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Full Length Article

Hierarchical Ni_3S_2-NiOOH hetero-nanocomposite grown on nickel foam as a noble-metal-free electrocatalyst for hydrogen evolution reaction in alkaline electrolyte

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ABSTRACT

It is a challenge to explore inexpensive noble-metal-free catalysts with long-term stability at low overpotential for water electrolysis to produce hydrogen. Herein, we constructed hierarchical Ni_3S_2-NiOOH hetero-nanocomposite on nickel foam (NF@Ni_3S_2-NiOOH) through a two-step hydrothermal and electrodeposition method. The as-prepared NF@Ni_3S_2-NiOOH catalyst was capable of catalyzing hydrogen evolution reaction effectively with a low overpotential of 160 mV at a current density of 10 mA/cm^2 in 1.0 M NaOH, and maintained excellent performance for 45 h without obvious attenuation.

1. Introduction

Water splitting with complex electrochemical processes is recognized as a promising strategy for generating hydrogen, which is considered as an ideal objective for sustainable energy. Water splitting consists of two half reactions, namely hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) [1–3]. Electrocatalysts play significant role in decreasing the overpotentials of reactions, which enhance the electrolysis efficiency. So far, the developed HER catalysts are typically used under acidic conditions, while OER is usually carried out in alkaline media. Furthermore, the equipment of electrolysis is hard to work steadily for long time under acidic environments. As we know by now, noble metal catalysts (such as platinum and palladium) possess high activity for HER, however, they are severe exiguity and high cost, which hinders their large-scale commercial application [4–6]. Consequently, it is highly desirable to develop efficient and cheap noble-metal-free electrocatalysts in alkaline media [7–10].

In recent years, noble-metal-free catalysts based on Co [11–14], Ni [15–19], Fe [20–22], were intensively studied as HER catalyst due to their earth-abundance, low cost, and high catalytic activities. Wu et al. fabricated nitrogen-anion decorated Ni_3S_2 (N-Ni_3S_2) directly grown on nickel foam (NF), which exhibited a low overpotential (110 mV) at 10 mA/cm^2 and a stability period of 8 h tests at 20 mA/cm^2 [23]. Zhang et al. synthesized NiS_2 nanostructure film on carbon fiber through a vapor-phase hydrothermal route, which displayed an overpotential (210 mV) at 10 mA/cm^2 and a stability period of 13 h [24]. Nevertheless, these non-noble metal catalysts still have many challenges, such as low efficiency and poor stability.

Great efforts have been devoted to enhance the HER catalytic activity by designing nanostructure, controlling heterogeneous composite as well as metal-doping [25–28]. In particular, three-dimensional (3D) NF has attracted much attention, not only owing to its intrinsic characters (such as superior conductivity, porosity, flexible and self-supported electrode), but also its function as flexible matrix for fabricating hierarchical nanostructures [29–31]. Numerous Ni-based catalysts have been introduced into 3D NF, including oxides, sulfides, hydroxides and diselenides [32–36]. On the other hand, hierarchical hetero-nanocomposites demonstrate a synergistic effect for improving the catalytic performance for HER [37]. Although the above strategies have been proved to be effective, the hierarchical Ni-based hetero-nanocomposite on 3D NF with long-term stability (especially more than 40 h) is still urgently demanded.

In this contribution, we reported hierarchical Ni_3S_2-NiOOH hetero-nanocomposite on nickel foam (NF@Ni_3S_2-NiOOH) through a two-step hydrothermal and electrodeposition method for efficient HER. The obtained NF@Ni_3S_2-NiOOH catalyst demonstrates superior HER performance with a overpotential of 160 mV when the current density was 10 mA/cm^2 in 1.0 M NaOH and maintained excellent

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performance over 45 h without obvious attenuation. Furthermore, the relationship between the intrinsic characters of NF@Ni_3S_2-NiOOH and the electrocatalytic properties for HER were also discussed in detail.

2. Experimental

2.1. Materials and chemicals

All chemicals and materials, including NF, sodium sulfide (Na_2S, 99.0%), sodium tetraborate (pH 9.18), hydrochloric acid (HCl) and sodium hydroxide (NaOH, 85.0%), were purchased from Aladdin Corporation and used without further purification. All aqueous solutions were prepared with Milli-Q water (18 MΩ cm).

2.2. Synthesis of NF@Ni_3S_2-NiOOH

The NF substrates were cut into 1 cm × 2 cm squares, which were cleaned by ultrasonication successively in acetone for 10 min to remove organic impurities, 6 M HCl for 10 min to remove surface oxide layer, water sequentially and finally dried at 60 °C for 10 min. The treated NF was placed vertically in a reaction kettle containing 0.3 M Na_2S aqueous, and the reaction was carried out at 120 °C for 10 h to form NF@Ni_3S_2.

After hydrothermal reaction, the NF@Ni_3S_2 was taken out and washed by water. Electrodeposition of NiOOH nanoparticles onto the NF@Ni_3S_2 (NF@Ni_3S_2-NiOOH) was carried out in a three-electrode cell in borate buffer (pH 9.18), with NF@Ni_3S_2 as working electrode, Pt plate as counter electrode and Ag/AgCl electrode as reference electrode. As a control, NF@NiOOH was prepared by the same method except that NF was used as the working electrode.

2.3. Characterizations

Scanning electron microscopic (SEM, Hitachi 4800) images and energy dispersive spectroscopy (EDS, FEI) analyses were obtained using Nova NanoSEM 450 instrument. X-ray diffraction (XRD, Rig-aku) results were examined on a D/tex-Ultima TV wide angle X-ray diffractometer equipped with Cu Kα radiation (λ = 0.154 nm). X-ray photoelectron spectra (XPS) were performed with an ESCALAB MARK II spherical analyzer using an aluminum anode (Al 1486.6 eV) X-ray source.

2.4. Electrochemical measurements

All electrochemical measurements were performed using a standard three-electrode electrochemical system controlled by AUTOLAB PGSTAT302N electrochemical workstation (Metrohm, Switzerland) in 1.0 M NaOH aqueous solution at room temperature. The as-prepared NF@Ni_3S_2 or NF@Ni_3S_2-NiOOH was used as working electrodes directly. A platinum plate and Ag/AgCl electrode was used as counter and reference electrode, respectively. The electrochemical activities of samples toward HER were examined by linear sweep voltammetry (LSV) at room temperature with a scan rate of 5 mV/s. The stability of NF@Ni_3S_2-NiOOH electrode was performed by amperometric i-t curve. The electrochemical impedance spectroscopy (EIS) measurements of samples were carried out in the same configuration from 10^6 to 0.01 Hz with an AC voltage of 5 mV. All potentials reported in this work were calibrated as reversible hydrogen electrodes (RHE) according to the Nernst equation ($E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059 \times pH$).

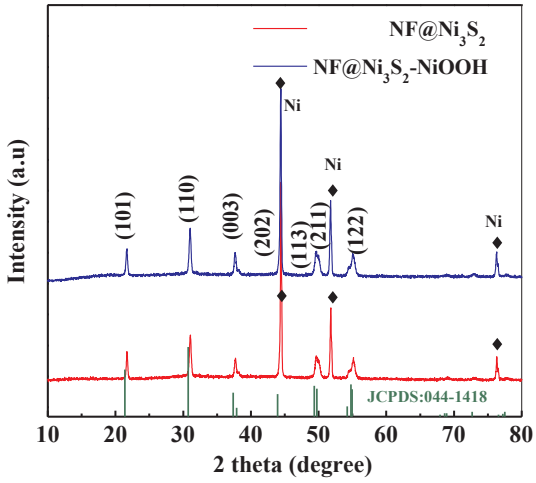

Fig. 1. XRD patterns of NF@Ni_3S_2 and NF@Ni_3S_2-NiOOH as well as the standard XRD pattern of Ni_3S_2.

3. Results and discussion

3.1. Preparation and characterizations of NF@Ni_3S_2 and NF@Ni_3S_2-NiOOH

The hierarchical NF@Ni_3S_2-NiOOH hetero-nanocomposite was prepared through a two-step hydrothermal and electrodeposition method. Firstly, Ni_3S_2 nano-trees directly grew on NF (NF@Ni_3S_2) was obtained by hydrothermal route in 0.3 M Na_2S solution using the NF as Ni resource. Then, the Ni_3S_2 nano-trees were covered with an amorphous NiOOH component after electrodeposition process.

The crystalline structure of NF@Ni_3S_2 and NF@Ni_3S_2-NiOOH was examined by XRD. The two patterns share similarly diffraction peaks at 2θ = 21.7°, 31.1°, 37.8°, 50.2° and 55.2° corresponding to (*1 0 1*), (*1 1 0*), (*0 0 3*), (*1 1 3*) and (*1 2 2*) reflection planes of Ni_3S_2 (JCPDS no. 44-1418), respectively (Fig. 1). And the sharp characteristic peaks at about 44.5°, 52.1° and 76.6° marked with asterisks are from the NF substrate (JCPDS no. 65-2865). These results manifested the partial sulfuration of NF after the hydrothermal reaction in both NF@Ni_3S_2 and NF@Ni_3S_2-NiOOH [38–42]. While the presence of NiOOH was not judged by XRD, possibly due to the NiOOH was poorly crystalline, even amorphous, it was further confirmed by EDX (Fig. 2), HRTEM (Fig. 4) and XPS (Fig. 5).

The 3D NF was fully covered by Ni_3S_2 nano-trees after the hydrothermal reaction. Some of the Ni_3S_2 grew densely, which exhibited an uneven nano-tree arrays structure (Fig. 2A and B). In the subsequent electrochemical deposition, NF@Ni_3S_2 was utilized as substrate for the growth of NF@Ni_3S_2-NiOOH hetero-nanocomposite, which displayed a vertically and uniformly distributed nano-pillar arrays (Fig. 2C and D). Moreover, the EDS results suggested that the NF@Ni_3S_2 and NF@Ni_3S_2-NiOOH samples were composed of Ni and S elements majorly (Fig. 2E and F). The atomic ratio between O and S in NF@Ni_3S_2 and NF@Ni_3S_2-NiOOH was 2.9 and 12.2, preliminarily proving the NiOOH probably existing in NF@Ni_3S_2-NiOOH hetero-nanocomposite. In addition, Fig. 3 shows elemental-mapping of Ni, S and O of NF@Ni_3S_2-NiOOH. In mapping photographs, the distribution of Ni, S and O element was very uniform after hydrothermal and electrodeposition process.

The NF@Ni_3S_2-NiOOH was a hierarchical hetero-nanostructure,