



Design and synthesis of Cu modified cobalt oxides with hollow polyhedral nanocages as efficient electrocatalytic and photocatalytic water oxidation catalysts



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ABSTRACT

Cobalt oxides have been modified with Cu using different methods to obtain the catalysts of Cu-ZIF-400 (copper-doped cobalt oxide), CuO/Co₃O₄ and Co₃O₄ with identical morphology of hollow polyhedral nanocages. These catalysts were investigated simultaneously for electrocatalytic and photocatalytic water oxidation for the first time. Among them, Cu-ZIF-400 can act as the best electrochemical water oxidation catalyst with a low oxygen evolution reaction (OER) overpotential of 342 mV at 10.0 mA cm⁻² in alkaline electrolyte. At the same time, a high turnover frequency (TOF) of $2.1 \times 10^{-3} \text{ s}^{-1}$ per metal atom was obtained over Cu-ZIF-400 at neutral conditions, which is comparable to those documented cobalt based catalysts. The different performances of catalysts can be attributed to the different doping methods. We hypothesize that the electrophilic Cu²⁺ makes the Co more electron-drawing and facilitates the nucleophilic addition of water, which enhanced OER activity of Cu-ZIF-400 catalyst.

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1. Introduction

The growing global energy requirement, combined with the consumption of fossil fuels and the related negative environmental influence, are boosting intense research into the pursuit and utilization of multitudinous types of sustainable and clean energy conversion technologies. Photo-driven and electricity-driven water splitting to generate hydrogen fuels and oxygen are regarded as the most promising and attractive strategies to accomplish the conversion from solar/electric energy to chemical energy. Therein, water oxidation is a rate-determining step ascribed to the inherent difficulties in multiple-electrons transfer and depressed kinetics of the oxygen evolution [1–5]. For this matter, the exploration of effective, stable and inexpensive oxygen evolution reaction (OER) photo/electrocatalyst is urgently requisite in order to facilitate the reaction, accelerate the evolution kinetics and thus meliorate the energy-conversion efficiency.

The first transition metal oxides as one kind of inexpensive, efficient and stable water oxidation catalysts (WOCs) have been widely studied [6–10]. Among them, Co₃O₄ catalyst with excellent water oxidation catalytic performance causes widespread interest [11–18]. So many factors can affect the catalyst performance such as morphology, particle size, crystallite structure, cation distribution and so on [19–21]. The influences of different modification methods are not explicit. Porous carbon supported-metal oxide hybrid nanomaterials with metal-organic frameworks (MOFs) as suitable precursors achieve the uniform distribution of metal oxide species on carbon matrix [22]. During the calcination of MOFs, the chemical decomposition of organic components and the forming process of metal oxide nanocrystals from metallic nuclei are thermally triggered and occur spontaneously. The reaction rate of these two processes is a vital factor affecting the final textural properties (e.g., pore size and morphologies) of the target metal oxide materials [23,24]. This strategy defends metal oxide nanoparticles from agglomeration, and thus inherits the high surface areas from MOFs that are extremely favorable to the photocatalytic and electrocatalytic performance for water oxidation.

Here, we reported a series of materials Cu-ZIF-*T* (Cu_{0.2}Co_{2.8}O₄), CuO/Co₃O₄ and Co₃O₄ with similar morphology of hollow polyhedral nanocages (HPNCs) to explore the influences of different modified methods on the catalytic performance for electrocatalytic and

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photocatalytic water oxidation reaction. Catalyst Cu-ZIF-400 with Cu^{2+} incorporated in Co_3O_4 crystal lattice and the catalyst $\text{CuO}/\text{Co}_3\text{O}_4$ with CuO loading on the Co_3O_4 performed better catalytic activities than Co_3O_4 in the water oxidation reaction. Moreover, the experimental results indicate that incorporation of Cu^{2+} into Co_3O_4 phase is a better approach to modify Co_3O_4 in order to obtain perfect activity. A low OER overpotential of 342 mV at 10.0 mA cm^{-2} in alkaline electrolyte (1 M KOH) and a high turnover frequency (TOF) of $2.1 \times 10^{-3} \text{ s}^{-1}$ per metal atom at neutral conditions were obtained over Cu-ZIF-400 for electrocatalytic and photocatalytic water oxidation, respectively. The superior stabilities of catalysts for electro/photocatalytic water oxidation were also investigated. At the same time, by varying the calcination temperature, the catalysts of Cu-ZIF-*T* showed distinguishable catalytic activities.

2. Experimental section

2.1. Materials and reagents

All chemicals were analytically pure and used without purification. Purified water ($18.25 \text{ M}\Omega\text{cm}$) for all experiments was obtained from a Molecular Lab Water Purifier.

2.2. Synthesis of Cu-ZIF-*T* hollow polyhedral nanocages

In total, the formation of Cu-ZIF-67 templates for the porous Cu-ZIF-*T* hollow polyhedral nanocages was as follows [25]. 5.0 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 5.0 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were dissolved in 100.0 mL of anhydrous ethanol (marked as A). 40 mmol of 2-methylimidazole was added into 100.0 mL of anhydrous ethanol (marked as B). Solution B was decanted slowly into solution A under stirring intensely to obtain a uniform solution. The uniform solution was refluxing for 8 h using water bath under constant stirring. After standing for 3 days in room temperature, the generated precipitation was collected by centrifugation and washed by anhydrous ethanol several times, and then dried in an oven at 60°C for 12 h. Then, the product was annealed at 350°C , 400°C , 450°C , 500°C for 2 h with the speed of $2^\circ\text{C}/\text{min}$ under air atmosphere to obtain the materials named Cu-ZIF-350, Cu-ZIF-400, Cu-ZIF-450, Cu-ZIF-500, respectively. This whole procedure is schematized in Fig. 1.

2.3. Synthesis of Co_3O_4 hollow polyhedral nanocages

Typically, 1.31 g (16.0 mmol) of 2-methylimidazole was dissolved in 100 mL methanol, and the solution was slowly poured into 100 mL methanol purple solution containing 0.996 g (4.0 mmol) of cobalt nitrate hexahydrate. After aged for 3 days, a purple solid was collected by centrifugation, washed with methanol several times and dried at room temperature.

Then, the Co_3O_4 was obtained by annealing the precursor ZIF-67 powder in air at 400°C for 2 h with a ramp rate of 2°C min^{-1} .

2.4. Synthesis of $\text{CuO}/\text{Co}_3\text{O}_4$ hollow polyhedral nanocages

For ZIF-67/Cu hydroxide (HD) [26], 1.2 g of ZIF-67 templates was first dispersed in 750 mL of ethanol, and 180 mg of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was added into the former solution and the obtained solution was refluxed for 3 h. ZIF-67/Cu HD was collected by centrifugation and finally dried at 60°C for 12 h. Then, the $\text{CuO}/\text{Co}_3\text{O}_4$ was obtained by annealing the as-obtained ZIF-67/Cu HD particles in air at 400°C for 2 h with a ramp rate of 2°C min^{-1} .

2.5. Material characterization

Thermogravimetric analysis (TGA) data were recorded on a NETZSCH STA 449F3 between 25 and 600°C , with a heating rate $10^\circ\text{C min}^{-1}$. Powder X-ray diffraction (PXRD) data were conducted on a PANalytical X'Pert Pro Diffractometer operating at a voltage of 40 kV and a current of 40 mA with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) from 5 to 90 degrees (2θ). Specific surface areas were calculated from the N_2 adsorption/desorption data obtained at 77 K (Micromeritics ASAP 2020 M system) using the BJH (Barrett–Joyner–Halenda) and BET methods. Field emission scanning electron microscopy (FESEM) observations were gathered on a Hitachi S-4800 microscope performing at an accelerating voltage of 20.0 kV. Transmission electron microscopy (TEM) images were collected with a JEOL JEM-2010 instrument operating at 200 kV. The GC–MS spectral analysis of isotope labeled O_2 was operated on an Agilent Series 7890A model chromatograph interfaced with an Agilent Series 5975C model mass spectrometer. X-ray photoelectron spectroscopy (XPS) spectra were acquired using an ESCALab220i-XL electron spectrometer.

2.6. Electrochemical water oxidation

All electrochemical experiments were performed using CHI760D Instrument Potentiostat at room temperature. The Ag/AgCl electrode (3 M KCl, 0.21 V vs NHE) was used as the reference electrode, Pt wire as the counter electrode, and glassy carbon electrode as the working electrode. An amount of 2.0 mg of catalysts was dispersed in the mixed solution of 1.0 mL of ethanol and 200 μL Nafion by sonication for 1 h. Then 10 μL of catalyst ink was dropwise added on a glassy carbon electrode (diameter 3 mm), which was then dried in air. Linear sweep voltammograms and cyclic voltammetric curves were measured at scan rates of 10 mV/s and 5 mV/s, respectively. For calculation of roughness factor (R_f) and electrochemically active surface area (ECSA), CV results were collected in 1.0 M KOH under different scan rates from 5 to 80 mV/s in the non-Faradaic region. The double-layer charging current (C_{dl}) is equal to the slope of the current density versus scan rate at 1.1804 V. Then, the electrochemically active surface area was determined by $\text{ECSA} = C_{dl}/C_s$, where C_s is typically $40 \mu\text{F}/\text{cm}^2$, represented the specific electrochemical double-layer capacitance of an atomically smooth surface. Furthermore, the roughness factor was calculated using the function of $R_f = \text{ECSA}/S_{\text{geo}}$, where S_{geo} is the geometric surface area (0.071 cm^2) of the GC electrode.

Electrochemical impedance spectroscopy measurements were acquired using an potential of 1.60 V in 1.0 M KOH solution on a CHI760E electrochemical workstation with an AC amplitude of 5 mV. The impedance spectra were performed in the frequency range from 100 kHz to 0.01 Hz. The data were further fitted to a specific equivalent circuit using ZSimpWin software to confirm the resistance of the electrodes. All data were not correct for Ohmic drop.

2.7. Photocatalytic water oxidation

Photocatalytic water oxidation was investigated using a dye-sensitized system consisted of 1 mM $[\text{Ru}(\text{bpy})_3]^{2+}$, 5 mM $\text{Na}_2\text{S}_2\text{O}_8$ and 0.2 g L^{-1} catalysts in 10 mL of phosphate buffer (pH 7.0, 100 mM). The prepared solution was deaerated with Ar gas for 10 min in a glass reactor (24 mL) sealed with a rubber stopper. The photocatalytic water oxidation reaction started with the irradiation to solution by a LED light source (light intensity 16 mW, and beam diameter 2 cm) through a glass filter ($\lambda \geq 420 \text{ nm}$) at room temperature. After each sampling instant, 100 μL of Ar was injected into the headspace of the bottle and then the same volume of the gas sample in the bottle was got out and then analyzed by

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