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Electrochemically prepared cuprous oxide film for photo-catalytic oxygen evolution from water oxidation under visible light

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ABSTRACT

Photo-catalytic oxygen evolution from water oxidation is very important for solar energy utilization and fuel cell production. In this work, cuprous oxide film for photo-catalytic water oxidation and oxygen evolution under visible light was in-situ prepared on a copper foil with an anodization based method. The surface features of cuprous oxide film were characterized with X-ray diffraction and scanning electron microscopy. The oxygen evolution capacity of as-obtained cuprous oxide film was evaluated with a water photolysis system, and an oxygen yield of 233.27 μmol per milligram of cuprous oxide was achieved during 8 h of illumination. During the reaction, water was oxidized by the photo-generated holes in cuprous oxide, and the copper/cuprous oxide heterojunction can effectively separate the photo-generated electron-hole pairs, which promote the catalytic activity of cuprous oxide film. The oxygen evolution reaction was driven by the bending of energy band of cuprous oxide caused by the semiconductor-metal contact. The remaining protons by the water oxidation resulted in the acidizing of water.

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1. Introduction

Solar energy utilization and fuel cell production are attractive and crucial issues of the development of clean resources. Photo-catalytic O_2 evolution from water oxidation is an important reaction, because it is a key reaction to provide a large-scale source of electrons and protons for fuel cell production through either proton reduction to hydrogen or proton-assisted CO_2 reduction to hydrocarbons [1].

As a promising p-type semiconductor material, cuprous oxide (Cu_2O) has many advantages, and it has considerable ability to produce photo-generated holes for oxidation under light illumination [2,3]. Cu_2O has a band-gap of approximately 2.17 eV, which corresponds to the absorption wavelength of visible light [4]. All these make Cu_2O a potential catalyst for the oxidation of water and O_2 evolution under solar illumination. However, the valence band edge (+0.54 V vs. SCE at pH=7) is close to the oxidation potential of water [5], and the energy provided by visible light was so low that the photo-generated electron-hole pairs in Cu_2O may fast recombine before effectively oxidizing H_2O [6]. All these make Cu_2O unsuitable for direct photo-catalytic water oxidation and O_2 evolution both thermodynamically and kinetically [7]. Thus although it

has been widely used as a catalyst for H_2O splitting from water splitting in previous studies by the introduction of mechanical energy [8–15] or n-type co-catalysts [16–23], Cu_2O has rarely been reported as an efficient photo-catalyst for the oxidation of water and O_2 evolution without any additional energy or co-catalysts.

It is already known that by forming Cu/ Cu_2O contact, the photo-generated electron-hole pairs in Cu_2O can be effectively separated [20], while little effort has been reported to realize O_2 evolution from water-oxidation by Cu/ Cu_2O heterojunction catalyst under visible light. Therefore, a Cu_2O film on Cu substrate as a catalyst for O_2 evolution from water oxidation under visible light is reported in this work. The Cu_2O film was in-situ prepared on Cu foil with an original anodization based method. Efforts were made to alter the energy band structure of Cu_2O by fabricating Cu/ Cu_2O heterojunction, in order to enable Cu_2O to be a proper photo-catalyst for water oxidation and O_2 evolution under visible light.

2. Experimental

2.1. The preparation of Cu_2O film

According to previous reports [24–28], it was very difficult to prepare the Cu_2O film directly on Cu substrate by anodization, because Cu_2O was prone to peeling off Cu substrate during the

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electrochemical reaction. However, the intermediate products, such as $\text{Cu}(\text{OH})_2$ or CuCl , can stay tightly on the surface of anode after anodization. Therefore we designed a two-step preparation route, which included two steps. First, $\text{Cu}(\text{OH})_2$ film was prepared on the surface of Cu foil by electrochemical anodization. The anodization was performed in a 3-electrode system, which was constituted with one-compartment electrolytic cell, polycrystalline Cu foil (99.999%, carefully rinsed and polished, the exposed area of which was 16 cm^2) as the anode, platinum gauze as the cathode, and SCE as the reference electrode. The electrolyte was 0.2 M NH_4Cl aqueous solution, and the pH value of which was accurately adjusted to 8.00 with NaOH solution. The anodization process was under galvanostatic condition (5 mA/cm^2) precisely controlled by a CHI-660D electrochemical workstation, at room temperature for 20 min. The electrolytic cell was slowly stirred to avoid the formation of passive film on the surface of anode. The Cu foil was finally rinsed and dried immediately after anodization for the subsequent post-treatments.

Many methods were tested in order to form Cu_2O film from the intermediate film, and most of them turned out to be failures because the product cannot form intact film on the substrate. Finally only 3 different methods were proved to be suitable for Cu_2O film forming. The first method was hydrolysis in 3% H_2O_2 solution and irradiated by a Xenon lamp for 30 min, which was described in our previous work [29]. The second method was thermal-reduction in H_2 atmosphere at $280\text{ }^\circ\text{C}$ in a tube furnace for 10 min, the reaction condition was based on the thermal-analysis of $\text{Cu}(\text{OH})_2$, the data of which can be found in the supporting information. The third method was reduction in 10% glucose solution at $80\text{ }^\circ\text{C}$ with water bath, according to the Fehling method [13]. The numbering of samples and corresponding reaction equations are listed in Table 1.

2.2. Characterization

The morphology of Cu_2O film was characterized with an FEI Sirion 200 scanning electronic microscopy (SEM, 5 kV). The composition of Cu_2O film was identified with a Rigaku X-ray Diffractometer (XRD, $\text{Cu-K}\alpha$ radiation $\lambda=0.154\text{ nm}$, 35 kV, 100 mA) and an X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD). In order to estimate the mass of film, Cu_2O was scraped off the substrate and weighed by an electronic balance. The $\text{Cu}(\text{OH})_2$ samples for DSC/TGA and BET measurements were also prepared by scraping $\text{Cu}(\text{OH})_2$ film off substrate. The Mott–Schottky curves of Cu_2O film were characterized by an impedance-potential method of electrochemical workstation, with 3-electrode electrolytic cell (platinum gauze as the cathode, and saturated calomel electrode as the reference electrode) and 0.5 mol/L Na_2SO_4 as electrolyte, the scan range, potential amplitude, frequency were $-1.0\text{--}0\text{ V}$, 0.01 V and 10 Hz respectively.

2.3. The photo-catalytic oxidation of water

The reaction was carried out in a hermetic vessel made of Pyrex glass, which was attached to a closed gas circulation system (Lab Solar-H2 water photolysis system, Beijing PerfectLight Technology Ltd.) equipped with a vacuum pump and a gas chromatograph (GC 7890 II, Hongkong Techcomp Ltd., 0.3 MPa N_2 as the carrier gas, P/N 19091J-433, HP-5 capillary column). Before reaction, ultra-pure

water ($18.25\text{ M}\Omega\text{ cm}$) was boiled for at least 1 min to eliminate the dissolved air. The water in reaction vessel was 90 mL. The Cu_2O film was directly put at the bottom of the vessel, with the Cu_2O (16 cm^2) face up (schematically shown in Fig. 1). The reaction system was evacuated for at least 30 min by vacuum pump. The vessel was irradiated by a 300 W Xe lamp (PLS-SXE300, Beijing PerfectLight Technology Ltd., $\lambda \geq 420\text{ nm}$) from top side, the distance between the Xe lamp and Cu_2O film was about 15 cm. The yield of gas was sampled every hour for 6 h, and the accumulated yield of the evolved gas was analyzed by gas chromatography. The reaction vessel was cooled with a circulating water system.

3. Results and discussion

3.1. The characterization of Cu_2O film

The composition and morphology of the product films are shown in Figs. 2 and 3, respectively. According to Fig. 2(A) and Fig. 3(A), the Cu foil was covered with $\text{Cu}(\text{OH})_2$ micro-sheet structure after 20 min of anodization. And according to Fig. 2(B)–(D) and Fig. 3(B)–(D), $\text{Cu}(\text{OH})_2$ was basically converted to Cu_2O after post-treatments, and the surface of product films presented quite different morphologies.

The composition of sample #1 is illustrated in Fig. 2(B), in which the diffraction peaks of $\text{Cu}(\text{OH})_2$ disappear except one at 56.7° , and the peaks of Cu_2O 's (111) facets at 36.4° and (200) facets at 42.3° appear. According to Scherrer equation, it is found that the film consists of Cu_2O crystallites of about 27 nm. However, the Cu_2O film contains small amount of CuO impurity, which was oxidized by H_2O_2 . The surface of sample #1 presents spongy

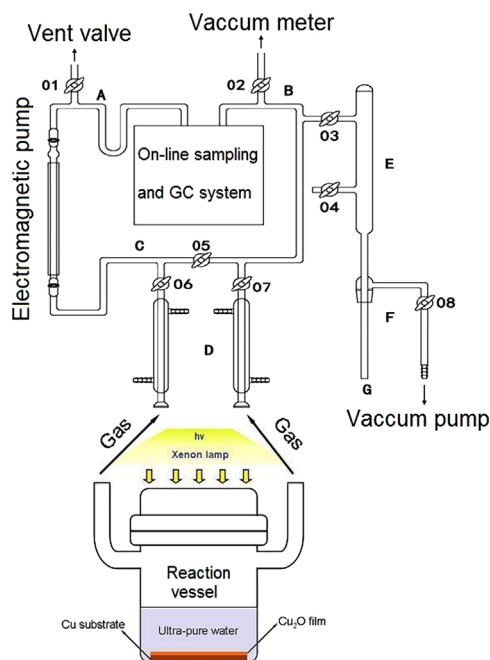


Fig. 1. Schematic image of photo-catalytic water oxidation system.

Table 1

The numbering of samples and corresponding reaction equations of samples.

The numbering of samples	The post-treatment methods	The reaction equation
#1	Hydrolyzed with H_2O_2 solution	$2\text{Cu}(\text{OH})_2 + \text{H}_2\text{O}_2 \rightarrow \text{Cu}_2\text{O} + \text{O}_2\uparrow + 3\text{H}_2\text{O}$
#2	Reduced at $280\text{ }^\circ\text{C}$	$2\text{Cu}(\text{OH})_2 + \text{H}_2 \rightarrow \text{Cu}_2\text{O} + 3\text{H}_2\text{O}$
#3	Reduced by glucose solution	$\text{CH}_2\text{OH}(\text{CHOH})_4\text{CHO} + 2\text{Cu}(\text{OH})_2 \rightarrow \text{CH}_2\text{OH}(\text{CHOH})_4\text{COOH} + \text{Cu}_2\text{O} + 2\text{H}_2\text{O}$

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