



# Insights into the superhydrophobicity of metallic surfaces prepared by electrodeposition involving spontaneous adsorption of airborne hydrocarbons



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## ABSTRACT

Electrochemical fabrication of micro/nanostructured metallic surfaces with superhydrophobicity has recently aroused great attention. However, the origin still remains unclear why smooth hydrophilic metal surfaces become superhydrophobic by making micro/nanostructures without additional surface modifications. In this work, several superhydrophobic micro/nanostructured metal surfaces were prepared by a facile one-step electrodeposition process, including non-noble and noble metals such as copper, nickel, cadmium, zinc, gold, and palladium with (e.g. Cu) or without (e.g. Au) surface oxide films. We demonstrated by SEM and XPS that both hierarchical micro/nanostructures and spontaneous adsorption of airborne hydrocarbons endowed these surfaces with excellent superhydrophobicity. We revealed by XPS that the adsorption of airborne hydrocarbons at the Ar<sup>+</sup>-etched clean Au surface was rather quick, such that organic contamination can hardly be prevented in practical operation of surface wetting investigation. We also confirmed by XPS that ultraviolet-O<sub>3</sub> treatment of the superhydrophobic metal surfaces did not remove the adsorbed hydrocarbons completely, but mainly oxidized them into hydrophilic oxygen-containing organic substances. We hope our findings here shed new light on deeper understanding of superhydrophobicity for micro/nanostructured metal surfaces with and without surface oxide films.

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## 1. Introduction

Superhydrophobicity of solid surfaces has attracted considerable attention from both academic and practical points of view, and remarkable progress has been achieved up to date. Superhydrophobic materials that exhibit static contact angles greater than 150° and low contact angle hysteresis for water droplets possess water-repellent self-cleaning property [1]. They have many important practical potential applications such as anti-adhesive coatings [2], anti-fogging coatings [3], self-cleaning surfaces [4,5], anti-corrosion coatings [6], microfluidic channels with reduced flow resistance [7], and so forth [8–10].

Inspired by the famous “lotus effect” of some plant leaves that have self-cleaning property [8,11–13], scientists have been able to fabricate artificial superhydrophobic surfaces by combination of two key factors: micro/nanoscale hierarchical

structures and low surface energy substances. On the basis of this principle, a number of strategies have been developed to fabricate artificial superhydrophobic surfaces through controlling both of surface chemical composition and surface morphological structures. For example, superhydrophobic cotton textiles by solution immersion of polymethylsilsesquioxane [14], superhydrophobic coatings of organic/inorganic composites by sol-gel processes [15], superhydrophobic rose-like mordenite zeolites by hydrothermal synthesis and surface modification with octyltrimethoxysilane [16], superhydrophobic polystyrene films by phase separation [17], superhydrophobic silica-sphere-coated substrates by fluorination treatment and layer-by-layer deposition of poly(diallyldimethylammonium chloride)/sodium silicate multilayer films [18], superhydrophobic substrates with dual-sized raspberry-like polystyrene/silica particles by colloidal self-assembly and surface modification with dodecyltrichlorosilane [19], superhydrophobic metal surfaces by electrodeposition [20,21] or electrooxidation [22] with organic modifications, superhydrophobic Si wafers with microstructures covered with chemically-modified graphene nanosheets by chemical vapor

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deposition [23], superhydrophobic aluminum alloy substrates by chemical etching in the presence of lauric acid [24], and so on [25,26].

Among them, electrochemical methods (especially electrodeposition) have been extensively used for preparing superhydrophobic metallic surfaces. It is well-known that electrodeposition is a very convenient method to create micro/nanostructures under mild conditions with cheap equipment, and the growth rate and micro/nanostructures can be readily controlled by adjusting deposition parameters. Generally, organic modification is required to obtain superhydrophobic metal surfaces prepared by this method. For example, Han's group prepared superhydrophobic ZnO films by cathodic deposition of Zn, gaseous oxidation and coating of perfluoroalkyl methacrylic copolymer [27], Jiang et al. obtained conductive superhydrophobic zinc oxide thin films by electrodeposition and (fluoroalkyl)silane modification [28], Zhang's group achieved a superhydrophobic Pt nanowire array by electrodeposition of Pt into the pores of an anodic aluminum oxide template and by fluoroalkylsilane modification [29]. Zhang et al. fabricated branchlike Ag aggregates, and a maximum water contact angle of 154° was achieved after modifying n-dodecanethiol [30]. Both Zhang's group [31] and Li's group [32] obtained superhydrophobic copper surfaces by electrodeposition of Cu and subsequent surface modification with tetradecanoic acid or lauric acid.

It has also been reported that superhydrophobic micro/nanostructured surfaces can be fabricated by electroless/electrodeposition without artificial modification of any organic substances. For example, cauliflower-like Ni–Cu–P alloy coatings [33], flower-like Co [34,35], cone-like Ni with round cap [36], flower-like Ag [37], aggregated nanoparticles of Au, CuCl and Cu<sub>2</sub>O [38], and multiscaled Cu [39–41]. We also found that the deposited dendritic Sn [42,43] and Bi [44] with surface oxides behaved superhydrophobic without artificial surface modifications. However, the origin still remains unclear why the smooth hydrophilic metal surfaces become superhydrophobic just by making micro/nanostructures without further surface modifications.

We conceive that airborne hydrocarbons might contribute to the superhydrophobicity of the micro/nanostructured metal surfaces by spontaneous adsorption to lower the surface energy. Airborne hydrocarbons exist almost everywhere, even inside a high-end nanofabrication clean room, the adsorption of airborne hydrocarbons at metallic surfaces can hardly be prevented in practice of wetting investigations. However, to our knowledge, few literatures related surface adsorption of airborne hydrocarbons to superhydrophobicity of metal surfaces up to date, except for supported graphene and graphite [45] and coatings of boron nitride nanotubes [46].

Ultraviolet (UV) treatment and dark storage for a few weeks were usually used to realize the transformation between superhydrophobicity and superhydrophilicity for micro/nanostructured oxides such as TiO<sub>2</sub> [47,48] and ZnO [1,48,49], which were also without additional organic modifications. There were different opinions on what happened during UV-treatment and dark storage. For example, some proposed that UV-photoinduced hydrophilicity of TiO<sub>2</sub> was due to the change of surface physical and chemical structure, not to photocatalytic oxidation of adsorbed organic compounds [48]. However, others argued that UV-induced hydrophilicity of TiO<sub>2</sub>(110)(1 × 1) surface was due to oxidation of simulated hydrocarbons (e.g. hexane) in the presence of O<sub>2</sub>, rather than production of surface oxygen vacancy defect sites, enhanced surface Ti–OH coverage on defect sites, or the modified surface bonding of bridging >OH groups [50]. Therefore, detailed surface analyses are required in order to make it clear if the airborne hydrocarbons also played some role in the initial and

recovered superhydrophobicity for the micro/nanostructured surfaces of oxides and metals without artificial surface modifications.

In this work, we aim at resolving two important unclear issues in literatures on superhydrophobicity at metal surfaces: (i) if the adsorption of airborne hydrocarbons at micro/nanostructured metal surfaces plays an important role in their superhydrophobicity, and (ii) if the transition between superhydrophilicity and superhydrophobicity by UV-O<sub>3</sub> treatment and dark storage also involves removal and/or oxidation and re-adsorption of airborne hydrocarbons. To do so, we fabricated a series of micro/nanostructured metal surfaces by electrodeposition, including non-noble and noble metals such as copper, nickel, cadmium, cobalt, zinc, gold, palladium and platinum, and detected the surface chemical composition especially the adsorbed airborne hydrocarbons by X-ray photoelectron spectroscopy (XPS) for the samples with superhydrophobicity, before/after UV-O<sub>3</sub> treatment of them, and before/after Ar<sup>+</sup>-etching in vacuum and re-exposure of them to air.

The metal surfaces under investigation in this work have diversity in surface composition. Surface oxide films occurred for the non-noble ones (e.g. Cu), which were absent for the noble ones (e.g. Au).

## 2. Materials and methods

### 2.1. Materials

CuSO<sub>4</sub>, NiCl<sub>2</sub>·6H<sub>2</sub>O, ZnSO<sub>4</sub>·7H<sub>2</sub>O, CdCl<sub>2</sub>·6H<sub>2</sub>O, HAuCl<sub>4</sub>·4H<sub>2</sub>O, PdCl<sub>2</sub>, and NH<sub>4</sub>Cl were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Sulfuric acid was purchased from the factory of Hunan Normal University. All the chemicals were of analytical grade and were used as received. Milli-Q water with a resistivity larger than 18.3 MΩ cm was used in the preparation of aqueous solutions.

### 2.2. Electrodeposition of metallic films

Electrodeposition of metals was performed on a CHI 660 C electrochemical workstation (Chenhua Instruments, Shanghai, China) with a three-electrode configuration. A platinum foil (geometric area 1 cm<sup>2</sup>) and a saturated mercurous sulfate electrode (SMSE) were employed as the counter and reference electrodes, respectively. The electrodeposition conditions for preparing superhydrophobic metallic surfaces of Cu, Au, Ni, Zn, Cd, and Pd are listed in Table 1. Prior to electrodeposition, the disk electrode was polished by 2000 grit carbimet paper and cleaned in Millipore water under ultrasonic waves. After electrodeposition, the disk electrode was washed several times with pure water to get rid of impurities, and was then fully dried under an infrared lamp or in a vacuum drying oven (at 65 °C) for about 12 h to present the superhydrophobic state. Then, the surface was ready for following characterization.

### 2.3. Characterization

The morphology images of prepared samples were taken with a Nova nanoSEM 230 scanning electron microscope (SEM) operating at 10 kV. Surface composition of samples was analyzed with a K-Alpha 1063 X-ray photoelectron spectroscopy (XPS). UV-O<sub>3</sub> treatment was carried out with a BZZ250G-T UV ozone washing machine at room temperature, and the treatment time was 1 h with a 250 W grid-Hg lamp of 185/254 nm. Contact angles (CAs) of sessile water droplets of 2 μL loaded at the center of the electrode surfaces were measured with freshly deionized water by a contact-angle meter (JC2000C) under static condition. The metal

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