



Co/CoO/C@B three-phase composite derived from ZIF67 modified with NaBH₄ solution as the electrocatalyst for efficient oxygen evolution

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ABSTRACT

Two kinds of three-phase composite materials, Co/Co(OH)₂/C@B directly from ZIF67 modified by NaBH₄ and Co/CoO/C@B through pyrolyzation of Co/Co(OH)₂/C@B material, are successfully synthesized and used as catalysts for the oxygen evolution reaction (OER). The structure and morphology are mainly characterized by X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), energy dispersive X-ray analysis (EDX), X-ray photoelectron spectroscopy (XPS). HBZ-1 sample with the structure of Co/Co(OH)₂/C@B has the best onset potential of 1.075 V vs. RHE at 0.1 mA cm⁻² and the best catalyst stability among all of the materials researched. Especially as its pyrolyzing product, the CBZ-1 sample with the structure of Co/CoO/C@B behaves the most excellent synthetically electrocatalytic performance with low onset potential of 1.444 V vs. RHE at 0.1 mA cm⁻² and a small overpotential of 390 mV at 10 mA cm⁻², which is better than that of RuO₂. This good catalytic activity is mainly attributed to the generation of CoO phase and synergistic effect of all the phases in the composite structure. Furthermore, the CBZ-1 sample has the appropriate catalytic stability which attributed to the three-phase structure of Co/CoO/C@B composite and the existing of a little B element.

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1. Introduction

The contradiction between the ever increasing energy needs and environmental pollution caused by fossil energy overuse is more and more prominent. Utilization of clean energy sources like solar and wind power worldwide can reduce our dependence on fossil fuels. However, due to the intermittence of these energy sources, efficient energy conversion and energy carrier are necessary for large scale applications of these kinds of energy forms. Hydrogen is an ideal energy carrier and the extensive application of hydrogen has already been realized through its efficient, low-cost, sustainable, and environmental-friendly production [1–4]. The water splitting by sunlight and electricity is found to be one of the very promising methods to produce hydrogen. However, the slow

kinetic process of oxygen evolution reaction (OER) restricts the energy efficiency and power consumption of the entire water splitting process [5,6]. To date, the noble-metal oxides such as IrO₂ and RuO₂ are known to be used as the best catalysts for the oxygen evolution reaction (OER) [7–9]. The large-scale application of noble metals is unrealistic due to scarce resources and high prices. A variety of earth-abundant, noble metal-free materials have been extensively investigated in recent years for OER catalysts, such as oxides, nitrides, borides, carbides, and so on [10–16]. Among them, the first-row transition-metal oxides and/or their carbon based composite materials [17–20] with high activity and durability may hopefully replace the noble-metal oxides. Especially, the cobalt (Co) based oxides and/or their carbonic composites have been most widely researched as the OER catalysts and behaved the excellent electrocatalytic performances. The group of Lu anchored crystalline Co₃O₄ densely and strongly onto mildly oxidized CNTs to obtain Co₃O₄/mMWCNT hybrid, which catalyses oxygen evolution reactions (OER) with an onset potential of 1.51 V vs. RHE and the overpotential only of 390 mV to achieve a current density of 10 mA cm⁻². The Co₃O₄/mMWCNT catalyst exhibits high Faraday efficiency (>99%) and long-term stability (>25 h) during bulk

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electrolysis of water [21]. The groups of Dou have shown that Graphene-like holey Co_3O_4 nanosheet, as a highly efficient OER catalyst, exhibits excellent OER catalytic performance with low onset potential of 0.617 V vs. Hg/HgO, high current density of 12.26 mA cm^{-2} at 0.8 V vs. Hg/HgO, and long-term stability with negligible fading in current density after 2000 cycles, significantly outperforming the performances of conventional Co_3O_4 nanostructures and commercial IrO_2 [22]. The group of Yang has synthesized highly acid-durable carbon coated Co_3O_4 nanoarrays as efficient oxygen evolution electrocatalysts. It is reported that the Co_3O_4 catalyst highly active toward the OER in 0.5 M H_2SO_4 has a small overpotential (370 mV) and can reach 10 mA cm^{-2} . The observed long life time for 86.8 h at a constant current density of 100 mA cm^{-2} , is among the best of the reported in literature so far, even longer than the state-of-art RuO_2 on CP [23]. The group of Xu has synthesized the carbon-encapsulated $\text{Co}_3\text{O}_4@/\text{CoO}/\text{Co}$ nano-composites for multifunctional applications in enhanced long-life lithium storage, super capacitor and oxygen evolution reaction [24]. In a word, the combination of cobalt oxide such as Co_3O_4 and carbon can improve conductivity, increase surface area and enhance cycling stability [25], and is a promising strategy for the development of next-generation of non-noble metal electrocatalyst for OER.

Metal organic frameworks (MOFs) materials, as a novel class of porous materials, have been given a lot of attentions because of their tunable structures controlled by modifying their own ligands, versatile functionalities, and attractive properties [26,27]. Further thermal treatment of MOFs can pyrolyze their carbon-containing ligands and result in the formation of carbon-coated metal or metal oxide nanoparticles [28,29]. Herein, it is very interesting that the cobalt-containing Metal-organic frameworks (MOFs) of ZIF67 mixed with NaBH_4 solution can transferred into a kind of $\text{Co}/\text{Co}(\text{OH})_2/\text{C}/\text{B}$ composite catalyst through hydrothermal reaction and another kind of $\text{Co}/\text{CoO}/\text{C}/\text{B}$ composite catalyst after further high temperature pyrolyzation. And the structures and electrocatalytic properties of two main composite catalysts are firstly discussed in this paper.

2. Experimental

2.1. Materials synthesis

ZIF67 (Zeolitic Imidazolate Frameworks) as a kind of excellent MOFs material was prepared by using a conventional synthesis method [30,31] at room temperature. In the typical synthesis, 5.997 mmol (1.745 mg) $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.0%, Tianjin Guangfu Technology Development Co. Ltd., Tianjin, China) and 21.786 mmol (1.789 mg) 2-dimethylimidazole(2-MIM, 99%, Aladdin) were respectively dissolved into 40 mL of solvent of ethanol and methanol (1:1, v/v) until they were completely dissolved. Then two kinds of solutions were mixed and thoroughly stirred for 30 min. The mixed solution was placed over there for 24 h at room temperature and then the solid product of ZIF67 synthesized was filtered and washed several times by ethanol and water. 100 mg of ZIF67 was dispersed in the 50 mL of solvent of ethanol and water (1:1, v/v). The certain quantity of NaBH_4 solution (6 mL, 2 M) was added into the ZIF67 dispersed solution in the ice water bath environment and then stirred for 2 min. The precursor solution was transferred into 250 mL Teflon-lined stainless steel autoclave. It was kept at 423 K in an isothermal oven for 7 h, yielding black composite. After cooling the autoclave to room temperature, the solid product was filtered and washed several times by ethanol and water. The product was then dried at 343 K in vacuum and the $\text{Co}/\text{Co}(\text{OH})_2/\text{C}/\text{B}$ composite was obtained and named as HBZ-1. Dried $\text{Co}/\text{Co}(\text{OH})_2/\text{C}/\text{B}$ composite was transferred to a ceramic boat, which was placed in a

quartz tube fixed in a tube furnace (3 KW, OTF-1200X-50, Ke Jing Materials Technology Co. Ltd., Hefei, China). And then the sample was pyrolyzed at 873 K for 3 h in continuous Argon flow of 120 mL min^{-1} . The product was denoted as the $\text{Co}/\text{CoO}/\text{C}/\text{B}$ composite catalyst and named as CBZ-1. In addition, through the change of the quantity of NaBH_4 solution addition (3 mL, 1 M), another contrast sample named as CBZ-2 was prepared well according to the above synthetic method.

2.2. Materials characterization

XRD (X-ray powder diffraction) patterns were recorded on a Philips 1830 diffract meter using Cu-K radiation source, 0.05 step size and 1s step in the 2θ ranges from 4 to 80° . The morphology was examined with field-emission scanning electron microscopy (FE-SEM, Hitachi, SU-8010) machine. Transmission electron microscopy (TEM) was performed on a JEM-2100F microscope at an accelerating voltage of 200 kV. An energy dispersive X-ray (EDX) instrument was attached to the TEM system. X-ray photoelectron spectroscopy (XPS) was performed on a K-Alpha spectrometer using an Al K α (1486.6 eV) photon source.

2.3. Electrochemical measurements

The electrochemical measurements were carried out in a conventional three electrode electrochemical cell with a platinum wire as the counter electrode, an Ag/AgCl (3 M KCl) electrode as the reference electrode, and an electrocatalyst modified glassy carbon electrode as the working electrodes, respectively. 4 mg catalytic material and 80 μL of 5 wt% Nafion solution were dispersed in 1 mL of ethanol. After ultrasonic bath for 15 min, 5 μL of suspensions were dropped onto glassy carbon electrode and dried at room temperature. The catalyst loading was $\sim 0.28 \text{ mg cm}^{-2}$ on glassy carbon electrode. For comparison, commercial RuO_2 modified electrode was prepared using the same method. The Electrochemical techniques, linear sweep voltammetry (LSV) and so on for the OER were performed using a PARSTAT[®]2273 instrument (Princeton Instruments, USA) in a standard three-electrode setup described above. For OER test in 0.1 M KOH solution, the corresponding LSVs were collected by sweeping from 0 V to 1 V vs. Ag/AgCl (3 M KCl) electrode and all the LSV curves were IR corrected. Stability was conducted at 1.6 V (vs. RHE). Electrochemical impedance spectroscopy (EIS) measurements were performed in 0.1 M KOH at 1.57 V (vs. RHE) within the frequency range of 100 kHz to 100 mHz. In this work, all of the potentials reported were calibrated to the reversible hydrogen electrode (RHE) using the following equation: $E(\text{vs. RHE}) = E(\text{Ag}/\text{AgCl}) + 0.197 \text{ V} + 0.059 \cdot \text{pH}$ [32]. Keeping a flow of O_2 over the electrolyte (0.1 M KOH) during electrochemical measurements could ensure the $\text{O}_2/\text{H}_2\text{O}$ approximately equal to the 1.23 V vs. RHE. The overpotential (η) was calculated by the following equation: $\eta = E(\text{vs. RHE}) - 1.23 \text{ V}$.

Electrochemical active surface area (ECSA) was represented by double-layer capacitance C_{dl} . The calculation of double-layer capacitance C_{dl} need to measure the capacitive current associated with double-layer charging from the scan-rate dependence of cyclic voltammetry (CV) among a potential window of 1.18–1.38 V vs. RHE and scan rates ranging from 10 to 100 mV s^{-1} . Then linear fitting of the charging current density differences ($\Delta j = j_a - j_c$ at the potential of 1.28 V vs. RHE) against the scan rate was done. The slope is twice of the double-layer capacitance C_{dl} .

3. Results and discussion

Fig. 1a shows the XRD patterns of the ZIF67 and HBZ-1 (HBZ-1 represents the $\text{Co}(\text{OH})_2/\text{Co}/\text{C}/\text{B}$ composite prepared through

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