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An ultrathin nickel-based film electrodeposited from a Ni-Tris molecular precursor for highly efficient electrocatalytic water oxidation

Hu Chen, Yan Gao*, Lu Ye, Ya'nan Yao, Yu Wei, Xuyang Chen

State Key Laboratory of Fine Chemicals, Institute of Artificial Photosynthesis, DUT-KTH Joint Education and Research Center on Molecular Devices, Dalian University of Technology (DUT), Dalian, 116024, China

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ABSTRACT

Water splitting is one of the important and effective routes to produce hydrogen as applicable alternative to conventional fossil fuels. As we all know, oxygen evolution reaction (OER) is a key and restricted part of the overall water-spitting process. Highly efficient electrocatalysts are essential components to accelerate the rate of the OER and lower the overpotential. In this paper, an ultrathin nickel-based film on FTO (NiO_x-Tris electrode) was prepared through five cycles of cyclic-voltammetry electrodeposition from a 0.1 M borate buffer solution (pH 9.2) that contained a molecular nickel complex as a precursor. The activity of the as-prepared catalyst film for OER was measured in near-neutral borate buffer solution (0.6 M, pH 9.2), and the results showed that the NiO_x-Tris electrode exhibits a better catalytic activity over the catalyst (NiO_x-aqua) that was derived from Ni^{2+} salts. In detail, the NiO_x-Tris ultrathin film achieved a stable catalytic current density of ~5.0 mA/cm^2 at 1.3 V versus a normal hydrogen electrode for OER in borate buffer solution.

1. Introduction

The depletion of fossil-fuel reserves coupled with the effects of global environmental issues are forcing major international endeavors to develop economically viable renewable and clean-energy sources (such as, solar energy, wind energy, hydraulic energy, geothermal energy, and hydrogen energy). Solar energy is an inexhaustible energy but because it is difficult to store, its large-scale application is hindered [1–3]. The search for effective and practical routes that can convert solar energy into other form of energy is required urgently. Hydrogen, as a potential clean energy, could contribute to efforts to replace conventional carbon-based fuels [4,5]. Hydrogen that is produced through water splitting that uses sunlight can be stored until it is required for use [6–8]. The overall water-splitting process includes two half reactions: the hydrogen-evolution reaction (HER) and the oxygen-evolution reaction (OER). However, the OER reaction that includes multiple protons and electrons limits the overall reaction [9–11]. Hence, the development of efficient, cheap and stable water-oxidation catalysts has attracted the attention of researchers globally.

The method to fabricate the materials is critical to obtain a highly efficient OER catalyst. Many effective methods have been developed by scientific researchers to prepare OER catalysts. The electrocatalysts in the form of nanoparticles have been synthesized by hydrothermal treatment, codeposition, chemical oxidation and other means. Then, the powder catalysts were dispersed in the solvents and attached to the substrate (glassy carbon electrode, carbon fibre paper, Ni foam) with adhesive (such as nafion) [12–15]. The use of adhesive provides a significant increase in the resistance of the assembled electrode, which weakens the catalytic activity for OER. Moreover, the catalysts peel off from the substrates easily, which would affect the stability of the catalysts. To avoid the above disadvantages, catalysts that are grown directly on the substrates can enhance the OER efficiency by accelerating the electron transfer between the catalysts and the substrates. Many ways exist for loading catalysts onto substrates. Electrodeposition is an effective approach to fabricate different kinds of catalyst materials [16–21]. This strategy has several key advantages: firstly, the technique is suitable for the production of large surface areas and can be performed in the laboratory and industrially with comparatively cheap equipment and straightforward procedures. Secondly,

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* Corresponding author.
E-mail address: dr.gaoyan@dlut.edu.cn (Y. Gao).

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many controllable factors can be used during the catalyst-deposition process. For example, the amount of material deposited can be controlled easily by the amount of charge passed during a deposition. The morphology of catalyst film can be regulated through different deposition conditions, which affect the catalytic activity. Very recently, Symes et al. summarized some OER electrocatalysts based on first-row transition metals through electrodeposition [22].

Several reports developed the molecules [23–26] and materials [27–29] based on precious metals (ruthenium and iridium) for OER, however, their high price and low earth reserves limit their large-scale application. Scientific researchers are committed to the development of new and highly efficient water-oxidation catalysts based on non-noble metals (such as iron [16,30–33], cobalt [17,34–37], copper [18,38–40], nickel [19,21,41–43], manganese [20,44], and some mixed metals [45–48]). In 2010, Nocera et al. [19] discovered a nickel-based film that was prepared by electrodeposition in borate buffer solution (0.1 M, pH 9.2) that contained 1.0 mM Ni^{2+}, which performed well for OER and exhibited a low onset potential of 1.15 V vs. a normal hydrogen electrode (NHE) in a borate buffer solution (0.1 M, pH 9.2). In 2014, Joya et al. [21] reported that a water oxidation catalyst film (Ni-Ci) formed via electrodeposition in a CO_2-saturated 0.2 M bicarbonate electrolyte that contained 1.0 mM Ni^{2+} showed an onset potential of ~1.30 V vs. NHE and obtained a current density of ~1.85 mA/cm^2 at 1.40 V vs. NHE in a HCO_3^-/CO_2 electrolyte (pH 6.8). The above catalyst films were all deposited from a buffer solution that contained nickel salt. A number of nickel-based molecules were used as precursors to electrodeposit catalyst films. Because of the low solubility of nickel salt in the buffer solution, the application of molecular nickel complexes (high solubility) as precursors to prepare catalyst films is very practical [49–51]. Moreover, ligands of molecular precursors can regulate the formation of catalyst films, which leads to an enhancement of the catalytic efficiency.

Moreover, ultrathin is indeed an important advantage of the electrode [31], on one hand, the ultrathin electrode indicates that the amount of electrocatalyst loaded on the substrate is extremely low, which is critical for high atom efficiency. On the other hand, the ultrathin electrode enables the optically transparent property, which makes the NiO_x-Tris film maybe a good candidate for preparation of a photoanode for photocatalytic OER and does not affect the light absorption of the photosensitizer.

Inspired by the above discussions, the tris(hydroxymethyl) aminomethane (Tris) ligand was applied to combine with Ni^{2+}, and the Ni-Tris complex was formed in-suit in the borate buffer solution. Therefore, the Ni-Tris complex with good solubility in the buffer solution was used as precursor to electrodeposit a high-efficiency water-oxidation catalyst film (denoted as a NiO_x-Tris film). The as-prepared ultrathin film exhibited a low onset potential of ~1.1 V vs. NHE and achieved a stable catalytic current density of ~5.0 mA/cm^2 at 1.3 V vs. NHE in borate buffer solution.

2. Experimental section

2.1. Materials

All chemical reagents, including $NiSO_4 \cdot 6H_2O$, Boric acid (H_3BO_3), NaOH, Tris(hydroxymethyl) aminomethane (Tris), Amberlite® IRC-748 were purchased from commercial suppliers and were used without further purification. Fluorine-tin-oxide (FTO) coated glass slides was purchased from Wuhan Geao science (thickness ~ 2.2 mm, transmittance > 90%, resistance ~ 50 mΩ/cm^2). FTO glass was ultrasonic washed by the aqueous solution with detergent, acetone, ethanol and deionized water each 30 min, and then was dried in the oven for future use.

2.2. Preparation of the buffer solutions

The borate buffer solutions (0.1 M or 0.6 M, pH 9.2) were prepared by dissolving H_3BO_3 (0.1 M or 0.6 M) in deionized water and the pH values of the solutions were adjusted to 9.2 by NaOH (solid). In order to rule out the influence of other metal impurity ions on the experiment, the borate buffer solutions we have prepared were washed with Amberlite® IRC-748. The washing procedure for the electrolyte was as follows. Firstly, the Amberlite resin was stirred for 45 min in ultrapure water and then filtered, in order to remove any unbound iminodiacetic acid. After drying in air, 5.0 g of this cleaned Amberlite resin were added to 400 mL of electrolyte and the mixture stirred for 5 min. After this time, the resin was removed by filtration and the electrolyte was for further use.

2.3. Preparation of nickel-based films

Nickel-based films were generated by a cyclic voltammetry (CV) electrodeposition method with FTO (1.0 cm^2) as working electrode, saturated Ag/AgCl as reference electrode and Pt wire as auxiliary electrode. FTO was immersed in borate buffer solution (0.1 M, pH 9.2, 25.0 mL) containing $NiSO_4$ (1.0 mM) and Tris (2.0 mM). The potential was cycled with 5 times between 0.2 V and 1.5 V (vs. NHE) (without iR compensation) in the static solution. The scan rate was 25.0 mV/s unless otherwise noted. After the CV electrodeposition, the catalyst film was polarized in borate buffer solution (0.6 M, pH 9.2, 25.0 mL) within 3 h.

2.4. The characterizations of the as-prepared electrodes

The scanning electron microscopy (SEM) images and the energy-dispersive X-ray (EDX) spectra were obtained using FEI Nova NanoSEM 450 instrument equipped with EDX detector. Images were obtained with an acceleration voltage of 3–5 kV and EDX spectra were obtained with acceleration voltages between 15 and 20 kV. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained using FEI TF30 equipment. To obtain enough samples to test, the film was electrodeposited via 10-cycles CVs. Then, the as-prepared film was carefully scraped off using a doctor blade, the powder material was dispersed in ethanol. After the mixture was treated with ultrasound for 30 min, a drop of the mixture was dried on a carbon-coated copper grid for analysis. The X-ray diffraction (XRD) results were collected with a D/max-2400 diffractometer from 20° to 80° with a scan-rate of 8°/min. X-ray photoelectron spectroscopy (XPS) measurement was performed on Thermo VG ESCALAB 250X using an aluminium anode (Al $K\alpha = 1486.6$ eV) operating at 150 W and a spot size of 500 μm. Typically the hydrocarbon C 1s line at 284.6 eV from adventitious carbon is used for energy referencing. Survey scans were measured at the constant pass energy of 50.0 eV. The nickel coverage of film was ascertained by the inductively coupled plasma atomic emission spectrometer (ICP-AES) using the Optima 2000DV (America Perkin Elmem Corp.). The as-prepared sample was dissolved in HNO_3 (0.1 M, 25.0 mL). The prepared electrodes were used to record the Raman spectra on a DXR laser confocal microscopic Raman spectrometer at an excitation wavelength of 532 nm.

2.5. Electrochemical measurements

All electrochemical experiments were carried out at room temperature (25 ± 2 °C) using CH Instruments (model CHI 630E Electrochemical Analyzer). CV curves were performed in the aqueous solution (35.0 mL) with a conventional three-electrode configuration: a FTO (1.0 cm^2) working electrode, a saturated Ag/