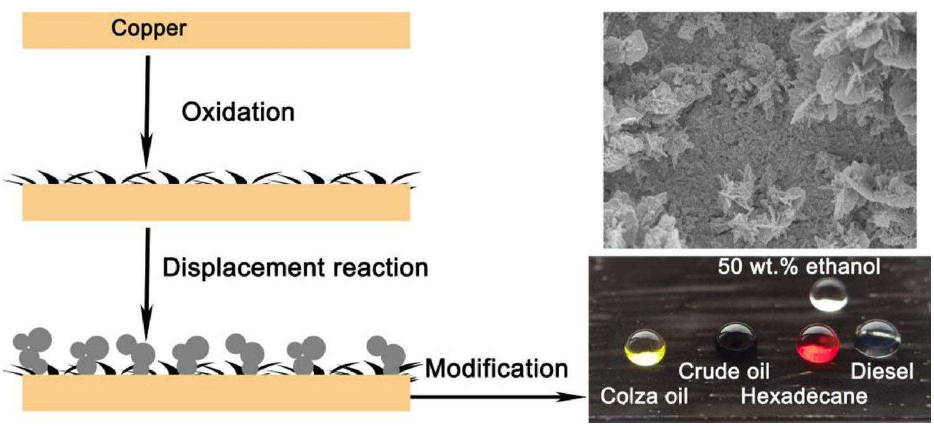
## GRAPHICAL ABSTRACT

Herein, we reported the simple fabrication of the superamphiphobic copper surfaces via a simple oxidation process and displacement reaction to create multilevel structures, followed by modification. The prepared superamphiphobic copper surfaces exhibit high contact angles (> 150°) of water, various oil and ethanol-water droplets with different mass fraction, which have great self-cleaning, oil resistant, anticorrosion properties.

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## ABSTRACT

Copper is widely used in various fields owing to its great electrical and thermal conductivity and so on. Once Coper is endowed with other properties, such as superamphiphobic, and the corresponding applications can be broadened. Hereby, we presented a convenient and cost-effective method to fabricate a superamphiphobic surface on the copper sheet. By virtue of scanning electron microscope (SEM), it is clear that hierarchical structures composed of micrometer-scale flake-like CuO and nanometer-scale Ag particles were formed on the copper surface by an alkali assistant oxidation process and a displacement reaction. After chemical modification of 1H,1H,2H,2H-perfluorodecanethiol, the surface with dual-scale structures was endowed with super-repellent ability towards water and several organic liquids with much lower surface tension, such as diesel, crude oil, colza oil and so on. Such superamphiphobic copper surfaces exhibit high contact angles (> 150°) of water, various oil, and ethanol-water (with different mass fraction) droplets, as well as corresponding low sliding angles (< 10°),

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which possess excellent self-cleaning and oil-resistant properties. In addition, enhanced corrosion resistance of the as-prepared surface was found in potential-dynamic polarization measurement.

## 1. Introduction

Inspired from nature, by recognizing the roles of the two key factors, appropriate roughness and low-surface-energy chemistry composition [1–3], superhydrophobicity has been widely investigated and achieved on various material surfaces due to its numerous functions including drag reduction [4], self-cleaning property [5–7], anti-icing [8], oil/water separation [9–11], and so on. Among these materials with anti-wetting behavior, superhydrophobic metallic materials have attracted increasing interests because metal substrate is more readily to construct rough structure than other materials and superhydrophobicity can greatly facilitate the metallic anticorrosion performance and prolong service life [12,13]. For examples, Cho and co-workers fabricated a superhydrophobic steel surface with improved anticorrosion performance through simply coating superhydrophobic nanocomposites on the bare steel [14]. Liu et al. reported a one-step electrodeposition method to prepare biomimetic superhydrophobic magnesium alloy with corrosion resistance ability [15]. Brassard and co-workers electrodeposited a thin Zn film on steel substrates, followed by modification with ultra-thin films of commercial silicone rubber, getting superhydrophobic surface for prevention of corrosion [16]. At the same time, copper, as an important engineering metallic material, has been widely used in many industrial applications owing to its excellent properties, such as great ductility, high electrical and thermal conductivity. However, when exposed to high humidity or elevated temperature, it can be easily contaminated and corroded despite of its good corrosion resistance, which greatly hamper its performance. Superhydrophobicity offers an efficient strategy to protect copper surface from corrosion and many superhydrophobic copper surfaces have been prepared for broad applications [17–23].

But, superhydrophobic copper surface only exhibits self-cleaning and antifouling abilities towards aqua-based liquid and cannot exhibit oil repellency property due to much lower surface tension of oil, which would seriously hinder applications of superhydrophobic copper such as oil resistance, oil transportation, and so on. Therefore, it is necessary to prepare superamphiphobic copper surface. However, compared to superhydrophobic surface, the demand on constructing superamphiphobic surface is higher. It is prerequisite to construct smaller or more special structure and to be modified with much lower surface energy. Aiming at these problems, many research groups have tried various techniques to create superamphiphobic surfaces and some promising results have been reported [24–28]. It is found that some special morphologies with dual-scale roughness (such as micrometer-scale and nanometer-scale surface roughness) make great sense to enhance the superamphiphobic property [29]. By controlling both surface energy and appropriate roughness, superamphiphobic surface can be fabricated [30–35]. Based on that, some superamphiphobic copper have been successfully prepared and researchers have reported a few methods for their development [34,36,37]. For examples, Li et al. prepared superamphiphobic CuO with hierarchical flower-like structures via electrodeposition and solution-immersion process, followed by fluorinated modification for 7 days [24]. Li and co-workers fabricated superamphiphobic surface on a copper substrate through chemical base deposition method and perfluorothiolate modification [36]. However, most of the preparation methods involved in complex steps and are time-consuming. So, it is necessary to obtain superamphiphobicity on copper surface through convenient and time-saving ways to meet the demand of industrial applications.

It has been reported that the transition metals and their oxides (Groups VIII and IB such as Cu and Ag) can easily coordinate with thiols [38,39]. Based on this, the F-rich thiol was introduced to the copper substrate to lower the surface energy. In this study, in order to get a convenient approach to equip the copper with better performances, such as oil resistance, anticorrosion and so on, the superamphiphobic copper surface was prepared through an oxidation process and a displacement reaction to obtain multilevel structures (CuO/Ag multilevel structures), followed by chemical modification of 1H, 1H,2H, 2H-perfluorodecanethiol. The overall fabrication process time is less than 3 h, which is time-saving. Importantly, without the procedure of immersing in the $AgNO_3$ solution to obtain multilevel structures, the superhydrophobic copper surface was only prepared. The superamphiphobic copper surface exhibits high water contact angle (WCA) more than 150° and low sliding angle (SA) less than 10°. In addition, it also shows high oil contact angle (OCA) more than 150° and low sliding angle (SA) less than 10°. The great anticorrosion resistance of the superamphiphobic surface was tested via electrochemical method. It is proved that the prepared superamphiphobic surface may have potential applications in self-cleaning, oil transportation, corrosion resistance, oil resistance, and so on.

## 2. Experimental section

### 2.1. Materials

Copper sheet was used after cleaning process. Anhydrous ethanol, sodium hydroxide (NaOH), ammonium persulfate ($(NH_4)_2S_2O_8$) and silver nitrate ($AgNO_3$) were analytical grade reagents and were used as received. 1H,1H,2H,2H-perfluorodecanethiol was used as a low-surface-energy modifier.

### 2.2. Fabrication of CuO flake-like structures

The copper sheet (2 × 3 cm) was ultrasonically cleaned by ethanol and deionized water respectively and dried at room temperature. Then the copper sheet was immersed in 20 mL aqueous solution including NaOH (1 mol/L) and $(NH_4)_2S_2O_8$ (0.05 mol/L) in water bath of 60 °C for 30 min. After the oxidation, the copper sheet was taken out and washed with water, followed by drying at 60 °C.

### 2.3. Fabrication of CuO/Ag multilevel structures

The copper sheet with CuO flake-like structures was immersed in the 20 mL $AgNO_3$ solution (1 g/L) for 30 min at room temperature. Then the copper sheet was taken out and dried at 60 °C for 30 min. In order to remove the residual reagent, the dried copper sheet was washed with deionized water and dried at room temperature to obtain CuO/Ag multilevel structures.

### 2.4. Modification

The copper sheets coated with CuO/Ag multilevel structures were immersed into ethanol solution of 1H,1H,2H,2H-perfluorodecanethiol for 30 min at room temperature. Afterwards, the copper sheets were washed with ethanol and dried at room temperature to obtain superamphiphobic copper surface. As a contrast, before immersed in the $AgNO_3$ solution, the copper sheet with CuO flake-like structures was directly immersed into the ethanol solution of 1H,1H,2H,2H-perfluorodecanethiol for 30 min to obtain superhydrophobic copper surface.