



Full Length Article

Intrinsically water-repellent copper oxide surfaces; An electro-crystallization approach



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ABSTRACT

Use of metal oxide thin layers is increased due to their good durability under environmental conditions. In this work, the repeatable nanostructured crystallite Cu_2O thin films, developed by electrodeposition method without any physical and chemical modifications, demonstrate good hydrophobicity. Copper (I) oxide (Cu_2O) layers were fabricated on gold/Si(1 0 0) substrates by different electrodeposition methods i.e. galvanostatic deposition, cyclic voltammetry, and pulse potentiostatic deposition and using copper sulfate (in various concentrations) as a precursor. The greatest crystalline face on prepared Cu_2O samples is (1 1 1) which is the most hydrophobic facet of Cu_2O cubic structure. Indeed, different crystallite structures such as nanotriangles and truncated octahedrons were formed on the surface for various electrodeposition methods. The increase of the contact angle (θ_w) measured by the rest time, reaching to about 135° , was seen at different rates and electrodeposition methods. In addition, two-step deposition surfaces were also prepared by applying two of the mentioned methods, alternatively. In general, the morphology of the two-step deposition surfaces showed some changes compared to that of one-step samples, allowing the formation of different crystallite shapes. Moreover, the wettability behavior showed the larger θ_w of the two-step deposition layers compared to the related one-step deposition layers. Therefore, the highest observed θ_w was related to the one of two-step deposition layers due to the creation of small octahedral structures on the surface, having narrow and deep valleys. However, there was an exception which was due to the resulted big structures and broad valleys on the surface. So, it is possible to engineer different crystallites shapes using the proposed two-step deposition method. It is expected that hydrophobic crystallite thin films can be used in environmental and electronic applications to save energy and materials properties.

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1. Introduction

As communities grow around the globe, finding better ways to reduce pollution and fuel consumptions is more felt. Recently, water-repellent and hydrophobic surfaces have attracted substantial interests due to their excellent applications in environmental and industrial fields. However, hydrophobic surfaces have potential applications as easy to clean, anti-bacteria, drag force reduction, corrosion resistance and marine applications [1,2].

In fact, for a smooth surface, following the Young–Dupré equation [3], θ^Y cannot “experimentally” exceed around 130° . Two developed version of the Young–Dupré equation (Wenzel [3] and Cassie–Baxter [4] equations) are very often used to predict the

effect of surface roughening on the surface hydrophobicity. In the Wenzel state, the liquid penetrates in all the surface roughness, so the surface roughness can increase the surface hydrophobicity but only if $\theta^Y > 90^\circ$ (intrinsically hydrophobic materials). For the Cassie–Baxter equation, there is some air trapped inside the surface roughness between the water droplet and the surface. With this equation, it is possible to increase the surface hydrophobicity whatever θ^Y if the surface structures present on the surface are able to trap some air.

Different processes were employed in the literature to control the surface structures and energy [1,2,5,6]. The electrodeposition allows an easy and fast control of these properties allowing the formation of various surface morphologies, such as spheres [7], tubes [8–10] and fibers [11] in polymers, for example. Metals and conducting polymers can be deposited and the surface properties can be tuned, with many electrochemical parameters such as the

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deposition method, deposition time, solvent or electrolyte [12,13]. Among the metal usages, copper and copper oxides are excellent choices for different applications in electrical, environmental, and optical fields such as electrical circuits and technology, sensors, anticorrosion surfaces, catalysts and photocatalysts, water purification and antifouling systems and solar cells, due to their good electrical and optical properties [12,14–19]. Moreover, copper is a highly sensitive material to different stimuli because different oxides and hydroxides can be formed, which change the surface energy [20].

Recently, the researchers have focused on observed hydrophobicity in copper and copper oxides (Cu_2O and CuO) [15,16,21–23]. It is shown that the structure and surface energy of copper oxide samples depend on the amount of oxygen and the most growth crystal facet on the surface. The decrease of surface energy is reported by decreasing the amount of oxygen in copper oxide samples which cause the increase of surface hydrophobicity [24]. On the other hand, in cubic Cu_2O structure the surface energy of various facets varies as: $\{1\ 1\ 1\} < \{1\ 1\ 0\} < \{1\ 0\ 0\}$ [14]. So, the most hydrophobic surface of Cu_2O is $\{1\ 1\ 1\}$.

However, it is observed that Cu_2O may be grown at large crystal shapes in various truncated or driven structures of octahedrons or cubes by controlling the conditions [14,17–19,25–31]. The observed structures are in the form of cubic, octahedral and their truncated structures. In fact, the structured surface will result to the well-defined surface energy or may give a scale of roughness which helps to study wettability. In addition, it was already reported that sometimes the measured θ_w on metal oxide surfaces increases to a saturation θ_w with the rest time [32,33]. Though, it may be explained by adsorption of contamination on the surface, change in oxygen amount of near surface layers and drying time needed for the sample especially when water is used as a solvent. In recent studies, Cu_2O samples were prepared by various methods such as radio frequency (RF) sputtering [34], thermal oxidation [35–37], chemical vapor deposition [38,39], electrodeposition [12,14,17,20,40–47], and sol gel methods [48]. Among them, the electrodeposition method is an inexpensive and fast deposition technique that provides a close control on stoichiometry and crystallinity. Moreover, it is possible to have control on the surface structure as well as the orientation of the grown thin films by controlling electrochemical conditions.

Here, copper with different surface structures such as nanotriangles is prepared by electrodeposition using different methods (galvanostatic deposition, cyclic voltammetry, and square pulse deposition). Finally, some binary compositions of all the used deposition methods were prepared to make two-layered samples. The effect of the deposition method on the chemical components (surface energy), the surface structures, and hydrophobicity are studied by X-ray diffraction, scanning electron microscopy (SEM), optical profilometry, and goniometry. The surfaces were also analyzed after storage for a few weeks in order to analyze the change of their θ_w by the rest time.

2. Experimental

2.1. Electrodeposition conditions

An Autolab potentiostat of Metrohm was used for the electrochemical experiments in different methods (galvanostatic deposition, cyclic voltammetry, and square pulse deposition). A three-electrode system was connected to the potentiostat: gold-coated silicon wafers (150 nm gold $\{1\ 1\ 1\}$) on 10 nm chromium on silicon wafer ($\{1\ 0\ 0\}$) as a working electrode, a carbon rod as a counter-electrode and a saturated calomel electrode (SCE) as reference electrode. An electrolytic solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Sigma Aldrich)

in ultra-pure water at different concentrations was prepared. 10 mL of this solution was added to the electrochemical glass cell and let degassing during 15 min under argon. After the electrodeposition, the samples were washed in distilled water and let drying for one week at ambient conditions before the characterization.

2.2. Surface characterization

The water contact angle (θ_w) was measured using a DSA30 goniometer (Krüss) for a 2 μL water droplet ($\gamma_{\text{LV}} = 72.8\ \text{mN/m}$) at five different positions on each sample. The θ_w was also measured to investigate the saturation θ_w , weekly. X-ray diffraction (XRD) pattern of the samples were studied by Philips XRD X'pert MPD Diffractometer (Cu $K\alpha$ radiation-1.54 Å) with step size of 0.02° and count time of 1 s per step in 2θ range from 10° to 80° at grazing incidence mode. A 6700F microscope (JEOL) was used to obtain the SEM images. In addition, a NT-MDT atomic force microscopy (AFM) was used in non-contact mode (window size: 1–10 μm) to study surface features more precisely. The average surface roughness was determined using a Wyko NT 1100 optical microscope (Bruker) with High Mag. Phase Shift Interference (PSI), field of view 0.5X and objective 50X.

3. Results and discussion

3.1. Galvanostatic deposition

Samples at five deposition times (10, 20, 40, 80, and 160 s) were prepared using 1 mA as current density (I) and four different CuSO_4 concentrations ($C = 0.03, 0.05, 0.1,$ and $1.0\ \text{M}$ with $\text{pH} = 4.96, 4.93, 4.66$ and 3.88 , respectively). A linear increase in surface roughness (R_a) relative to the deposition time was shown in Fig. S11 (see Supporting Information). The observed enhancement is very slight in the case of $C = 0.03$ and $0.05\ \text{M}$; however, it is much more intense for $C = 0.1\ \text{M}$. Moreover, a saturation behavior was observed for $C = 1.0\ \text{M}$ at $t = 40\ \text{s}$. As expected, for concentrations lower than $1\ \text{M}$, the roughness increases with the increase in CuSO_4 concentration [12].

According to XRD patterns of galvanostatic method samples, Cu_2O is the main phase on the surface (Fig. 1). It grows on $\{1\ 1\ 1\}$ direction, which is the most hydrophobic face of Cu_2O cubic structure [14]. At $0.05\ \text{M}$, the ratio between $\text{Cu}(4\ 2\ 0)$ and $\text{Cu}_2\text{O}(1\ 1\ 1)$ is larger than that of $0.1\ \text{M}$. However, more hydrophobicity of $0.05\ \text{M}$ galvanostatic method samples may be rise from the less tendency of the layer to adsorb oxygen during the growth.

All the samples are hydrophobic with θ_w up to 115° in the case of $C = 0.05$ and $0.1\ \text{M}$ (Fig. S12-up). Moreover, θ_w evolves with resting time due to the change of surface energy. Therefore, an increase in θ_w was observed up to around 120° (Fig. S12-down). It seems that in the case of using water as a solvent; the layer needs a few weeks to dry and reach the maximum θ_w .

SEM pictures as a function of CuSO_4 concentration and deposition time are given in Fig. 2. At $0.05\ \text{M}$, the surface is covered by very small and distinct octahedral pyramids and some big vertical sheets. By increasing the deposition time the size of the structures has increased, but their amount on the surface has decreased. In addition, at more than 80 s deposition, some large cubic structures at different orientations are also appeared on the surface (Fig. 3). In the case of $0.1\ \text{M}$ and $1\ \text{M}$, the surface morphology is the same whatever CuSO_4 concentration and deposition times with the presence of octahedral crystallites with triangle facets (nanotriangles).

The existence of triangle facets parallel to the substrate surface shows the crystal growth perpendicular to $\{1\ 1\ 1\}$ planes. It can also be confirmed by the XRD results (Fig. 1). As showed by Siegfried and Choi, triangle faceting was grown along the surface in

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