



Cuprous oxide thin film directly electrodeposited from a simple copper salt on conductive electrode for efficient oxygen evolution reaction



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ABSTRACT

Catalysts made of earth-abundant elements for water splitting have attracted increasing attention in recent years. Herein we report that inexpensive cheap copper oxide thin film material can be used as an excellent electrocatalyst precursor for the oxygen evolution reaction (OER). Cuprous oxide (Cu_2O) thin films were facilely electrodeposited on conductive fluorine doped tin oxide (FTO) substrates from a simple Cu(II) salt solution under a very low applied potential (-0.17V or -0.23V). Two kinds of morphologies (dendritic branching and cluster-like) of Cu_2O were obtained just by altering the deposition potentials. Both Cu_2O films can be used for OER, and the dendritic branching Cu_2O material exhibits better performance. Under optimal conditions, OER was achieved under an onset potential at $\sim 0.92\text{V}$ (vs. Ag/AgCl) in 0.1M borate solution at $\text{pH } 9.2$. A catalytic current density of $\sim 0.1\text{ mA/cm}^2$ required a low overpotential of $\sim 430\text{ mV}$ using the electrodeposited Cu_2O material under an optimal condition. The slope of the Tafel plot is $\sim 59.9\text{ mV/dec}$ and the Faradaic efficiency was close to 93%. The samples were well characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS).

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1. Introduction

In nature, the cube-like CaMn_4O_5 cluster is the active site for oxygen evolution reaction (OER) in photosystem II to release oxygen with moderate activity [1–4]. The important role of CaMn_4O_5 in photosystem II inspired researchers to design and create new catalysts with structure and function similar to CaMn_4O_5 for the purpose of OER [5–7]. As an alternative to the well-known catalysts based on precious metals (such as RuO_2 [8] and IrO_2 [8–11]), catalysts made of earth-abundant elements for water oxidation have attracted increasing attention in recent years [12–14]. Since nature uses Mn as one of the key elements to assemble the catalytic center, many studies have reported using this metal to construct artificial OER [15–17]. Besides the OER catalysts based on Mn, much progress has also been made to explore catalysts based on other first-row transition metals such as cobalt [13,14,18–23], nickel [24–29], and iron [30,31].

Compared with the abovementioned metals, copper-based catalysts have attracted much less attention to be used for water oxidation, although since 2013, a few copper(II)-based

homogeneous systems have been reported for this purpose [32–36]. More recently, heterogeneous copper oxide (CuO) has also been used as an active OER catalyst [37–39]. Our group reported that CuO thin film electrodeposited from an organic copper complex catalyzed water oxidation with an overpotential at $\sim 470\text{ mV}$ (0.1 mA/cm^2) in 0.1M KBI electrolyte at $\text{pH } 9.2$, but the catalytic performance was much lower when the precursor was switched to a simple copper salt [37]. A following study reported by the Sun group showed that electrodeposition of CuO -based Cu-Bi film from CuCl_2 solution enhanced the OER catalytic performance (overpotential for OER at $\sim 440\text{ mV}$ to achieve catalytic current density at 0.1 mA/cm^2) when the concentration of KBI electrolyte was increased to 0.2M [39]. Meanwhile, Cu-based bifunctional catalyst for both hydrogen production and water oxidation was also reported [40], in which an overpotential of $\sim 490\text{ mV}$ was required to achieve 0.1 mA/cm^2 in 0.1M KBI electrolyte at $\text{pH } 9.2$. Besides above studies, it is still necessary to simplify the fabrication method to prepare copper-based catalysts under a low applied potential, while also seeking to further enhance the catalytic properties and lower the overpotentials toward OER.

In this present study, we report on the use of Cu_2O thin films, directly electrodeposited from cheap copper(II) salts under very

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low applied potentials (-0.17 V and -0.23 V), as the precursor for OER catalysis. These Cu₂O materials with varying morphologies (dendritic branching and cluster-like) were facily prepared in a Cu(II) acetate solution without using any template or surfactants. All the materials showed good catalytic activities for OER, even after a long term of electrolysis (> 10 h). A catalytic current density of ~0.1 mA/cm² required a low overpotential of ~430 mV using the electrodeposited Cu₂O material under an optimal condition. The Cu₂O material was characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS).

2. Experimental Details

Materials. All chemicals, including Cu(OAc)₂·H₂O (99.0%), NaOAc·3H₂O (99.0%), NaOH (96.0%), potassium acetate (KOAc, 92.0%), boric acid (HBI, 99.99%), potassium phosphate (99.0%), Cu₂O powder (99.0%), and K₂CO₃ (99.0%) were commercially purchased (Aldrich or Acros) and used without further purification unless otherwise noted. All electrolyte solutions were prepared with millipore water (resistivity: ~18 MΩ·cm).

2.1. Electrochemical methods

All electrochemical experiments were performed in a standard three-electrode system at room temperature by a CHI602E potentiostat (purchased from Shanghai Chen Hua Instrument Co., Ltd.). In this three-electrode system, an Ag/AgCl electrode (3 M KCl, 0.21 V vs. NHE) and Pt wire were used as the reference electrode and the counter electrode, respectively. The working electrode was fluorine doped tin oxide (FTO) coated with Cu₂O. Bulk electrolysis (BE) under variable potentials and cyclic voltammograms (CVs) were measured in 0.1 M KBI electrolyte with mild stirring (200 rpm). In addition, there were *iR* compensations and no stirring was used for the CV tests.

2.2. Electrodeposition of Cu₂O thin films on conductive FTO electrode

In a typical method,[41] Cu₂O films were electrodeposited from an aqueous solution containing 0.1 M copper(II) acetate and 0.1 M sodium acetate under an applied negative potential. In detail, the deposition was performed potentiostatically under the applied potentials of -0.23 V or -0.17 V vs. Ag/AgCl at room temperature. The applied charge was variable to optimize the Cu₂O films. After deposition, the films were rinsed with deionized water and ethanol three times each, and dried in air. All potentials are reported with reference to Ag/AgCl.

2.3. Commercial Cu₂O for electrocatalysis

10 mg of commercial Cu₂O was dispersed in 0.9 mL ethanol and 100 μL 5% Nafion solution. The resulting solution was homogenized by ultrasonication for 20 min to make Cu₂O ink. Then, 20 μL of the above ink solution was dropped onto a clean FTO electrode (1 cm²), which is equivalent to the mass of electrodeposited Cu₂O after 0.3 C/cm² charge that passes through the electrode. The as-prepared electrode was further used for cyclic voltammograms and bulk electrolysis.

2.4. Electrochemically Active Surface Area (ECSA). Cu₂O-OEC1 and Cu₂O-OEC2

Catalysts were firstly electrodeposited on glass carbon electrode (GC, with diameter of 3 mm) in an aqueous solution containing 0.1 M copper(II) acetate and 0.1 M sodium acetate by controlling the same charge (0.3 C/cm²) passed through the

electrode at -0.17 V and -0.23 V, respectively. Then, CVs of **Cu₂O-OEC1** and **Cu₂O-OEC2** catalysts at various scan rates are obtained in 1.0 M KOH. The ECSA was calculated using the function $ECSA = C_{dl}/C_s$. In this equation, C_{dl} is the electrochemical double layer capacitance, which was determined by measuring the CVs at various scan rates in the non-Faradaic region. The double layer charging current is equal to the product of scan rate (ν) and C_{dl} . [42–46] Thus, a plot of i_c as a function of ν yields a straight line with a slope equal to C_{dl} . C_s is specific electrochemical double layer capacitance of an atomically smooth surface, which could be typically 15–50 μF/cm². [46–48]

2.5. Tafel plot

The Tafel plot was obtained by a function of overpotential (η) vs. the Nernstian potential for the H₂O/O₂ half-reaction. Each stable current density (j) under various potentials was obtained in 0.1 M KBI solution at pH 9.2. The overpotential is defined as $\eta = V_{app} - iR - E_{pH}$. V_{app} is the applied potential vs. NHE, i is the stable current, R is the uncompensated resistance, and E_{pH} is the thermodynamic potential for water oxidation under this pH ($E_{pH} = 1.23 \text{ V} - 0.059 \text{ pH V}$ vs. NHE)

2.6. Faradaic efficiency

The quantitative detection of O₂ was recorded by a fluorescence-based oxygen sensor (Ocean Optics). The experiment used a gas-tight electrochemical cell equipped with Cu₂O/FTO electrode as the working electrode, an Ag/AgCl electrode as the reference electrode, and Pt wire as the counter electrode. Before the measurement, the electrolyte was degassed by bubbling with high purity N₂ for 20 minutes. The percentage of O₂ in the headspace was recorded at 2s intervals and converted into the partial pressure of O₂. Accompanied by the detecting process of oxygen, bulk electrolysis was initiated at 1.10 V without *iR* compensation.

2.7. Scanning electron microscopy (SEM)

A SIRION200 Schottky field emission scanning electron microscope (SFE-SEM) was used to obtain SEM images with an acceleration voltage of 5 kV or 10 kV or 20 kV. All the detected samples were rinsed by deionized water and dried in the air. Au was sprayed onto these samples to make the samples conductive before loading into the instrument.

2.8. X-ray photoelectron spectroscopy (XPS)

The ESCALAB 250 X-ray photoelectron spectroscopy (XPS) instrument was used to probe the elemental composition and the valence states of the samples. All the spectra obtained by the instrument are referenced to the C 1s peak (285.0 eV).

2.9. X-ray diffraction spectroscopy (XRD, D/max-TTR III)

The crystal phase analysis of the samples was performed by X-ray diffraction (XRD, D/max-TTR III) via graphite monochromatized Cu K α radiation of 1.54178 Å, operating at 40 kV and 200 mA. The scanning rate was 5° min⁻¹ from 10° to 80° in 2 θ .

3. Results and discussion

Two kinds of Cu₂O films were facily electrodeposited on FTO conductive electrode separately under -0.23 V and -0.17 V when the charge of 0.3 C/cm² passed through the electrode in 0.1 M aqueous copper(II) acetate solution containing 0.1 M sodium acetate. These two as-prepared Cu₂O films were characterized

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