



Full Length Article

One-step electrochemical deposition of Schiff base cobalt complex as effective water oxidation catalyst



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ARTICLE INFO

Article history:

Received 16 September 2016

Received in revised form 29 October 2016

Accepted 4 November 2016

Available online 6 November 2016

Keywords:

Electrochemical deposition

Schiff base cobalt complex

Water oxidation catalyst

ABSTRACT

Schiff base metal complexes have been applied in many fields, especially, a potential homogeneous catalyst for water splitting. However, the high overpotential, time consumed synthesis process and complicated working condition largely limit their application. In the present work, a one-step approach to fabricate Schiff base cobalt complex modified electrode is developed. Microrod clusters (MRC) and rough spherical particles (RSP) can be obtained on the ITO electrode through different electrochemical deposition condition. Both of the MRC and RSP present favorable activity for oxygen evolution reaction (OER) compared to the commercial Co_3O_4 , taking an overpotential of 650 mV and 450 mV to drive appreciable catalytic current respectively. The highly active and stable RSP shows a Tafel plot of 84 mV dec^{-1} and negligible decrease of the current density for 12 h bulk electrolysis. The synthesis strategy of effective and stable catalyst in this work provide a simple method to fabricate heterogeneous OER catalyst with Schiff base metal complex.

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1. Introduction

Water splitting is one of the most promising ways to generate a clean and renewable fuel that can meet the need of environmentally friendly energy sources in the future. A crucial factor that limits the efficient water splitting is the high overpotential for oxygen evolution reaction (OER), thus, it is urgently needed for the fabrication of highly active and stable catalyst. Although Ir- and Ru- based materials [1,2] demonstrate excellent catalytic activity towards OER, the high cost and scarcity limit their widespread and large-scale application. To replace the noble metal catalysts, numerous efforts have been done with the nonprecious earth-abundant elements, that are, Co [3–5], Fe [6,7], Mn [8], Cu [9] based materials. Metal based inorganic materials work as heterogeneous catalyst usually show low overpotential and high activity, but they always consist in amorphous states and are rarely easy to be characterized [9,10]. Therefore, it is difficult to control the exact structure of this kind of catalyst. Another way, though the metal species are generally considered to be the active sites of those heterogeneous catalysts, there are still lots of questions about how the system operates during the complex electrochemical process. In contrast, catalyst based on cobalt [4] and iron [6,7] with certain molecular structure,

work in a homogeneous solution, has a much clear mechanism of electrocatalysis water splitting. However, the high overpotential, complicated synthesis process, hard to recycle, difficult to reuse and lots of them operate in non-aqueous solution all be the shortcoming of their application. Therefore, efficient, stable, easily fabricated and nonprecious elements based catalyst is continuing needed.

Schiff base metal complexes are an important series of complexes that widely use in biological fields [11], analytical fields [12,13] and organic catalyst [14]. Recently, they have been studied as an electrochemical catalyst towards hydrogen evolution reaction (HER) [15,16] and OER [17]. Though the structure of these catalyst can be accurately controlled, their high overpotential ($\eta = 560 \text{ mV}$ for OER [17]), complicated synthesis process, large consumption and sacrifice largely limit their application. In contrast, a modified electrode works in much simple conditions and their performance can be easily controlled by adjusting the loading amount of catalyst or electrode surface. In order to inherit the low overpotential and high efficient of the heterogeneous catalyst and the accurately controllable structure of Schiff base metal complex, a simple one-step process to fabricate Schiff cobalt complex/ITO electrode for OER through electrochemical deposition is worthy developed.

In the present work, we developed a simple process to synthesize a modified ITO electrode for efficient water oxidation using salophen and cobalt through electrochemical deposition. By changing the deposited conditions, different shapes of particles can be obtained on the ITO surface. The as prepared particles were suc-

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cessfully characterized and confirmed to be Schiff base cobalt complexes, while the microrod clusters (MRC) correspond to CoL and the rough spherical particles (RSP) correspond to H_2CoL_2 (H_2L : Bis[Salicyldene]-1,2-Iminophenylenediamine, Co: cobalt). The catalytic activity towards OER in a pH 9.02 borate solution shows an overpotential of 650 mV for MRC and 450 mV for RSP. For a constant current density of 2 mA cm^{-2} , 900 mV and 650 mV is required for MRC and RSP respectively. The highly active and stable RSP catalyst shows a tafel plot of 84 mV per decade and negligible degradation after 12 h electrolysis. The pH dependent performance of RSP shows a slope of -92 mV per pH unit of the potential-pH curve demonstrates a $2\text{e}^- - 3\text{H}^+$ couple transfer process during the electric catalytic reaction [18–20], and Co^{IV} is considered as the active species [4,20]. The RSP coated electrode exhibits higher active than the homogeneous Schiff base cobalt complex which with similar structure [4]. The facile synthesis strategy of effective and stable catalyst in this work may widen the research of Schiff base metal complexes as a heterogeneous catalyst for OER.

2. Experimental section

2.1. Reagents and materials

Cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), o-Phenylenediamine (AR), salicylaldehyde (AR), tetrabutylammonium perchlorate ($[(n\text{-Bu})_4\text{N}]\text{ClO}_4$), acetonitrile, *N,N*-Dimethylformamide (DMF), potassium hydroxide (KOH), boracic acid and sodium borate were commercially available (obtained from Aladdin Industrial Co. (China)) and used without further purification. All solutions were prepared with acetonitrile (GC) or deionized water (resistivity: $18 \text{ M}\Omega \text{ cm}^{-1}$).

2.2. Synthesis of bis[Salicyldene]-1,2-Iminophenylenediamine

Bis[Salicyldene]-1,2-Iminophenylenediamine (defined as H_2L) was synthesized according to a previous report [21]. Briefly, a sample of 1.08 g o-phenylenediamine mixed with 2.44 g salicylaldehyde in ethanol and stirred with reflux for 4 h to get a yellow precipitate, which was separated and further purification by recrystallized in ethanol. H_2L was analyzed by HRMS using methanol as the solvent. M/z was found: 317.1293, calculated for $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}_2$ [$M+\text{H}^+$]: 317.1285 (Fig. S1 in Supplementary material).

2.3. Preparation of modified electrodes

The modified electrodes were prepared by electrochemical deposition according to our previous work [22]. MRC was deposited onto ITO in a water-acetonitrile (acetonitrile containing 3 wt% deionized water) solution containing 27 mM H_2L and 27 mM CoCl_2 when the potential was held at -1.15 V for 30 min. RSP/ITO was obtained in anhydrous acetonitrile containing 27 mM H_2L and 27 mM CoCl_2 using the same deposited procedure. For these deposition experiments, 0.1 M $[(n\text{-Bu})_4\text{N}]\text{ClO}_4$ was applied as the supporting electrolyte. Co_3O_4 coated ITO electrode ($\text{Co}_3\text{O}_4/\text{ITO}$) was prepared as the following procedure. Firstly, Co_3O_4 was distributed into ethanol-Nafion (ethanol containing 0.25 wt% Nafion) by 30 min of ultrasonication to get a 0.1 g mL^{-1} suspension. Then, the suspension was dropped onto the ITO surface and dried under an infrared lamp to obtained $\text{Co}_3\text{O}_4/\text{ITO}$ with a loading amount of 20 mg cm^{-2} .

2.4. Characterizations

Scanning electron microscopy (SEM) images were carried out with a Hitachi SN-3400 scanning electron microscope. Fourier Transform Infrared spectroscopy (FTIR) was obtained on a Thermo

Fisher iS10 equipped with a liquid nitrogen cooled MCT detector. UV–visible spectroscopy was recorded on a Shimadzu UV-2450 spectrophotometer. High resolution mass spectrometer (HRMS) data was obtained by LC–MS (Agilent 1290/Bruker maxis Impact). X-ray photoelectron spectra (XPS) were performed using an ESCALAB 250 X-ray electron spectrometer microprobe using Al $K\alpha$ radiation.

2.5. Electrochemical measurements

All electrochemical experiments were done with a IGS 4030 potentiostat (Guangzhou Ingsens sensor technology Co. Ltd, China) at room temperature. A three-electrode system was applied with a platinum wire as the counter electrode. A saturated Ag^+/Ag (1 M $[(n\text{-Bu})_4\text{N}]\text{ClO}_4$) electrode and an Ag/AgCl (3 M KCl) electrode were used as the reference electrode for deposition experiments and experiments in aqueous solution, respectively. Indium tin oxide (ITO) electrode was used as the working electrode for deposition experiments in acetonitrile, in which 0.1 M $[(n\text{-Bu})_4\text{N}]\text{ClO}_4$ was used as the supporting electrolyte. A ferrocenium/ferrocene ($\text{FcH}^{+/0}$) couple was used as an internal standard and $E_{1/2}$ of $\text{FcH}^{+/0}$ under experimental conditions was 0.52 V. The catalytic activity of RSP and MRC towards OER was measured in 0.1 M borate solution.

3. Results and discussion

3.1. Characterization of the deposition

SEM images in Fig. 1a–b revealed the well-separated microrod clusters obtained from electrochemical deposition that held in water-acetonitrile solution (acetonitrile contains 3% deionized water in volume, 0.1 M $[(n\text{-Bu})_4\text{N}]\text{ClO}_4$) containing 27 mM H_2L and 27 mM CoCl_2 with a constant potential at -1.15 V for 30 min. The smooth rods grown in clusters with a length from 20 to 50 μm come out from a same site of the electrode surface and appear as flowers. Obviously, each flower is developed from the well separated nuclei sites where the charge transfer takes place [23]. A higher magnification image (Fig. 1b) shows that these rods are smooth with width of 1 μm . In contrast, deposition obtained from an anhydrous acetonitrile solution of 27 mM Co^{2+} and 27 mM H_2L after a -1.15 V 30 min electrolysis process reveals a total different appearance. As shown in Fig. 1c, the electrode surface is coated with rough spherical particles in diameters of 5–8 μm . This result is consistent with our previous report [22]. The particles are not smooth but present a multi-layer surface (Fig. 1d, Fig. S2 in Supplementary material) and some of them are found to grow together. This phenomenon can be associated to the quickly deposition process. Moreover, a rough thin film can be observed on the electrode surface at the foot of the particles, and it may results from a higher concentration of the Schiff base cobalt complexes [22,24]. The results demonstrated that the electrode surface could be modified with different shape of particles during a quickly electrochemical deposited process.

According to our previous study [22], the different morphology was considered as a result of different products obtained in different coordinated conditions. H_2O is a kind of Lewis base. In the water-acetonitrile solution, it is more likely for the ligand (H_2L , $\text{pK}_a = 8.10$ at 25°C) to exfoliate a proton and forms HL^- . In this condition, Co^{2+} combines with HL^- in forming two $\text{N}-\text{Co}^{2+}$ and a single $\text{O}-\text{Co}^{2+}$ coordinate bonds, results in the product of HCoL^+ . In the contrast, anhydrous acetonitrile inhibits the ionization of H_2L , coordinated bond between O atom and Co^{2+} is hard to be formed. The association between Co^{2+} and H_2L is constructed through the $\text{Co}^{2+}-\text{N}$ bonds. As a result, Co^{2+} forms 4 $\text{Co}^{2+}-\text{N}$ bonds with two H_2L molecules in generating H_4CoL_2 . During the electrodeposition process, HCoL^+ and H_4CoL_2 are reduced on the ITO electrode sur-

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