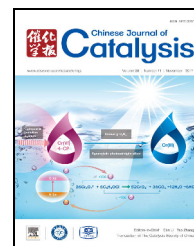


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## Article

# Electrocatalytic water oxidation by a nickel oxide film derived from a molecular precursor

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## ABSTRACT

In this study, we fabricated a NiO<sub>x</sub> film by electrodeposition of an ethanediamine nickel complex precursor (pH = 11) on a fluorine-doped tin oxide substrate. The resulting film is robust and exhibits high catalytic activity for electrochemical water oxidation. Water oxidation is initiated with an overpotential of 375 mV (1 mA/cm<sup>2</sup>) and a steady current density of 8.5 mA/cm<sup>2</sup> is maintained for at least 10 h at 1.3 V versus the normal hydrogen electrode. Kinetic analysis reveals that there is a 2e<sup>-</sup>/3H<sup>+</sup> pre-equilibrium process before the chemical rate-determining step. The low-cost preparation, robustness, and longevity make this catalyst competitive for applications in solar energy conversion and storage.

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## 1. Introduction

The massive consumption of fossil fuel is creating worldwide interest in searching for renewable energy sources [1,2]. Splitting water into oxygen and hydrogen by sunlight is a promising approach to achieve this goal [3,4]. However, water oxidation involves the release of 4e<sup>-</sup> and 4H<sup>+</sup>, and it requires a high thermodynamic overpotential (2H<sub>2</sub>O → O<sub>2</sub> + 4H<sup>+</sup> + 4e<sup>-</sup>, 1.23 V vs. the normal hydrogen electrode (NHE) at pH = 0) [5]. To efficiently drive this reaction, water oxidation catalysts (WOCs) with low overpotentials are crucial. Inspired by nature, great progress has been made in developing WOCs based on transition metals [6–14]. Although the activities of WOCs based on noble metals, such as ruthenium and iridium, are impres-

sive, their practical application is hampered by their scarcity and high cost. Consequently, development of efficient WOCs based on earth-abundant elements is urgently required in the field of solar energy conversion.

Great effort has been made to develop WOCs derived from first row transition metals. In 2008, Nocera and co-workers reported that electrodeposition of cobalt phosphate (Co-Pi) on conductive substrates gave highly efficient electrocatalysts for water oxidation [15]. This method has been extended to other metals, such as iron and nickel [16–23]. For example, electrochemical deposition of an oxide film from molecular complexes is a promising approach to fabricate active Ni-based WOCs [17,24,25]. Recently, Spiccia and co-workers reported a facile protocol for electrodeposition of a NiO<sub>x</sub> film from a nickel

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amine complex in borate buffer [24]. The film exhibited a steady current density of 1.8 mA/cm<sup>2</sup> at 1.3 V vs. NHE in borate buffer. More recently, Allen and co-workers reported that the combination of Ni<sup>2+</sup> and glycine could act as a precursor for an efficient nickel oxide electrocatalyst in phosphate buffer at pH = 11 [25]. However, the activity and durability of these catalysts needs to be improved. Here, inspired by this progress, we report a simple [Ni(en)<sub>3</sub>]Cl<sub>2</sub> (en = ethanediamine) complex for facile electrodeposition of a nickel oxide film in phosphate buffer solution. The resulting film is inert to corrosion and exhibits superior catalytic activity to other molecular complex-derived catalysts. A current density of 8.5 mA/cm<sup>2</sup> is maintained for at least 10 h at a constant applied potential of 1.3 V.

## 2. Experimental

### 2.1. Materials and methods

All of the chemicals were purchased from Aladdin Chemical Company and used without further purification. Deionized water (18.2 MΩ/cm) obtained from a Milli-Q system (Millipore, Direct-Q 3 UV) was used throughout. The phosphate buffer solution (0.25 mol/L, pH = 11) was prepared by dissolving appropriate amounts of Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O and Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O in deionized water. The [Ni(en)<sub>3</sub>]Cl<sub>2</sub> complex was prepared according to a reported procedure [26]. The fluorine-doped tin oxide (FTO) substrates were purchased from Dalian Heptachroma SolarTech Co., Ltd. (thickness ~2.2 mm, transmittance >90%, resistance ~8 mΩ). Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis were performed with a Nova NanoSEM 450 scanning electron microscopy. The SEM images and EDX spectra were obtained with acceleration voltages of 3 and 20 kV, respectively. The catalyst content on the surface of the working electrode (FTO) was determined by inductively coupled plasma mass spectrometry (ICP-MS, (Optima 2000DV, America PerkinElmer Co.). The sample used for ICP-MS was prepared by depositing the NiO<sub>x</sub> film on FTO with an applied bias of 1.2 V (vs. NHE). The sample was then gently rinsed with deionized water and dissolved in concentrated HNO<sub>3</sub>. The sample used for the measurement was diluted with water. X-ray photoelectron spectroscopy (XPS) was performed with a Thermo Scientific ESCALAB250 X-ray photoelectron spectrometer using 200 W K<sub>α</sub> radiation. The electrochemical measurements were recorded with a CHI 630D electrochemical potentiostat. The counter electrode was platinum wire. The reference electrode was an aqueous Ag/AgCl (3 mol/L NaCl) electrode. A glassy carbon electrode (diameter 3 mm) or FTO film was used as the working electrode. All of the potentials were measured against a Ag/AgCl reference and converted to the NHE by addition of 0.197 V to the measured potentials.

### 2.2. Fabrication of the catalyst film

The FTO substrates were ultrasonically cleaned in deionized water, ethanol, and acetone (30 min each), and then air-dried. The NiO<sub>x</sub> films for the water oxidation experiments were de-

posited by constant potential electrolysis (CPE) at 1.2 V (vs. NHE) using a solution of [Ni(en)<sub>3</sub>]Cl<sub>2</sub> (1 mmol/L) in phosphate buffer solution (0.25 mol/L). The films were then gently rinsed with deionized water and transferred to fresh 0.25 M phosphate buffer solution for anodization (1.3 V vs. NHE bias was applied for about 1.5 h).

### 2.3. Current–potential measurements for the Tafel plot

Current–potential data were obtained by performing controlled potential electrolysis in 0.25 mol/L phosphate buffer solution at pH = 11 with a variety of applied potentials. A FTO electrode (1 cm<sup>2</sup>) coated with a NiO<sub>x</sub> film (after anodization) was used as the working electrode. Ag/AgCl and Pt wire were used as the reference and counter electrodes, respectively. Before data collection, the solution resistance (35 Ω) was measured with a clean FTO working electrode using the potential loss for resistance (iR) test function to correct the Tafel plot for the iR drop. A catalyst film (1 cm<sup>2</sup>) was prepared by electrodeposition. Preconditioning the film by subjecting it to bulk electrolysis for several hours is necessary to obtain a reproducible Tafel slope value. A current density of 1.1 mA/cm<sup>2</sup> was applied for ~6 h before collecting data for the Tafel plot. The steady-state currents were measured at a variety of applied potentials while the solution was stirred. The Tafel plot measurements were performed in 10 mV steps between 0.88 and 0.97 V. In a typical experiment, the current reached a steady state at a particular potential in 3 min and the current values were recorded after 5 min. All of the measurements were performed twice. The obtained current values ranged from 22 μA/cm<sup>2</sup> to 1.84 mA/cm<sup>2</sup> in the applied potential range. The variation in the steady-state current of two runs at a particular potential was <5%. According to the current–potential data, the Tafel slope is 43 mV/decade.

### 2.4. Current–pH measurements

The current–pH data were collected by performing electrolysis at a fixed applied potential of 0.91 V (vs. NHE) in 0.25 mol/L phosphate buffer solution with a variety of pH values. A FTO electrode (1 cm<sup>2</sup>) coated with a NiO<sub>x</sub> film (after anodization) was used as the working electrode. Ag/AgCl and Pt wire were used as the reference and counter electrodes, respectively. The solution had an initial pH value of 10.4. The pH value gradually increased by adding small amounts of NaOH solution, and the current density was recorded after 5 min electrolysis at each pH value point. All of the data were collected with iR correction using a solution resistance value measured before each electrolysis. The pH values of the solution ranged from 10.4 to 11.6 and the measured currents ranged from 14 μA/cm<sup>2</sup> to 1.56 mA/cm<sup>2</sup>.

### 2.5. Determination of the faradaic efficiency

The faradaic efficiency measurements for oxygen evolution were performed in a gas-tight electrochemical cell. The cell was equipped with a FTO electrode coated with a NiO<sub>x</sub> film. Ag/AgCl

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