

## Full Length Article

# The anodization synthesis of copper oxide nanosheet arrays and their photoelectrochemical properties



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## ABSTRACT

We studied the growth of copper oxide nanosheet arrays on copper foil via a simple anodization method. The structures, morphologies, and elemental compositions of the specimens were characterized with an X-ray diffractometer, scanning electron microscope, high resolution transmission electron microscope, and X-ray photoelectron spectrometer. The copper oxide (Cu<sub>2</sub>O and CuO) nanosheet arrays were comprised of 30-nm-thick nanosheets that stand vertically on the Cu substrate. The anodizing parameters, such as the current density, temperature, and polyethylene glycol concentration, were optimized to obtain the regular nanosheet arrays. The optical absorption properties of the anodized products were evaluated using a diffuse reflectance spectrometer, and broad and strong optical absorption bands arising from the UV to visible region were observed. The photoelectrochemical performance of the nanosheet arrays was measured with chronoamperometry and cyclic voltammetry on an electrochemical workstation equipped with a Xe lamp (wavelength >400 nm). A negative photocurrent was obtained due to the p-type semiconductor of the copper oxides. The copper oxide nanosheet arrays achieve the highest photocurrent of 0.4 mA/cm<sup>2</sup> at the current density of 1.0 A/dm<sup>2</sup>, temperature of 70 °C, and polyethylene glycol concentration of 0.5 g/L.

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## 1. Introduction

There are two forms of copper oxide, cuprous oxide (Cu<sub>2</sub>O) and copper oxide (CuO); both are excellent semiconductors with a narrow band gap and have many potential applications in supercapacitors [1–4], photocatalysis [5,6], sensors [7], and solar-driven water splitting [8–10].

Copper oxides can be prepared by many methods, such as chemical or electrochemical deposition [11,12], anodization [13–15], and electrostatic spray deposition (ESD) [16]. Ma and coworkers adopted the polyol method to deposit a Cu<sub>2</sub>O film onto the Cu substrate and were the first report on Cu<sub>2</sub>O films with aligned 2-D single crystal nanosheets [17]. F-doped SnO<sub>2</sub> (FTO) glass, porous nickel nets, TiO<sub>2</sub> nanotube arrays, and other materials have been

adopted as the substrates for growing copper oxide nanostructures [18–21].

Copper oxide composite photocatalysts have garnered significant attention since these single-phase photocatalysts exhibit a very low quantum efficiency due to the high recombination rate of their photogenerated electrons and holes [22]. Many new structures have been studied, such as Cu-nanoparticle-covered Cu<sub>2</sub>O microspheres [23], CuO and Cu<sub>2</sub>O nanowires [24], MoS<sub>2</sub>/Cu<sub>2</sub>O composites [25], p-n Cu<sub>2</sub>O homojunction films [26], p-n Cu<sub>2</sub>O/ZnO heterojunction nanowires [27], and Cu<sub>2</sub>O/CuO hollow microspheres [28]. Unlike the single-phase CuO or Cu<sub>2</sub>O photocatalysts, the interface between CuO and Cu<sub>2</sub>O acts as a rapid separation site for photogenerated electrons and holes due to the different energy levels of their conduction bands and valence bands. Therefore, CuO/Cu<sub>2</sub>O composite hollow spheres exhibit a higher photocatalytic activity than that of the single-phase oxides [28].

Nevertheless, these copper oxide composites are all powdered materials. The development of commercially-viable copper oxides used for photocatalysis, sensors, solar-driven water splitting, and supercapacitors is still challenging work. The purpose of this paper is to focus on growing copper oxide nanosheet arrays using a sim-

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ple anodization method to optimize the anodization parameters, including the current density, temperature, and the content of polyethylene glycol (PEG), in order to obtain regular nanosheets that stand vertically on the Cu substrate and to achieve better photoelectrochemical properties of the anodization product, which can be potentially applied in water splitting and photocatalytic organic degradation.

## 2. Experimental

### 2.1. Chemical agents

High-purity copper foil (99.99%, 0.20 mm thick) was purchased from Tongling Nonferrous Metals Group Holding Co., Ltd. A titanium sheet (99.6%, 0.10 mm thick) was purchased from Beijing Nonferrous Metal and Rare Earth Application Research Institute and used as received without further treatment. Polishing liquid of copper (RY-522) was purchased from Shenzhen RunYuDH New Materials Co., Ltd. Sodium Hydroxide, sodium chloride, PEG 20000, and other chemicals of analytical reagent grade were purchased from Sinopharm Chemical Reagent Co., Ltd. All solutions were prepared with deionized water.

### 2.2. Synthesis

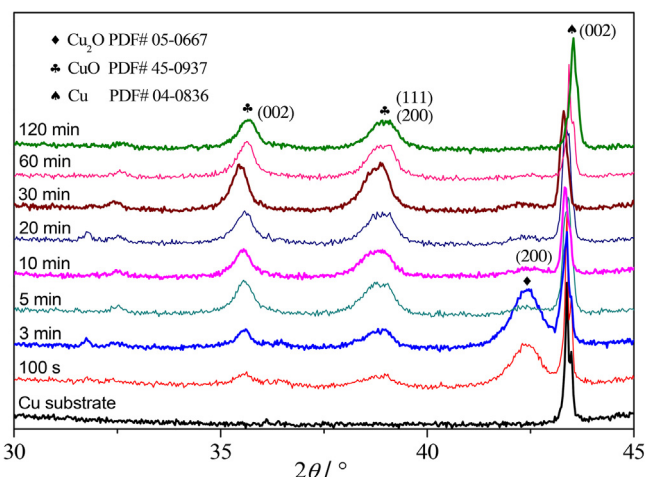
Copper foil was used as the substrate and source material for the copper oxide anodization. Prior to anodization, the copper foils were chemically polished with composite acidic solutions of RY-522 to remove the surface oil and then rinsed with deionized water, a dilute alkali solution, and deionized water again to remove surface impurities. Anodization was performed in a double-electrode cell with the copper foil as the working electrode and the titanium sheet as the counter electrode using a DC stabilized power supply (Sovotek, E5200-4). The electrolyte was an aqueous solution composed of 1 mol/L NaOH, 2.5 mol/L NaCl, and PEG, in which PEG is used for adjusting the solution's viscosity to control the growth process of the copper oxide nanosheet arrays [29]. After that, the copper foils with the anodization products were washed 3 times with deionized water and dried in an oven at 45 °C.

### 2.3. Characterization

The surface morphologies of the anodization products were observed with a scanning electron microscope (SU8020, Hitachi, Japan) and a transmission electron microscope (JEM-2100F, Japan). The phase structures of the anodization products were measured by an X-ray diffractometer (D/MAX2500V, Rigaku, Japan) with Cu-K $\alpha$  radiation (0.15418 nm). The elemental compositions of the products were analyzed with an X-ray photoelectron spectrometer (ESCALAB 250, Thermo, USA) with a monochromatic Al K $\alpha$  (1486.60 eV) X-ray source. The ultraviolet-visible diffusion reflection/absorption performances were recorded by a spectrophotometer (UV-3600, Shimadzu) using BaSO $_4$  as the reference.

### 2.4. Photoelectrochemical performances

The photoelectrochemical performances of the anodization products were examined on an electrochemical workstation (CHI760E) combined with a Xe lamp (wavelength  $\lambda > 400$  nm). All measurements were performed in a 3-electrode system using copper oxide as the working electrode, Pt wire as the counter electrode, and the Ag/AgCl electrode as the reference electrode. The chronoamperometry method was used for measuring the photocurrents of the specimens; it had a bias potential at  $-0.2$  V under the illumination of visible light and the interval time of light on/off is 50 s. The impedance-potential spectroscopy tests



**Fig. 1.** XRD patterns of the anodization products on the Cu foils obtained at different times, with a current density of 1.0 A/dm $^2$ , PEG concentration of 0.5 g/L, and temperature of 70 °C.

(Mott-Schottky) were performed in the dark and under illumination, respectively, with an ac-amplitude of 10 mV and frequency of 3 kHz.

## 3. Results and discussion

### 3.1. Mechanism of the anodization process

**Fig. 1** shows the X-ray diffraction (XRD) patterns of the anodization products on the Cu foils obtained at different anodization times from 100 s to 120 min. The anodization parameters are a current density of 1.0 A/dm $^2$ , PEG concentration of 0.5 g/L, and temperature of 70 °C. For comparison, the XRD pattern of the Cu substrate without anodization is also shown in **Fig. 1**. The diffraction peak at 43.4° corresponds to the (002) crystalline plane of metallic Cu (PDF #04-0836). With the elapse of the anodization time, the surface color of the Cu substrate changes from luminous red to brick red, indicating the formation of the anodization products on the surface of the substrate. Besides the substrate's diffraction peak, the anodization product obtained at 100 s shows a broad diffraction peak at 42.4°, which corresponds to the (200) lattice plane of Cu $_2$ O (PDF #05-0667). Three diffraction peaks with a relatively low intensity at 35.6°, 38.7°, and 38.9° are observed, which correspond to the (11-1), (111), and (200) lattice planes of the monoclinic CuO (PDF #45-0937), respectively, indicating that both Cu $_2$ O and CuO coexist in the anodization products. When the anodization time is 3 min, the diffraction intensities of Cu $_2$ O and CuO are enhanced at the same time, indicating the continuous growth of the copper oxides.

When the anodization time was increased to 5 min, the diffraction intensities of Cu $_2$ O and CuO showed different change tendencies, i.e., the diffraction intensity of CuO increases and the diffraction intensity of Cu $_2$ O decreases, indicating the conversion of Cu $_2$ O to CuO with the increasing anodization time.

When the anodization time is prolonged to 10, 20, 30, 60, and 120 min, the diffraction patterns are almost the same: there are 2 strong diffraction peaks for CuO and a weak peak of Cu $_2$ O, in addition to the diffraction peaks of the Cu substrate. The relative diffraction intensity between the copper oxides and the Cu substrate reflects the amount of the anodization products. Almost no change of those diffraction patterns means no change of the product amount, indicating that the growth of the copper oxides have ceased.

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