



Short communication

Nanostructured copper oxide electrodeposited from copper(II) complexes as an active catalyst for electrocatalytic oxygen evolution reaction



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ABSTRACT

In this report we show that nanostructured copper oxide thin films electrodeposited from copper(II) complexes can catalyze the oxygen evolution reaction. Cyclic voltammetry and bulk electrolysis with copper oxide film electrode in alkaline aqueous solutions showed significant catalytic currents. The catalyst film was characterized by scanning electron microscopy, X-ray photoelectron spectroscopy, energy-dispersive X-ray analysis and X-ray diffraction. The results identify that nanostructured copper oxide is an active electrocatalyst for water oxidation.

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1. Introduction

An efficient catalytic oxygen evolution reaction (OER, $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$) is a requirement for one half of a water splitting system and still remains a great challenge in the conversion of electricity or solar energy into chemical fuels [1–3]. Synthetic complexes and metal oxides of ruthenium and iridium have been developed as water oxidation catalysts (WOCs) since the late 1970s [4–8]. However, owing to the low abundance and high cost of these noble metals, limitations may arise for the use of these catalysts in real applications. Therefore, efforts have also been made to find efficient and robust first-row transition metal-based WOCs, such as manganese [9], cobalt [3,10], nickel [11], copper [12–15], and iron [16]. Among these elements, copper is a very cheap metal but has been less explored for catalytic water oxidation. Since 2013, Cu(II) complexes have been reported as novel homogeneous WOCs for oxygen evolution. Cu(II) complexes with a 2,2'-bipyridine [12] or a triglycylglycine macrocyclic ligand [15] showed good catalytic activity in alkaline solution. Simple inorganic copper ions can also catalyze water oxidation in a carbonate solution at pH = 10.8 [14].

In contrast to the above-mentioned homogeneous systems for oxygen evolution reaction in copper(II) solutions, herein we report a heterogeneous system for catalytic water oxidation based on a nanostructured copper oxide catalyst, which can be electrodeposited from molecular

copper(II) 2-pyridylmethylamine complexes (Fig. 1a). To the best of our knowledge, these types of copper(II) complexes have not been previously reported for electrocatalytic water oxidation and the formation of copper oxide nanoparticles as an active electrocatalyst.

2. Experimental

2.1. Materials and characterization

All chemicals were obtained from Aldrich and used without any further purification. All electrolyte solutions were prepared with deionized water (resistivity: 18 M Ω ·cm). The synthesis of 2-pyridylmethylamine ligands and copper complexes was carried out according to a reported method [17]. Scanning electron microscopy (SEM) images and energy-dispersive X-ray analysis (EDX) data were obtained with a SIRION200 Schottky field emission scanning electron microscope equipped with a Rontec EDX system. X-ray photoelectron spectroscopy (XPS) data and the valence states of metal elements were probed with an ESCALAB 250 instrument. Powder X-ray diffraction (XRD) was measured by 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 in 2 θ .

2.2. Electrochemical methods

All electrochemical experiments were performed at room temperature with a CHI602E potentiostat (Shanghai Chenhua Instrument Co., Ltd.) and an Ag/AgCl reference electrode (3 M KCl, 0.210 V vs.

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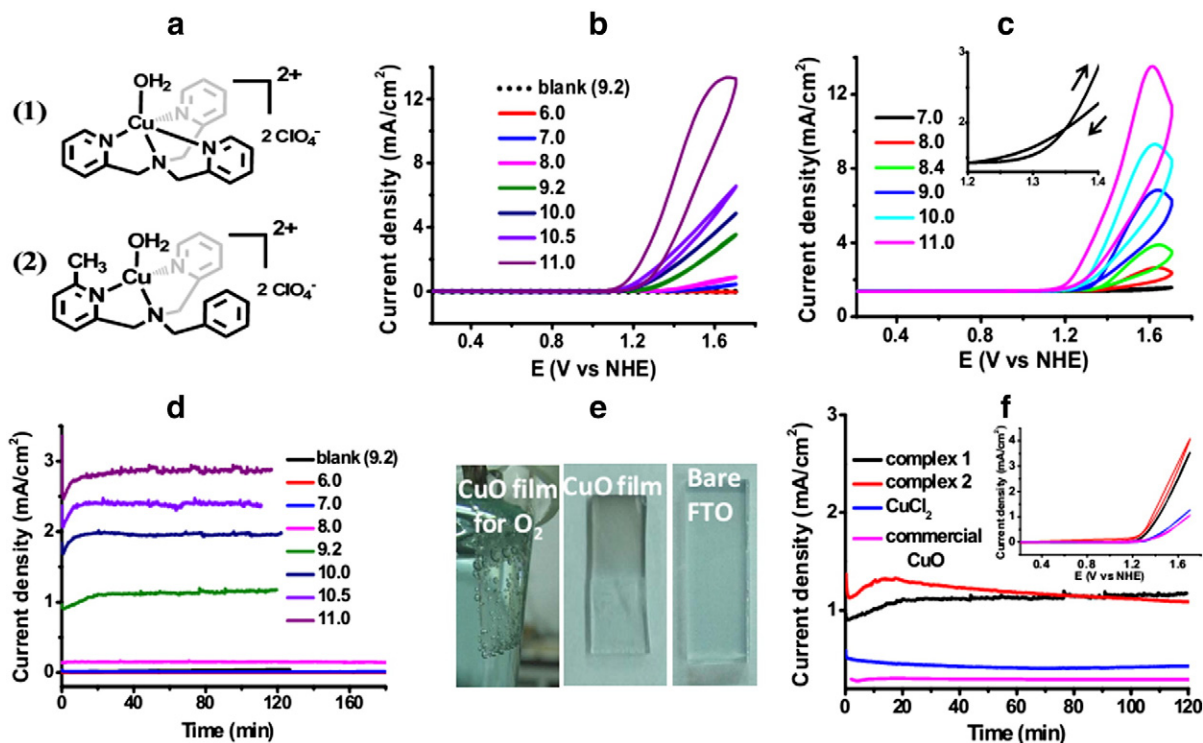


Fig. 1. (a) Molecular structures of copper(II) complexes. (b) CVs of 0.68 mM **1** in a 0.1 M borate solution (pH 6.0–11.0) using FTO as the working electrode; (c) the same as (b) but using glassy carbon as the working electrode (inset: the CV obtained at pH 9.0); (d) Bulk electrolysis of **1** at 1.41 V under different pH values. (e) Pictures of the FTO during O₂ evolution, the catalyst film and bare FTO. (f) Bulk electrolysis of the catalyst film obtained from compounds **1**, **2**, CuCl₂ and commercial CuO in a 0.1 M borate solution at 1.41 V (inset: the CVs of **1**, **2**, CuCl₂ and commercial CuO).

NHE). All the potentials are quoted versus NHE. Pt wire was used as the counter electrode, and a fluorine doped tin oxide (FTO) electrode was used as the working electrode. Bulk electrolysis was carried out at variable potentials in a 0.1 M borate electrolyte. The concentrations of the copper(II) complexes **1–2** and CuCl₂ were fixed at 0.68 mM. The Faradaic efficiency was determined using a fluorescence based oxygen sensor (Ocean Optics) for the quantitative detection of O₂.

3. Results and discussion

The cyclic voltammograms (CVs) of compound **1**, [Cu^{II}(TPA)H₂O](ClO₄)₂ (TPA = tris(2-pyridylmethyl)amine), were run in a 0.1 M borate solution using a FTO electrode (Fig. 1b). The onset of an oxidation wave was observed at about 1.2 V in a pH 9.2 solution, and gas bubbles were clearly observed on the FTO surface. The bubbles were further confirmed to be oxygen by both gas chromatography and a fluorescence based oxygen sensor, indicating that water oxidation reaction occurred during the anodic scan. The current densities for catalytic water oxidation are highly dependent on pH. Higher catalytic current intensities were observed when the pH was increased to 11.0. The black plot in Fig. 1b shows no appreciable catalytic wave in the absence of a copper(II) complex, indicating that the existence of **1** is essential for the catalytic reaction. Fig. 1c shows the CVs using a glassy carbon electrode, which presents an oxidative catalytic current peak at $E_{p,a} = \sim 1.65$ V ($E_{p,a}$ is the oxidative peak potential), and in the reverse scan a current crossover appears (Fig. 1c, inset). The values of $E_{p,a}$ have only slight differences (1.60–1.65 V) but the catalytic current densities increase from pH 7.0 to 11.0. As discussed in the earlier studies [12–14], the crossover feature may result from re-oxidation of an intermediate and all these observations probably indicate the formation of a high oxidation state Cu intermediate(s) during water oxidation.

Bulk electrolysis of **1** was performed at 1.41 V (Fig. 1d). The catalytic current densities increased with the pH, and a significant amount of oxygen gas bubbles were produced on the FTO. From pH 9.2 to 11.0, a

gray catalyst film (Fig. 1e) appeared on the FTO electrode in 1 h, and it became darker after a longer electrolysis time. Furthermore, when the film was used for bulk electrolysis in a borate solution containing no copper(II) complex, similar catalytic performance and gas bubbles were observed, indicating the high activity of the as-deposited film. To confirm the above observations, complex **2** was further examined for electrocatalysis. The CV data showed that complex **2** was also active for electrocatalytic water oxidation (Fig. 1f). Meanwhile, a similar heterogeneous film could be observed. To provide more insight into the advantage of using these copper complexes to generate an active catalyst film, we carried out experiments with a 0.68 mM CuCl₂ solution and commercial CuO (45 μL from 10 mg/mL CuO-ethanol suspension dispersed on the FTO electrode) for electrocatalytic water oxidation in a 0.1 M borate solution at pH 9.2 (Fig. 1f). Both exhibited much lower catalytic currents and higher overpotentials than the catalyst films electrodeposited from a Cu(II) organic complex.

Fig. 2a–c shows the SEM images of the catalyst films deposited on the FTO surface at 1.41 V after a 9 C charge passed through the electrode at pH 9.2 (all films < 0.1 mg). Fig. 2a shows the film obtained from compound **1**, which contains noticeable nanoparticles on the FTO with the size at ~30 nm. The inset is the cross-section image of the film, illustrating that its thickness is ~280 nm. These results clearly demonstrate that nanostructured materials were formed during the catalytic water oxidation reaction. Fig. 2b is the film obtained from compound **2**, which shows the thickness of ~280 nm. Comparing this to the former two films, a more disordered layer with a film thickness of ~300 nm was obtained from the film obtained by using CuCl₂ (Fig. 2c). The EDX data in Fig. 2d shows that the film obtained from compound **1** deposited at pH 9.2 mainly contains Cu, O, Sn and Au. Cu and O resulted from the deposited catalyst film. In addition, Sn was from the FTO substrate, and Au was artificially sprayed on the film. X-ray diffraction study showed that only the substrate SnO₂ peaks were observed on the electrode but no peaks from copper species, indicating the amorphous character of the electrodeposited catalyst film (Fig. 2d, inset).

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