# Synthesis of cuprous oxides thin film with different morphologies by electrodeposition

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**Keywords:** Cuprous oxide; electrochemical growth; thin film.

**Abstract.** Cuprous oxides thin film with different morphologies were formed on F-doped tin oxide (FTO) covered glass substrates by potentiostatic deposition of cupric acetate. The effects of electrodeposition temperature and $Br^-$ on the crystal morphologies of cuprous oxide were studied. Different crystal morphologies of cuprous oxides were obtained by the change of electrodeposition temperature or the concentrations of $Br^-$. The network-like and tetrahedron morphologies of $Cu_2O$ crystals were obtained when using higher deposition temperature and concentration of KBr, respectively. Photoelectrochemical behavior of the cuprous oxides thin films prepared in the system was also studied.

## 1. Introduction

As a direct band-gap semiconductor, cuprous oxide ($Cu_2O$) with its environmentally benign nature of copper and low cost is desirably used in many ways including catalysis [1], sensors [2] and energy conversion such as solar cells for both its relatively high light absorption coefficient in visible region [3,4] and appropriate band gap ($E_g$ = 1.9~2.2 eV). Recently, it has been documented that chemical and physical properties depend greatly on the microstructures, such as crystal size, orientation of inorganic nanomaterials [5], and morphological characters, e.g., the photoelectrochemical properties $Cu_2O$ have been greatly influenced by their morphologies [6]. Because the electronic structure, surface energy and chemical reactivities of micro- or nanomaterials are greatly related to their surface morphologies [5,7], the development of micro- or nanomaterials may open new opportunities for exploring the physical and chemical properties. The conduction band edge (ca. -1.35 V vs. Ag/AgCl at pH = 7) and valence band edge (ca. -0.61 V vs. Ag/AgCl at pH = 7) of $Cu_2O$ are located near the reduction and oxidation potentials of water respectively, thus it is feasible to use $Cu_2O$ for hydrogen generation from visible light-induced photocatalytic water splitting [8,9].

Various methods such as electrodeposition route [10], wet chemistry method [11] and gas phase deposition techniques [12], have been developed for the synthesis of $Cu_2O$ with different microstructures. Among these methods, electrochemical deposition which presents a gentle, simple and economical method with the advantage of allowing patterned and controlled crystal growth has shown the advantage to control the crystallization engineering of large area $Cu_2O$ films.

There are two steps in the process of electrodeposition of $Cu_2O$. Reduction of $Cu^{2+}$ ions to $Cu^+$ ions is the first step (eq 1); Due to the solubility limitation of $Cu^+$ ions, precipitation of $Cu^+$ ions to $Cu_2O$ is the second step (eq 2) [13].

"$Cu^{2+} + e^- \longleftrightarrow Cu^+$ $E^o = 0.159$ V (1)

$2Cu^+ + H_2O \longleftrightarrow Cu_2O + 2H^+$ $\log[Cu^+] = 0.84 - pH$ (2)

$2Cu^{2+} + H_2O + 2e^- \longleftrightarrow Cu_2O + 2H^+$ (overall reaction)"

In previous studies, during the process of crystal growth of Cu2O by electrodeposition, the influences of anion, cation or surfactant on the growth of cuprous oxide such as NH4+ [14], SDS [15], have been explored and it has been reported that Cl- ions are preferentially adsorbed on {100} planes and sodium dodecyl sulfate ions on {111}. Generally, in electrodeposition process, the dendritic branching growth can be induced when deposition rate is increased to form depletion zone of nutrient

 

ions (i.e., Cu2+ for Cu2O deposition) around a growing crystal [6]. However, in cupric acetate system, the influences of Br- on the crystal growth of Cu2O have been rarely studied with continuous concentrations during electrodeposition process. Usually, Cu2O is prepared as a p-type material, while only a handful of synthesis method such as electrodeposition have been reported to prepare n-type Cu2O [16], which may be beneficial to build photoelectrochemical cells based on a p-n Cu2O homojunction [17]. In this study, the influences of deposition temperature and Br- on the crystal morphology of cuprous oxide were investigated in the process of electrodeposition, and the photoelectrochemical properties of the samples were also investigated.

## 2. Experimental Section

### 2.1. Preparation of $Cu_2O$ film

Synthesis of Cu2O thin film was carried out in a glass cell equipped with a 15 × 20 mm2 platinum plate as the counter electrode and a saturated calomel electrode as the reference electrode at different temperatures. The working electrode was a FTO glass with a surface area of 15 × 10 mm2 exposed to the electrolyte. The electrolytes are 0.02 M Cu(Ac)2 and 0.1 M NaAc aqueous solution and added with different concentrations of KBr. The pH values of electrolytes were 5.75 by adding acetic acid. The FTO glass electrode was carefully washed with acetone and distilled water before experiments. Cu2O thin films were prepared through the electrodeposition route in a potentiostatic mode using a commercial electrochemical workstation (CHI633C, China). It is practiced at E= -0.2 V.

### 2.2. Characterization

The as-prepared samples were characterized by X-ray diffraction (XRD) for phase identification on a Rigaku D/MAX-Ultima III X-ray diffractometer with Cu Kα radiation (λ = 0.154 nm, 40 kV, 40 mA, a scan rate of 10 °·min-1). The microstructure of deposited particles was characterized by scanning electron microscopy (SEM, Philips XL30) with an electron accelerating voltage of 10 kV. With 500W xenon lamp (USHIO Optical Module X500) illumination, the photoelectrochemical properties were characterized by linear scanning voltampere (LSV) technique from -0.20 to 0.05 V with a scan rate of 0.02 V/s performed on a electrochemical workstation (CHI633C). The solutions were purged of O2 through the bubbling of N2 for at least 60 min before the measurements. The LSV measurements were performed in a 0.02 M K2SO4 aqueous solution in a standard three-electrode configuration coupled with the as-prepared sample film (working electrode), a high purity platinum (counter electrode) and an Ag/AgCl electrode (reference electrode).

## 3. Results and Discussion

The representative XRD pattern of as-deposited Cu2O film on the FTO-glass substrate using the electrolyte containing 0.02 M copper acetate, 0.1 M sodium acetate at room temperature is shown in Fig. 1. According to JCPDS card No. 65-3288, the XRD result indicate that the crystallographic phase of the as-deposited film could be indexed to Cu2O with the cubic structure (Pn-3m). There are no other peaks observed in the XRD result except for the diffraction peaks of Cu2O and FTO-glass, which means single-phase Cu2O can be obtained route in this system through electrodeposition.

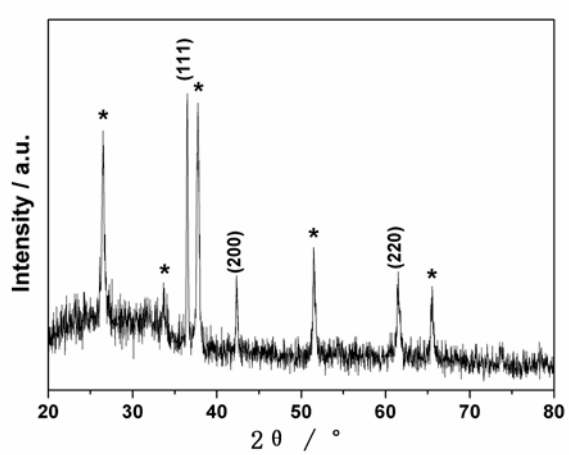


Fig. 1 XRD pattern of Cu2O thin film deposited in 0.02 M copper acetate, 0.1 M sodium acetate at room temperature; The label (*) represents the diffraction peaks from FTO-substrate (JCPDS card no. 41-1445).

Fig. 2 shows the SEM images of Cu2O crystals deposited at E= -0.2 V for 20 min in solutions containing 0.02 M copper acetate, 0.1 M sodium acetate at different temperatures. The results show obvious change in Cu2O crystal morphologies with the increase of temperature. From Fig. 2a and b, the low- and high-magnification SEM images show the Cu2O film prepared at room temperature has compact and uniform structure. From Fig. 2c and d, Cu2O with dendric morphology is deposited when the temperature was increased to 40 ℃. From Fig. 2e and f, the network-like Cu2O appears when the temperature was increased to 70 ℃. Based on these results, the temperature of the electrodeposition system is supposed to play a key role in controlling the morphologies of the as-prepared Cu2O films.

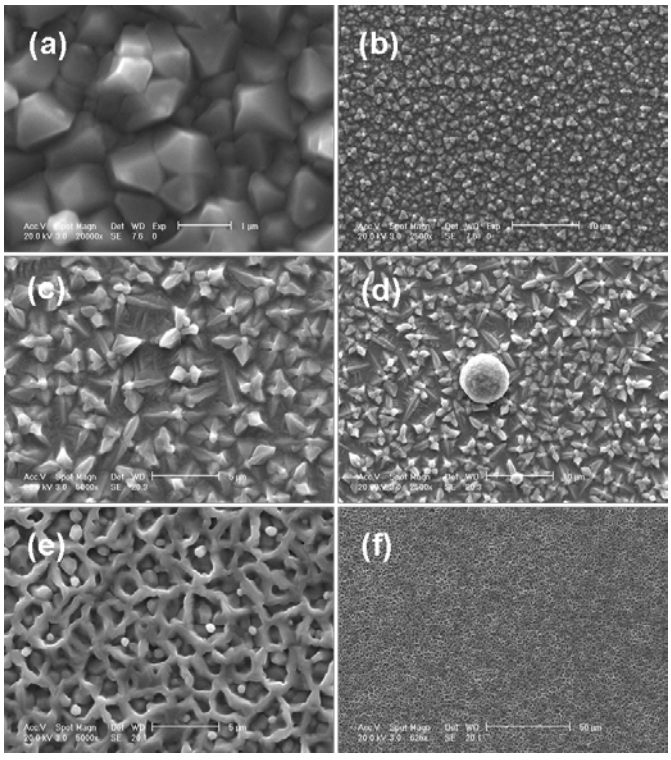


Fig. 2 Low- and high-magnification SEM images of Cu2O deposited for 20 min in the electrolyte containing 0.02 M copper acetate, 0.1 M sodium acetate and different temperatures: (a,b) room temperature; (c,d) 40 ℃; (e,f) 70 ℃.

The SEM images of the products deposited in the electrolyte composed of NaAc and Cu(Ac)2 with different concentrations of KBr are shown in Fig. 3. From Fig. 3, the observed morphology of Cu2O particles was changed from polyhedron-like shape to tetrahedron-like shape with increasing the concentration of KBr. With adding less KBr, the polyhedron-like structure was shaped (Fig. 3a, b). With the increase of the concentration of KBr, tetrahedron-like shape appeared (Fig. 3c, d). The results indicated that, in addition to the reactants, the morphology of the Cu2O films highly depended on the concentration of KBr in electrolyte. Thus, the formation mechanism of Cu2O morphological changes might be attributed to the adsorption of Br- ions on some planes, which in turn changed the surface energies and hindered the crystal growth of some planes, resulting in the changes of the Cu2O crystal morphology.

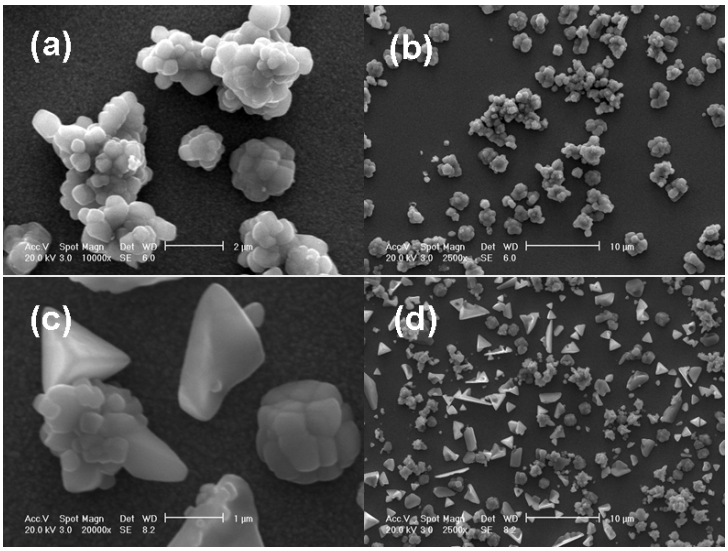


Fig. 3 Low- and high-magnification SEM images of Cu2O deposited for 5 min in the electrolyte containing 0.02 M copper acetate, 0.1 M sodium acetate and different concentrations of KBr: (a,b) 1.5 mM; (c,d) 3.0 mM at room temperature.

Taking Cu2O film deposited in the electrolyte at room temperature as the example, the photo-electrochemical properties of the as-deposited Cu2O films were studied and the result is shown in Fig. 4. From Fig. 4, it is clearly shown that the as-deposited Cu2O film can produce anodic photocurrent, which indicates that Cu2O prepared by electrodeposition in this system is n-type semiconductor photoelectrode [6] and it is possible to form p-n homojunction with p-Cu2O.

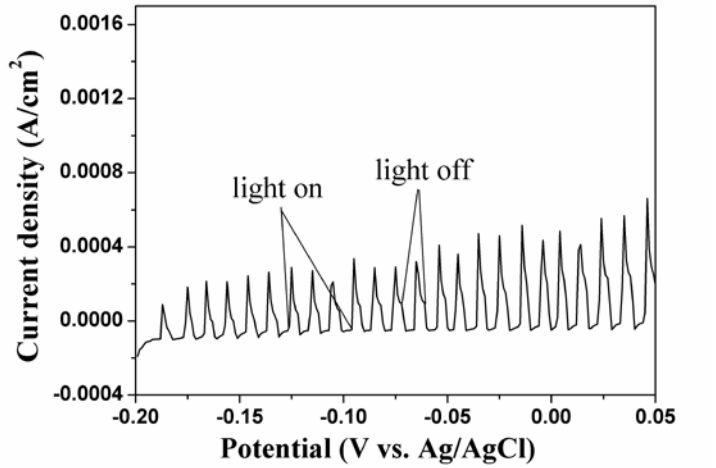


Fig. 4 Photocurrent curve from -0.2 to 0.05 V for $Cu_2O$ films deposited for 20 min at room temperature.

## 4. Conclusions

In summary, crystal morphologies of Cu2O by electrodeposition can be modulated in cupric acetate system with different concentrations of Br- or temperature. With the increase of deposition temperature, the morphologies of Cu2O change from compact, dendric to network-like shapes. Br- shows great influence on the microstructure of Cu2O. Cu2O tetrahedron-like crystals appear when the concentration of KBr increases. Cu2O prepared in this electroposition system is n-type semiconductor photoelectrode, which may be useful by forming p-n homoconjunction with p-Cu2O in various fields such as solar cells.


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