Facile Synthesis of Fe-Doped Ni$_3$S$_2$ Nanoparticles Supported on Ni Foam as Highly Active Electrocatalyst for Water Splitting

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Abstract. Novel Fe-doped Ni$_3$S$_2$ nanoparticles have been synthesized in situ on Ni foam (NF) through a facile one-step hydrothermal method. The structure and composition of the as-synthesized samples were characterized by XRD, XPS and SEM technique. The Fe-Ni$_3$S$_2$/NF shows excellent electrocatalytic activity toward both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Moreover, assembled as an electrolyzer for overall water splitting, this material delivers a current density of 10 mA cm$^{-2}$ at a quite low cell voltage of 1.59 V, and it also shows remarkable stability for continuously working over 24 h with nearly negligible deactivation. We expect that the Fe-doping can be an effective way to enhance the catalytic performance of metal disulfides for overall water splitting.

1. Introduction

To achieve sustainable production of H$_2$ fuel, electrochemical water electrolysis a promising strategy because it utilizes the abundant water resources and produces high-purity H$_2$.[1, 2] The water electrolysis process involves two half reactions: the cathodic hydrogen evolution reaction (HER) and the anodic oxygen evolution reaction (OER).[3, 4] To date, Pt-based materials are still the most efficient HER catalysts with a near-zero overpotential, whereas Ir and Ru oxides hold the benchmark for OER catalysts.[5] Unfortunately, the high cost and low abundance of these noble-metal based catalysts greatly impede their widespread applications in commercial electrolyzers.[6] Therefore, it is highly attractive to exploit alternative, low-cost and efficient noble-metal-free eletrocatalysts to expedite the sluggish HER/OER kinetic processes.[7-9]

Recently, Ni-based dichalcogenides nanostructures show impressive potential in water splitting.[10] Especially Ni$_3$S$_2$ nanostructures have attracted increasing attention for the application as electrocatalysts due to their rich existent in nature, much lower cost, unique structure configuration and high conductivity.[5] However, pure Ni$_3$S$_2$ nanostructures are still have limited activity for water electrolysis reaction. To improve their catalytic performance, Ni$_3$S$_2$-based hybrid composites, such as MoS$_2$/Ni$_3$S$_2$ and MoO$_x$/Ni$_3$S$_2$, have been reported.[11, 12] Although these hybrid composites can improve the activity of Ni$_3$S$_2$, their fabrication processes are greatly prohibited by the harsh, multi-step and time-consuming synthetic procedures.

In this work, we present a facile hydrothermal method to fabricate Fe-doped Ni$_3$S$_2$ nanoparticles with outstanding HER and OER catalytic activity. We find that introducing ferric nitrate reactant into solution results in not only the Fe-doping but also the generation of Ni$_3$S$_2$ nanoparticles uniformly grown on the Ni foam surface. We show that the catalytic activity of Ni$_3$S$_2$/NF is greatly enhanced by...
Fe-doping, such as reduced onset overpotential. Moreover, when assembled as an electrolyzer for overall water splitting, this Fe-Ni3S2/NF electrode delivers a current density of 10 mA cm\(^{-2}\) at a quite low cell voltage of 1.59 V, it also shows remarkable stability for continuously working over 24 h with nearly negligible deactivation.

2. Experimental section

2.1. Preparation of Ni\(_3\)S\(_2\)/NF and Fe-Ni\(_3\)S\(_2\)/NF

A piece of commercial Ni foam (NF, thickness: 1.5, bulk density: 0.23 g cm\(^{-3}\)) was carefully pre-treated complying following steps before each experiment: firstly rinsed with acetone to remove surface oxides for 5 min, then dipped in 3 M HCl solution in an ultrasonic bath for 10 min, and finally washed with ethanol and distilled water, respectively. In a typical synthesis of Fe-Ni\(_3\)S\(_2\)/NF, the fresh-treated NF (1 × 3.5 cm, ~80 g) was dipped fully in a 50 mL Teflon-lined autoclave containing 20 mL distilled water solution consist of 0.75 mmol thiourea (CH\(_4\)N\(_2\)S) and 0.25 mmol ferric nitrate (Fe(NO\(_3\))\(_3\)•9H\(_2\)O). The mixture was ultra-sonicated for 10 min to form a homogeneous suspension around Ni foam. Subsequently, the autoclave was sealed, and then heated at 140°C for 5 h. After the autoclave was cooled down to room temperature, the NF with black precipitates on the surfaces was rinsed with ethanol for 5 times and then dried in a vacuum at 30°C overnight. For comparison, pure Ni\(_3\)S\(_2\)/NF was fabricated by the same process without adding ferric nitrate in the solution. All chemicals mentioned above were purchased from Aladdin and were used without further purification.

2.2. Material characterization

X-ray diffraction (XRD) was carried out in X’Pert PRO MPD system using a Cu K\(_\alpha\) source. Field-emission scanning electron microscopy (FESEM) was taken with a Hitachi S-4800 accelerating voltage of 15 kV. X-ray photoelectron spectroscopy (XPS) was analyzed through an AMICUS ESCA 3400 with K\(_\alpha\) radiation

2.3. Electrochemical measurements

All the measurements were performed on an electrochemical workstation (CHI 660E, CH Instruments Inc., Shanghai) with a standard three-electrode setup. A graphite rod and Ag/AgCl electrode in saturated KCl were used as the counter electrode and the reference electrode, respectively. Linear sweep voltammetry (LSV) was carried out with a scan rate of 5 mV s\(^{-1}\). The long-term durability measurement was conducted using the chronopotentiometric methods. All the currents presented in this work were compensated with IR-correction.

3. Results and discussion

As shown in Fig.1a, the X-ray diffraction (XRD) profiles of the as-synthesized pure and Fe-doped samples exhibit the same peaks at 23.7°, 34.3°, 38.0°, 38.5°, 49.0°, 49.5° and 55.0°, which are indexed to the (101), (110), (003), (021), (113), (211) and (122) planes of hexagonal Ni\(_3\)S\(_2\) (JCPDS no:44-1418), respectively. The other two strong peaks at 44.5° and 52.0° are well assigned to Ni foam (JCPDS no:04-0850). Next, the X-ray photoelectron spectroscopy (XPS) spectrum was used to investigate the chemical states of Fe element. As presented in Fig. 1b, there is no spectrum peak of Fe element for bare Ni\(_3\)S\(_2\)/NF. However, For the Fe-doped Ni\(_3\)S\(_2\)/NF, two main peaks located at 711.0 and 726.2 eV, which are assigned to Fe 2p\(_{3/2}\) and 2p\(_{1/2}\),[13] respectively. Combine XRD with XPS analysis, these results confirm the successful fabrication of Fe-doped Ni\(_3\)S\(_2\) on Ni foam.
From the field-emission scanning electron microscopy (FESEM) images in Fig. 2, it can be seen that in contrast to a smooth and clean surface of pristine Ni foam (Fig. 2a), hydrothermal process led to the formation of triangle-shaped spikes Ni3S2 scattered on the Ni foam surface (Fig. 2b). Moreover, after adding ferric nitrate into the solution, the generated Fe-doped Ni3S2/NF material is consist of plenty of nanoparticles uniformly grown on the Ni foam surface, and the average diameter of the nanoparticles is about 200 nm (Fig. 2c-d).

To evaluate the electrocatalytic performance, Ni3S2/NF and Fe-Ni3S2/NF were then tested in 1.0 M KOH electrolyte purged with N2 using a standard three-electrode cell, in which the Ni foam with dimensions of 1.0 × 1.0 cm was used as the working electrode, along with bare Ni foam for comparison. We first tested the HER activity, as shown in Fig. 3a, the linear sweep voltammetry (LSV) curves with iR correction exhibits that the onset overpotentials of bare NF and Ni3S2/NF are approximately 250 and 180 mV, respectively. However, the onset overpotential of the Fe-doped Ni3S2/NF is substantially lower at a round 82 mV. Moreover, The overpotential required for current density ($j$) values of 10 mA cm$^{-2}$ is about 110 mV, substantially superior to those of Ni3S2/NF (ca. 205 mV) and bare NF (ca. 300 mV). Next, we further investigated the OER activity in 1.0 M KOH. Fig.3b displays the LSV cures measured within 1.2-1.8 V vs. RHE. Similar to the HER performance, Fe-Ni3S2/NF exhibits the highest OER activity and delivers a current density of 20 mA cm$^{-2}$ at low overpotential of about 1.57 mV. In contrast, Ni3S2/NF and bare NF require overpotentials of 1.62 and 1.75 mV to drive the same current density, respectively. Encouraged by the highly catalytic activity of the Fe-Ni3S2/NF toward both the HER and OER in 1.0 M KOH, we further utilized it as a bifunctional electrocatalyst for overall water electrolysis in a single electrolyzer. Fig. 3c displays the polarization
curve tested at a scan rate of 0.1 mV s\(^{-1}\). Impressively, Fe-Ni\(_3\)S\(_2\)/NF delivers an quite low cell voltage of 1.59 V to achieve a current density of 10 mA cm\(^{-2}\), which is much superior to those of Ni\(_3\)S\(_2\)/NF (ca. 1.68 V) and bare NF. The high activity for overall water splitting manifests the compatible integration of HER and OER. The stability of Fe-Ni\(_3\)S\(_2\)/NF was examined by chronoamperometry \((j-t)\) with constant applied voltage of 1.60 V vs. RHE, in which excellent water splitting stability was observed for 24 h with a negligible deactivation (Fig. 3d).

Fig.3. Polarization curves with iR correction for (a) HER, (b) OER and (c) overall water splitting. Electrolyte: 1 M KOH; scan rate: 1 mV s\(^{-1}\).

4. Summary
In summary, we present a facile hydrothermal synthesis method for the fabrication of Ni\(_3\)S\(_2\) nanoparticles doped with Fe. The obtained Fe-Ni\(_3\)S\(_2\)/NF exhibits excellent catalytic activity toward both HER and OER under alkaline solutions. Moreover, the corresponding electrolyzer constructed by the obtained material exhibits an impressive overall-water-splitting efficiency.

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