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Full Length Article

Facile synthesis of Fe-doped Co_9S_8 nano-microspheres grown on nickel foam for efficient oxygen evolution reaction

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ABSTRACT

Cobalt sulfides have drawn enormous attention as earth-abundant alternatives to precious-metal electrocatalysts capable of catalyzing oxygen evolution reaction (OER) in alkaline medium. Although significant progresses have been realized in the development of various composite modulation to improve their properties for oxygen evolution, to boost their poor catalytic activity for oxygen evolution reaction is still challenging, which unambiguously limits the wide utilization of cobalt sulfides. Here, we present the facile growth of metal-doping (Fe, Ni) into Co_9S_8 supported on nickle foam (NF) through a one-step simple hydrothermal process. The effect of (Fe, Ni)-doping on the morphology and the catalytic activity of Co_9S_8 has been thoroughly investigated. Fe-Co_9S_8 nano-microspheres supported on NF (Fe-Co_9S_8 NM/NF) have been obtained with the remarkable electrocatalytic activity, which only requires a lower overpotential of 270 mV to reach a current density of 10 mA cm^{-2} and exhibits the smaller Tafel slope of 70 mV dec^{-1} as well as robust stability. The excellent OER performance of Fe-Co_9S_8 NM/NF could be attributed to the synergistic interaction of Fe dopants with Co_9S_8 nano-microspheres and faster charge transfer rate derived from NF support. This work provides a new and effective way to design metal-doped Co_9S_8-based heterostructures supported on conductive support as efficient OER electrocatalysts.

1. Introduction

The problem of global energy shortage and sustainable economic development have greatly stimulated comprehensive study on contamination free, zero carbon emissions and the renewable energies, such as the solar energy, wind power, water splitting batteries and rechargeable metal-air cells [1–3]. However, major renewable energies are discontinuous, seasonal and regional with significant variability in the course of utilization [4]. This instability in energy utilization could be solved by connecting regional energy storage to the electricity producing equipment [5]. Because of the water abundantly existing in the earth and with low-carbon emissions, an efficient and novel technology of water electrolysis applied to separate out O_2 and H_2 ($2H_2O \rightarrow 2H_2 + O_2$) is considered as a promising approach to deal with the environmental pollution issue and the crisis of energy shortage [6–10]. The anodic OER that is the half-reaction of water splitting with sluggish reaction rate due to its intricate four electrons transfer with high overpotentials, which seriously impeded the entire conversion efficiency of the water splitting [11–13]. As we all know, RuO_2 is the standard catalyst for OER, but the low output and high cost of the noble metal extremely impedes its large-scale applications. Therefore, it is of vital importance to exploit non-noble metal based electrocatalyst with remarkable activity and extraordinary stability to decrease the overpotential for water oxidation electrolysis and promote the OER kinetics [14–18].

In recent years, non-noble transition-metal (Fe, Co, Mo, Ni, V, W and so on) based sulfides (TMSs) are demonstrated as the ideal electrocatalysts to catalyze water splitting in alkaline electrolytes [19,20]. Especially for the Co_9S_8, several researchers have concentrated on investigating the diversified morphologies of Co_9S_8, such as metallic nanoflakes, hollow cubes, nanocages, branch arrays and so on [21–24]. Moreover, the metal doping catalytic material without any structure change has been a significant strategy to enhance the conductivity and generate the synergistic effect among the diverse ions [25–27]. The doping of nontoxic and inexpensive elements of Fe can expose numerous electrochemically active sites for OER and further perfect the catalytic activity [27,28]. Therefore, the enhanced OER performance of Co_9S_8-based materials can be realized through metal doping, which can promote the synergistic effect among ions and further improve catalytic activity [16,29–31]. However, limited by the uncontrolled morphology

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and doped ratio of binary metal, developing the unique metal-doped Co_9S_8 nanostructures still remains a challenge [32,33].

Herein, we report an efficient and straightforward hydrothermal method to prepare the Fe-doped Co_9S_8 nano-microspheres loaded on NF. The Ni-Co_9S_8 NM/NF has been synthesized as a convincing contrastive sample to reveal the effect of Ni and Fe for the nanostructure and catalytic activity of Co_9S_8. NiS_x/NF and Co_9S_8 NM/NF have been fabricated to confirm the synthetic effect between Fe and Co_9S_8 for catalytic activity. The resulting electrochemical measurements demonstrate that the Fe cluster-coupled with Co_9S_8 possess excellent electrocatalytic activities for oxygen evolution reaction along with lower overpotential, smaller Tafel slope and charge-transfer resistance than those of Co_9S_8 NM/NF, NiS_x/NF and Ni-Co_9S_8 NM/NF. The spherical-like nanostructures of the binary metal composition (Fe-Co_9S_8 NM/NF) has been regarded as one of the most promising candidates to substitute the noble metal catalysts due to its impressing catalytic activity and long-term stability for OER in alkaline medium.

2. Experimental

All materials and chemical reagent were purchased from the Sinopharm group or Aladdin and used without any further purification. All the chemicals including cobalt(II) acetate tetrahydrate ($Co(CH_3COO)_2{\cdot}4H_2O$), nickel acetate tetrahydrate ($Ni(CH_3COO)_2{\cdot}4H_2O$), thioacetamide (TAA, CH_3CSNH_2), glutathione (GSH), iron (II) acetate tetrahydrate ($Fe(CH_3COO)_2{\cdot}4H_2O$), deionized water (resistivity: ~18.5 MΩ cm), and 1.0 M KOH (PH: ~13.8) solution were used as electrolyte solutions.

Prior to the following experiment, three pieces of nickel foams (NF, 1 × 2 cm, surface density: 350 g m^{-2} and the thickness: 1.01 mm) were washed by sonication in dilute hydrochloric acid, acetone and absolute ethanol for 30 min consecutively, then dried in 60 °C under the vacuum conditions for 4 h.

In the typical synthesis, 2 mmol Cobalt(II) acetate tetrahydrate and 2 mmol thioacetamide were dissolved in 60 mL deionized water under intensely stirring at indoor temperature for about 20 min. And then 0.08 g glutathione was added into the hybrid homogenous solution under mightily stirring for 5 min. Then the brown hybrid solution was transferred in 100 mL Teflon-lined autoclave added with three slices of pre-treated NF and heated at 140 °C for 12 h. Finally, the sealed autoclave was cooled to indoor temperature in naturally. The obtained product was thoroughly washed with deionized water and absolute ethanol for several times, respectively. And the sample was dried in 60 °C under the vacuum conditions for 6 h, which were donated as Co_9S_8 NM/NF.

In order to fabricate the sample of Fe-Co_9S_8 NM/NF, 2 mmol Cobalt (II) acetate tetrahydrate, 2 mmol thioacetamide and 2 mmol iron (II) acetate tetrahydrate were dissolved in 60 mL deionized water under intensely stirring at indoor temperature for about 20 min. And then 0.08 g glutathione was added into the hybrid homogenous solution under mightily stirring for 5 min. Then the hybrid solution was transferred in 100 mL Teflon-lined autoclave added with three slices of pretreated NF and heated at 140 °C for 12 h. Finally, the sealed autoclave was cooled to indoor temperature in naturally. The obtained product was thoroughly washed with deionized water and absolute ethanol for several times, respectively. And the sample was dried in 60 °C under the vacuum conditions for 6 h.

The synthetic procedure for the compound of Ni-Co_9S_8 NM/NF is analogical to that for the synthesis of Fe-Co_9S_8 NM/NF. The differences between them lie in replacing iron (II) acetate tetrahydrate with nickel acetate tetrahydrate. And the synthetic procedure for the compound of NiS_x/NF is analogical to that for the synthesis of Co_9S_8 NM/NF without adding Cobalt (II) acetate tetrahydrate. The approximately estimated loading mass of Co_9S_8 NM/NF, Fe-Co_9S_8 NM/NF, Ni-Co_9S_8 NM/NF and NiS_x/NF on NF is 2.83, 3.32, 3.84 and 1.06 mg cm^{-2}, respectively.

The powder X-ray diffraction (XRD, X'Pert PRO MPD, Cu KR) patterns was recorded on 2θ range from 5° to 70° to explore the crystalline structure of the as-prepared samples. The X-ray photoelectron spectroscopy (XPS, VG ESCALAB MK II, the spectrometer with Al Ka of 1486.6 eV as a photon source) was carried out to authenticate the valence states of the elements of as-prepared specimen. Energy dispersive X-ray fluorescence spectrometer analysis (EDX) was taken advantage of the representative areas to identify the dominating elements on the surface of as-prepared samples. The scanning electron microscope (SEM, Hitachi, S-4800) images were used to explore the morphology of as-prepared specimen. The transmission electron microscope (TEM) and the high-resolution transmission electron microscopy (HRTEM) were used to explore the morphology and crystal structure of sample.

All the electrochemical measurements were executed through a standard three-electrode setup (Gamry Reference 600 Instruments, USA), in which all the as-prepared specimens were used as the working electrodes, a saturated calomel electrode (SCE) and the Pt plate was used as the reference electrode and counter electrode, respectively. 1 M KOH solution was utilized as the electrolyte solutions (degassed by O_2 continuously in advance to kept saturation). Linear sweep voltammetry (LSV) was carried out with a scan rate of 5 mV s^{-1} and conducted from 0 to 0.7 V (vs. SCE). The electrochemical impedance spectroscopy (EIS) measurements were maintained at 0.44 V (vs. SCE) with frequency from 10^5 Hz to 0.01 Hz with an AC voltage amplitude of 5 mV. The long-term stability of the as-prepared Fe-Co_9S_8 NM/NF was employed by the chronoamperometry (CA) at 0.46 V (vs. SCE) in 36000 s and the consecutive cyclic voltammetry (CV) obtained specimen from 0.42 V to 0.52 V (vs. SCE) for 10,000 circles at the scan rate of 100 mV s^{-1}. All the electrochemical data were iR corrected automatically on Gamry Framework.

The conversion of potentials from vs. SCE to vs. RHE is on the basis of the following equation: E (vs. RHE) = E (vs. SCE) + 0.244 V + (0.059 V) pH.

3. Results and discussion

The schematic illustration of synthesis process is shown in Fig. 1. In the synthesis, the NiS_x/NF with irregular surface, Ni-Co_9S_8 NM/NF with hill-shaped bulges morphology and Co_9S_8 NM/NF, Fe-Co_9S_8 NM/NF nanospheres are obtained through a facile hydrothermal process. Typically, the doping of Fe into Co_9S_8 could significantly improve electrocatalytic activity of Co_9S_8 NM/NF without changing its unique nanosphere morphology. To the contrary, after doping Ni into Co_9S_8, the spherical nanostructure of Co_9S_8 is totally destroyed. Therefore, the effect of doping Ni and Fe into Co_9S_8 for morphology and activity of Co_9S_8 is thoroughly investigated. Besides, the synthetic effect between Fe and Co_9S_8 for oxygen evolution is also confirmed by comparing the electrochemical measurement results.

XRD diffraction patterns of Co_9S_8 NM/NF, Fe-Co_9S_8 NM/NF, Ni-Co_9S_8 NM/NF, blank NF and NiS_x/NF are shown in Figs. 2 and S1. The distinct diffraction peaks of four as-prepared samples approximated at 44.8°, 52.2° and 76.8° corresponds to (1 1 1), (2 0 0), (2 2 0) crystal planes of metallic NF substrate (PDF No. 00-003-1051), respectively. And the dominating diffraction peaks of Co_9S_8 NM/NF, Fe-Co_9S_8 NM/NF and Ni-Co_9S_8 NM/NF at about 31.1°, 36.8° and 47.5° belongs to the (3 1 1), (3 3 1), (4 4 0) crystal planes of Co_9S_8 (PDF No. 03-065-6801), respectively. Because that all samples are synthesized by hydrothermal sulfuration reaction, all the as-prepared samples contain NiS (PDF No. 00-001-1286) crystal phase, which can be attributed to the partial sulfurization of NF substrate. It should be noted that the XRD patterns of Fe-Co_9S_8 NM/NF shows no peaks of iron, which imply its amorphous characteristic in Fe-Co_9S_8 NM/NF.

The surface elemental compositions and chemical valence state of Fe-Co_9S_8 NM/NF have been investigated by the X-ray photoelectron spectroscopy (XPS), as shown in Fig. 3. The XPS survey spectrum in Fig. 3a further demonstrates the presence of Co, Fe, Ni and S in the as-prepared sample. The existences of O signal peak may be attributed to