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One-step construction of porous Ni/Co metal/oxide nanocubes for highly efficient oxygen evolution

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ABSTRACT

A one-step method to synthesize porous Ni/Co metal/oxide as highly efficient oxygen evolution reaction (OER) catalysts is presented. Using Ni-Co Prussian blue analogue as both the precursor and the template, a simple oxidation in air at low temperatures results in the formation of Ni/Co metal/oxide nanocubes with fine particles. The optimized porous $NiCoO_x$-400 exhibits excellent OER activity with a low onset of 1.40 V (vs. RHE), an overpotential of 280 mV at 10 mA/cm^2 and a small Tafel slope of 74 mV/decade in 0.1 M KOH solution, significantly superior to those of the state-of-the-art noble-metal OER catalyst IrO_2/C. This approach offers the potential to generate highly active and low-cost OER catalysts on a large scale.

1. Introduction

Sustainable energy conversion and electrochemical energy storage techniques, such as water splitting, metal-air batteries and fuel cells, have been widely considered as next generation sustainable energy technologies that may ease the global energy crisis, due to their advantages of low environmental impact and excellent conversion efficiency and capacity [1–3]. Among these techniques, oxygen evolution reaction (OER) is one of the key electrode half reactions but it turns out to be the bottleneck for practical applications due to its sluggish kinetics of this reaction. Currently, noble metal Ir- and Ru-based materials are benchmarked OER catalysts which are, however, too expensive to allow their wide applications [4–6]. As a result, it is imperative to develop highly active and cost effective OER catalysts.

Among a variety of potential OER catalysts, earth-abundant Ni/Co oxides have drawn attention due to the large number of active centres and low cost. Single Ni and Co based transition metal oxides are regarded as low cost OER catalysts [7–9], but more and more researchers found that bimetal oxides may over-perform single metal oxides [10–12]. Ni/Co oxide can be generally chemically formed from their inorganic salts precursors such as metal carbonates, hydroxides, and so on [13–15]. Recently, it is reported that metallic Ni/Co or its combination with their oxides are excellent OER catalysts [16–18].

Metal-organic frameworks (MOFs) are a typical type of porous crystalline materials with easily tailorable structures. Early efforts have been devoted to exploring MOF-derived materials for electrochemical applications [19–24], and their performance can be significantly affected by the control of their morphology, topology and chemical composition [25–27]. As a special class of MOFs, Prussian blue analogues (PBA) are in the formula of $M_3^{II}[M^{III}(CN)_6]_2 \cdot nH_2O$ (where M stands for Fe, Ni, Co, etc.) and have been explored as versatile precursors to generate different metal hydroxides, sulfides or oxides with tunable nanostructures for various energy related applications [28–30]. However, additional chemicals such as NaOH [28] and Na_2S [29] or multi-step annealing treatments [30] were generally required to produce the target materials.

Herein, for the first time we report a simple one-step technique for the synthesis of Ni/Co oxide based nanocubes derived from PBA, and we further demonstrate that the resultant $NiCoO_x$ nanocubes are promising OER electrocatalysts with excellent electrochemical activity and stability.

2. Experimental

2.1. Synthesis of Ni-Co Prussian blue analogue nanocubes

Ni-Co Prussian blue analogue (PBA) nanocubes were synthesized by a modified literature method [29]. Typically, 1.35 mmol sodium citrate and 0.9 mmol nickel nitrate were dissolved in 30 mL deionized water. 0.6 mmol potassium hexacyanocobaltate was dissolved in another

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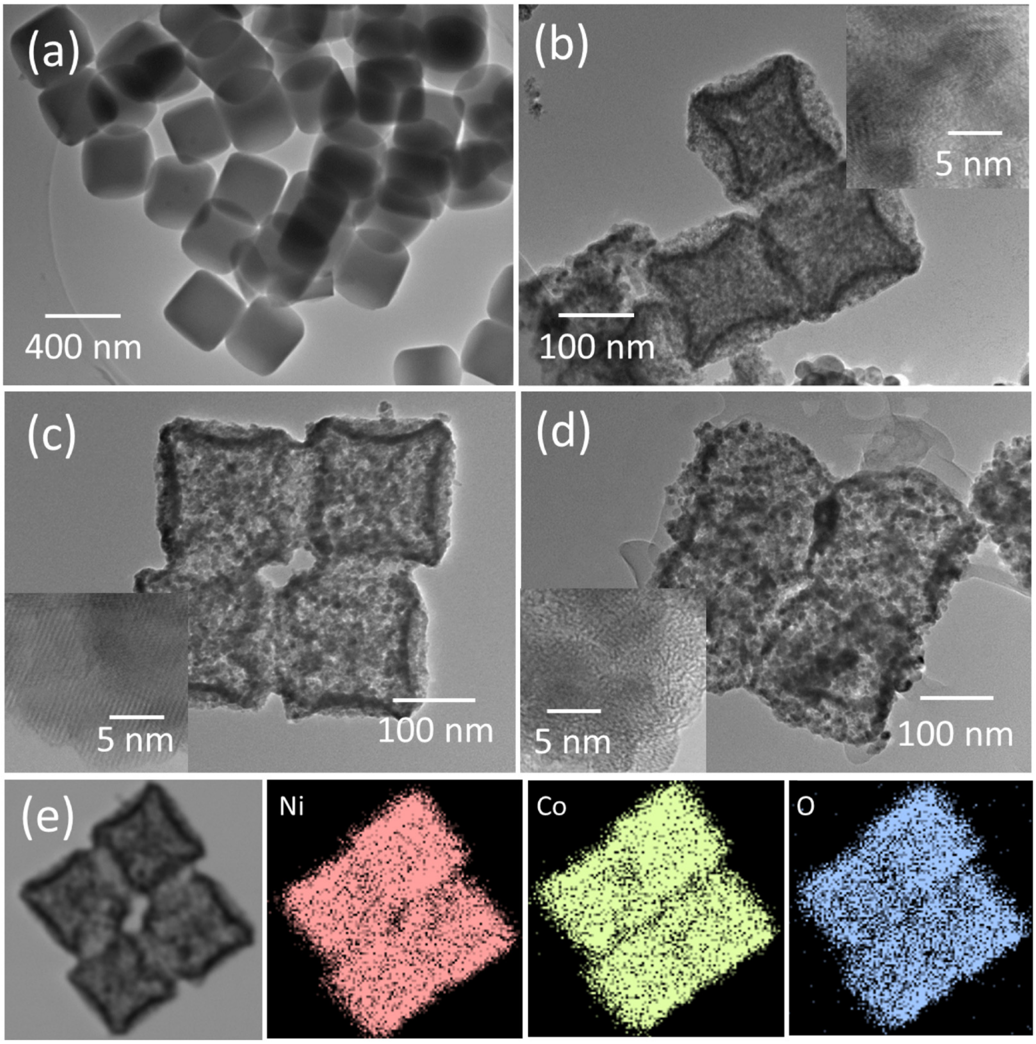

Fig. 1. TEM images of (a) Ni-Co PBA; (b) $NiCoO_x$-300; (c) $NiCoO_x$-400 and (d) $NiCoO_x$-500; insets are their corresponding high-magnification TEM images; and (e) elemental mappings of NiCoOx-400.

30 mL water. These two solutions were then mixed for 10 min under magnetic stirring. The mixed solution was aged at room temperature for 28 h. The Ni-Co Prussian blue analogue nanocubes were then collected by centrifugation, washing, and drying overnight.

2.2. Synthesis of Ni/Co metal/oxide complex polyhedral

Ni/Co metal/oxide complex polyhedral was prepared by a one-step thermal treatment of the as-prepared Ni-Co PBA. In a typical synthesis, Ni-Co PBA powders were evenly spread onto a ceramic boat, which was then transferred to the center of a flow-through tube furnace. The furnace was heated to the target temperature (300, 400, and 500 °C, respectively) in air atmosphere at a heating rate of 1 $°C\,min^{-1}$. The furnace temperature was kept at the target temperature for 1 h followed by cooled to room temperature naturally. The obtained black powders, (named as $NiCoO_x$-300, $NiCoO_x$-400, and $NiCoO_x$-500, respectively) were collected and ready for further characterizations and electrochemical measurements.

2.3. Materials characterization

X-ray diffraction (XRD) patterns were measured by a Bruker D8 advanced X-ray diffraction. X-ray photoelectron spectroscopy (XPS) was measured by a Kratos AXIS ULTRA spectrometer using a monochromated Al KR X-ray source (1486.6 eV) of 10 mA emission current and 15 kV anode potential. Transmission electron microscopy (TEM) images, elemental mapping, and diffraction pattern were all obtained by a JOEL-2100 at a 200 kV acceleration voltage. A Quantachrome Autosorb-iQ gas sorptometer was used to measure the N_2 gas sorptions of the materials.

2.4. Electrochemical tests

The electrocatalytic properties were measured by a three-electrode system in 0.1 M KOH aqueous solution using an electrochemical workstation (CHI 760D) coupled with a rotating disk electrode (RDE) system. A Ag/AgCl and a platinum wire was used as the reference electrode and counter electrode, respectively. A glassy carbon electrode (GCE) with a diameter of 3 mm covered by 5 μL catalyst ink was used as the working electrode. The catalyst ink was obtained by ultrasonically dispersing 1 mg catalyst into 0.5 mL 0.05 wt% Nafion alcohol solution. In this paper, the electrode potential reported is relative to the reversible hydrogen electrode (RHE) potential using the Nernst equation as follows:

$$E_{RHE} = E_{Ag/AgCl} + 0.059*pH + 0.197$$

Electrochemical impedance spectroscopy (EIS) was measured by using an AC voltage with amplitude of 5 mV in a frequency range from 100,000 to 0.1 Hz. The double-layer capacitance C_{dl} was determined by