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Article (Special Issue of Photocatalysis for Solar Fuels)

Highly effective electrochemical water oxidation by copper oxide film generated in situ from Cu(II) tricaine complex

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ARTICLE INFO

Article history:

Received 28 October 2017

Accepted 20 November 2017

Published 5 March 2018

Keywords:

Water oxidation

Oxygen evolution reaction

Electrodeposition

Copper oxide film

Electrocatalyst

ABSTRACT

Developing highly efficient and stable water oxidation catalysts based on abundant metallic elements is a challenge that must be met to fulfill the promise of water splitting for clean energy production. In this work, we developed an oxygen evolution reaction catalyst consisting of a nanostructured film electrodeposited from a phosphate buffer solution (0.2 mol/L, pH = 12.0) containing Cu-tricaine complex. A Tafel plot showed that the required overpotential for a current density of 1.0 mA/cm² was only 395 mV and the Tafel slope was 46.7 mV/decade. In addition, the Cu-tricaine film maintained a stable current density of 7.5 mA/cm² for the oxygen evolution reaction in phosphate buffer solution for 10 h, and a Faradaic efficiency of 99% was obtained.

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1. Introduction

Increasing energy consumption and environmental pollution caused by burning of traditional fossil fuels have stimulated global efforts to develop clean energy alternatives to fossil fuels [1,2]. Water splitting, involving the cathodic hydrogen evolution reaction and anodic oxygen evolution reaction (OER), is considered to be a highly efficient method for producing renewable and clean hydrogen energy [3–7]. However, because of its intrinsically sluggish reaction kinetics and the requirement for a high overpotential, the OER is the limiting step in water-splitting reactions [8,9]. The development of electrocatalysts with high OER activities is therefore needed to improve the reaction rate and reduce the overpotential. At present, complexes and oxides based on iridium and ruthenium are the best performing OER catalysts [10–16]. However, the scarcity and high cost of these noble metals greatly limits their

large-scale practical applications. It is therefore important to identify new efficient and cheap electrocatalysts for the OER. Recently, water oxidation catalysts based on non-precious metals, such as cobalt [17–23], nickel [24–28], copper [29–40], iron [41–43], and manganese [44,45] have been reported.

Because of their good redox properties and low cost, copper-based electrocatalysts show great potential in various catalytic applications. Several Cu(II)-based homogeneous catalysts for the OER have been reported in various buffered solutions with different pHs, including Cu(II)-bipyridyl [46,47] and Cu(II)-polypeptide [48] complexes. Highly efficient, stable copper-based heterogeneous electrocatalysts for the OER have also been reported and are listed in Table 1. In 2014, Du's group [29] reported that heterogeneous copper oxide electrodeposited from copper-tris(2-pyridylmethyl)amine was an active catalyst for the OER, with an overpotential of ~600 mV (1.0 mA/cm²). Du's group [31] also reported the use of an electro-

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This work was supported by the National Basic Research Program of China (973 Program, 2014CB239402), the National Natural Science Foundation of China (21573033), and the Basic Research Project of Key Laboratory of Liaoning (LZ2015015).

DOI: 10.1016/S1872-2067(17)62892-4 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 39, No. 3, March 2018

Table 1
Comparison of copper-based heterogeneous electrocatalysts for water oxidation.

Catalyst	Electrolyte	pH	η (mV vs. 1.0 mA/cm ²)	Tafel slope (mV/decade)	Ref.
CuO from Cu-TPA	Borate buffer 0.1 mol/L	9.2	600	56	[29]
Cu-bifunctional	Borate buffer 0.1 mol/L	9.2	749	85	[31]
CuO from Cu-TEOA	Acetate electrolyte 0.1 mol/L	12.4	780	130	[39]
Cu-Bi	Borate buffer 0.1 mol/L	9.2	530	89	[32]
CuO from Cu-en	PBS 0.2 mol/L	12.0	550	59	[36]
Annealed CuO	KOH electrolyte 1.0 mol/L	13.6	430	61.4	[40]
Cu(OH) ₂	Borate buffer 0.1 mol/L	9.2	640	78	[30]
CuO from Cu-Gly	PBS 0.2 mol/L	12.0	450	64	[33]
CuO from Cu-Tricine	PBS 0.2 mol/L	12.0	395	46.7	This work

Note: Overpotential (η) values at 1.0 mA/cm² are determined from Tafel plots.

deposited copper-based film as a bifunctional catalyst; the catalytic overpotential was 749 mV (1.0 mA/cm²) for the OER. In 2015, Sun's group reported a robust copper oxide film[32], prepared by a simple electrodeposition of Cu²⁺ from a borate buffer solution, which featured a current density of 1.0 mA/cm² at an overpotential of 530 mV in the OER. More recently, Chen's group [33,36] reported that CuO films electrodeposited from Cu-en and Cu-Gly complexes gave overpotentials of 550 and 450 mV, respectively, at a catalytic current density of 1.0 mA/cm² in 0.2 mol/L phosphate buffer solution (PBS, pH = 12.0).

2. Experimental

2.1. Materials

All chemical reagents used in this study, including CuSO₄·5H₂O, Na₂HPO₄·2H₂O, NaOH, *N*-[tris(hydroxymethyl)methyl]glycine (tricine), and Amberlite® IRC-748 were purchased from commercial suppliers. The chemicals were of analytical reagent grade and used without further purification. Indium tin oxide- (ITO-) coated glass slides were purchased from Zhuhai Kaivo Optoelectronic Technology Co., Ltd. (thickness ~1.6 mm, transmittance > 70%, resistance < 15 mΩ/cm²). All aqueous solutions were prepared with Milli-Q ultrapure water (>18 MΩ·cm) unless stated otherwise. The ITO-coated glass was washed by ultrasonication in aqueous detergent solution, acetone, ethanol, and deionized water for 30 min each, and then dried in an oven for future use.

2.2. Preparation of buffer solution

The PBS (0.2 mol/L, pH = 12.0) was prepared by dissolving Na₂HPO₄ (0.2 mol/L) in deionized water and the pH value of the solution was adjusted to 12.0 by addition of NaOH (solid). To rule out the influence of other metal impurity ions on the experiment, the PBS solution was washed with Amberlite® IRC-748. The washing procedure for the electrolyte was as follows. First, the Amberlite resin was stirred for 45 min in ultrapure water and then filtered to remove any unbound iminodiacetic acid. After drying in air, 5.0 g of the cleaned Amberlite resin was added to 400 mL of electrolyte and the mixture was stirred for 5 min. In this time, the resin was removed by filtration and the electrolyte was reserved for further use.

2.3. Formation of Cu-tricine complex

The copper complex was formed in situ by adding an aqueous solution of ligand (10.0 mL of 0.3-mol/L tricine) to an aqueous solution of CuSO₄ (10.0 mL, 0.3 mol/L) in molar ratio corresponding to the Cu/ligand stoichiometry of the final complex. The formation of the copper(II) complex was confirmed by UV/Vis spectrophotometry. Immediately, prior to deposition, the solutions were diluted in PBS (0.2 mol/L, pH = 12.0) to form a 1.0 mmol/L Cu-tricine complex in 0.2-mol/L PBS.

2.4. UV/Vis spectra

Solution UV/Vis spectra of the Cu-tricine complex were measured on a Varian 300 UV/Vis spectrophotometer in 1.0 cm cuvettes. The copper(II) complex was diluted in PBS (0.2 mol/L, pH = 12.0) for analysis.

2.5. Preparation of Cu-tricine catalyst films

The electrodeposition of the Cu-tricine films was performed in a two-compartment electrochemical cell with a glass frit junction to separate the two compartments. In the auxiliary chamber, the counter electrode was immersed in 30.0 mL PBS (0.2 mol/L, pH = 12.0). In the working electrode compartment, an ITO-coated glass electrode, with a 1.0-cm² electroactive area, was immersed in 30 mL PBS (0.2 mol/L, pH = 12.0) containing 1.0 mmol/L Cu-tricine complex. An Ag/AgCl reference electrode was also immersed in the working electrode compartment. After controlled-potential electrolysis for 6.0 h at 1.15 V (vs. normal hydrogen electrode (NHE)), without iR compensation or stirring, a layer of the catalyst film was formed on the ITO substrate.

2.6. Material characterization

The morphology of the prepared Cu-tricine films was observed with FEI Nova Nano SEM 450 instrument equipped with an energy-dispersive X-ray (EDX) analysis detector. Scanning electron microscope (SEM) images were obtained at an acceleration voltage of 3–5 kV and EDX spectra were obtained at accelerating voltages between 15 and 20 kV. Transmission electron microscopy (TEM) and high resolution TEM (HRTEM)

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