Electrochimica Acta 292 (2018) 88–97

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Synthetic strategy and evaluation of hierarchical nanoporous NiO/NiCoP microspheres as efficient electrocatalysts for hydrogen evolution reaction

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A R T I C L E I N F O

Article history:
Received 1 May 2018
Received in revised form
14 August 2018
Accepted 24 September 2018
Available online 25 September 2018

Keywords:
Hydrogen evolution reaction
Hierarchical nanoporous
Synergistic effects
Non-precious metal catalyst
Transition metal oxide/phosphide

A B S T R A C T

The development of efficient hydrogen evolution reaction (HER) catalysts based on non-precious metal alternative to noble metal is significant for booming energy conversion/storage systems. Here, we report a facile strategy to design a novel hierarchical nanoporous (HNP) HER electrocatalyst by incorporating transition metal oxide (TMO) NiO and complex phosphide (TMP) NiCoP. With the HNP $NiCo_2O_4$ products via a facile solvothermal and annealing method, the NiO/NiCoP composite was easily obtained through a simple subsequent phosphorization process at the optimized temperature. Owing to various factors such as the strong synergetic coupling effects between TMO and TMP, electron interaction between TMPs, unique HNP structure features and increased active sites, the resulting HNP NiO/NiCoP composite demonstrated significantly enhanced electrocatalytic HER activities with a current density of 10 $mA cm^{-2}$ at a small overpotential of 112 mV, a low Tafel slope of about 56 mV dec^{-1} and satisfactory stability. We expect that this facile synthetic strategy of active binary TMPs functionalized hierarchical porous TMOs will provide a promising prospect for the development of non-precious HER electrocatalysts.

1. Introduction

Due to abundant sources and sustainability as well as high energy density and no carbon emissions, hydrogen has been deemed to be a viable alternative to huge consumption of fossil fuels [1,2]. As a flexible and efficient means, electrocatalytic water splitting for highly pure hydrogen production has been extensively studied in recent years [3,4]. However, the low energy efficiency and sluggish kinetics of hydrogen evolution reaction (HER) on the cathode lead to a huge reaction overpotential, which are existing problems and urgently needed to be solved. In the view of reducing HER overpotential, precious metal Pt, Ru and Pd are often adopted ideal materials [5–7], but the expensive prices and scarcity have severely restrained their extensive applications. To this end, the design of low-cost, highly active, and durable HER electrocatalysts becomes a crucial research field.

Over the past decades, earth-abundant transition metal oxides have attracted considerable attention in the HER field due to low-cost, high stability and nontoxicity [8–11], but their poor intrinsic conductivity is still a nonnegligible drawback that limits their electrocatalytic activities. Up to now, more innovative HER catalysts based other transition metal compounds including sulfides, nitrides, carbides, phosphides and borides have been further exploited [12–15]. Especially, various transition metal phosphides (TMPs) own hydrogenase-like catalytic activity, good conductive structure effect and expected stability [15–17], which have been demonstrated as efficient HER catalysts in last few years [16–22]. It has been experimentally observed that TMO/TMP composite could also synergistically enhance electrocatalysis [23,24] and needs further development.

As the typical TMPs, nickel phosphides and cobalt phosphides are both highly active HER catalysts, which showed efficient electron density transfer between transition metal atoms and phosphorus (P) atoms [25–27] and thus facilitating electrochemical dehydrogenation in the subsequent HER [26–28]. Nevertheless, valence electron transfer from one kind of TMP only produced single anionic active site, which resulted in low-efficiency proton exchange during HER process. However, a few recent researches

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https://doi.org/10.1016/j.electacta.2018.09.159

have suggested that the strong electron interactions between binary TMPs could provide co-mediating active sites, which will be conducive to improving HER performance [25,29,30].

Furthermore, the optimization of morphology is also a valid strategy to accelerating HER rate [31]. Recently, micro/nano-porous materials have provided new opportunities for the innovation of electrocatalysts due to enlarged specific surface area for mass/charge transfer and other meaningful properties such as nano-confinement effect, ion-selective impedance, discriminative electrokinetics, electrical double layer overlapping, etc [28,32,33]. Especially, studies have indicated that two-dimensional porous nanosheets exhibited incredible properties due to their remarkable features such as lightweight, efficiently utilizing interior voids, and shortening diffusion lengths, which promoted the feasibility of exposed active sites and thus further enhanced the catalytic activities [15,34,35].

In light of the attractive properties of TMO/TMP composite, binary complex TMPs and micro/nano porous structure, we sought to develop a novel synthetic strategy to incorporate nano-TMO and binary complex NiCo phosphide into the micro/nano-porous hierarchical composite structures, which would be a promising approach to enhance the electrocatalytic properties for hydrogen evolution reaction. In this work, upon a simple phase conversion by phosphatizing spinel hierarchical nanosheet-assembled porous (HNP) $NiCo_2O_4$ at the optimized temperature, a highly-efficient HER electrocatalyst, NiO/NiCoP composite, has been successfully prepared. Due to stable HNP structure, synergistic effects, strong electron interactions and enriched active sites, the as-prepared NiO/NiCoP composite has exhibited with performance HER activities in an alkaline electrolyte with relatively positive onset overpotential, small Tafel slope, low interfacial reaction resistance, good mass transfer and conduction properties and long-term stability.

2. Experimental

2.1. Reagent

Cobalt acetate ($Co(AC)_2$), nickel acetate ($Ni(AC)_2$), polyvinylpyrrolidone (PVP, K30), sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$), ethylene glycol, ethyl alcohol and potassium hydroxide (KOH) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) with analytical grade, while 5 wt% Nafion ethanol solution from Sigma. Millipore ultrapure water was used to prepare the solution and wash the samples throughout the experiments.

2.2. Synthesis of HNP NiO/NiCoP

Firstly, two-step sequential operation was conducted to fabricate the HNP $NiCo_2O_4$. Briefly, 0.999 g $Ni(AC)_2$, 2 g $Co(AC)_2$ and 0.05 g PVP were added in 80 ml mixed solution with 79 ml ethylene glycol and 1 ml Millipore water. After the magnetic stirring for 30 min, the formative deep purple mixed solution was sealed in a 100 mL Teflon-lined autoclave, heated at 180 °C for 12 h and then naturally cooled down to room temperature. The precipitate samples were collected by centrifugation, washed with water and ethanol seven times, and dried at 60 °C for 12 h in an oven. The NiCo-containing precursors were finally calcined at 300 °C in air for 2 h. For comparison, HNP Co_3O_4 and HNP NiO were also prepared with the similar synthetic method.

For the synthesis of HNP NiO/NiCoP composite, the $NaH_2PO_2 \cdot H_2O$ crystalline powder and HNP $NiCo_2O_4$ samples were placed at the two separate positions of the tube furnace while the $NaH_2PO_2 \cdot H_2O$ near Ar inlet of the furnace. The molar ratio of transition element (Ni and Co) to P is 1:5. The furnace was heated in a high-purity Ar atmosphere to 300 °C with a slow heating rate of 2 °C min^{-1}, maintained at this temperature for 2 h, and then naturally cooled down to room temperature. On the other hand, NiCo-containing precursors, HNP Co_3O_4 and HNP NiO were phosphatized under these operating conditions. In order to investigate the effects of phosphorization temperature on the crystalline phase, element composition and morphology, HNP $NiCo_2O_4$ samples were also phosphatized by heating to 300 °C (immediately aborted), 250 °C for 2 h, 300 °C for 2 h, and 350 °C for 2 h, respectively.

2.3. Instruments and characterization

Composition and crystalline of the prepared samples were analyzed by a D8 ADVANCE X-ray diffractometer (XRD, German Bruker). Surface morphology images were taken on a Merlin Compact scanning electron microscope (SEM, Carl ZEISS), and the elemental composition measurement was performed with an attached Oxford energy dispersive X-ray (EDX) spectrometer. High-resolution transmission electron microscope (HRTEM) images and selected area electron diffraction (SAED) pattern were obtained on a JEOL 2100 TEM system. Surface composition and valence state of elements were investigated by a K-Alpha 1063 X-ray photoelectron spectrometer (XPS).

2.4. Electrode modification and measurements

Electrochemical measurements of as-prepared samples were operated on a CHI 660E electrochemical workstation (Chenhua Instruments, Shanghai) with a typical three-electrode system (including a piece of Pt foil as counter electrode, a saturated calomel electrode (SCE) as reference electrode and the sample modified glassy carbon electrode (GCE, 3 mm in diameter) as working electrode), while 1 M KOH aqueous solution as the supporting electrolyte. The modification of work electrode is described below: 5 mg catalyst samples, 1 mg carbon powder (Cabot Vulcan XC-72) and 40 μl 5 wt% Nafion ethanol solution were added in a mixed solution (containing 768 μl Millipore water and 192 μl ethyl alcohol) and then sonicated over 45 min; 5 μl formed catalyst ink was dropped on a polished GCE and naturally dried in the air. According to the Nernst equation: $E_{RHE} = E_{SCE} + E^{\ominus}_{SCE} + 0.059$ pH, all potentials in this work were converted to reversible hydrogen electrode (RHE) potential, where E_{RHE} is the converted potential vs. RHE, E_{SCE} is the experimentally applied potential against SCE, and $E^{\ominus}_{SCE} = 0.245$ V at 25 °C [33,36]. Linear sweep voltammetry at a scan rate of 2 mV s^{-1} was conducted, and the potential data are compensated according to the equation ($E_{compensated} = E_{applied} - IR_s$), since the potential difference of solution resistance (R_s) should usually be eliminated [23,24]. The value of R_s was obtained from the electrochemical impedance spectroscopy (EIS) measurement. EIS was measured from 100 kHz to 0.01 Hz at −0.2 V (vs RHE) with an amplitude of 5 mV. In order to evaluate the double layer capacitance of the as-prepared catalysts, cyclic voltammetry curves were measured at the different scanning rates of 20, 40, 60, 80, 100, 120 and 140 mV s^{-1}. All electrochemical experiments were operated at room temperature.

3. Results and discussion

3.1. The formative process of HNP NiO/NiCoP

As illustrated in Scheme 1, initially, the generated NiCo glycolate colloids through the chelation from Ni^{2+} ions and Co^{2+} ions dissolved in EG solution were derived to quickly oriented attachment of nanosheets under the appropriate viscosity of the EG/water solvent [37,38]; By the interaction of PVP, the formative nanosheets then self-assembled into irregular microsphere structures [39].