

Full paper

Identifying the electrocatalytic sites of nickel disulfide in alkaline hydrogen evolution reaction



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ABSTRACT

Transition-metal chalcogenides have attracted great attention for their superior catalytic activity towards hydrogen evolution reaction (HER) as an alternative to platinum. Here we report a facile method for synthesizing two-dimensional nickel disulfide (NiS₂) by using Ni(OH)₂ on nickel foam as substrate. The as-synthesized NiS₂ displayed an activation period during HER with a remarkable structural and compositional change under alkaline conditions. Electrochemical in situ X-ray absorption spectroscopy revealed that metallic Ni acted as catalytic active species with superior activity of 67 mV to reach 10 mA cm⁻². The in situ generated metallic Ni were easily oxidized to large-area ultrathin Ni(OH)₂ when exposed to air. The overall water splitting device was fabricated by using NiS₂-derived metallic Ni and Fe doped NiS₂-derived hydroxide as HER and OER electrode with a potential of 1.52 V to reach 10 mA cm⁻².

1. Introduction

Hydrogen (H₂) is considered to be the most promising clean energy carrier in the near future. Electrochemical or photoelectrochemical water splitting is an environmentally friendly approach for providing affordable H₂ [1]. The scalable water splitting requires efficient and stable non-noble metal electrocatalysts for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) beyond the state-of-the-art noble-metal catalysts [2,3]. Transition-metal dichalcogenides (TMD) have been emerging as one of the most efficient earth-abundant HER electrocatalysts [4] since the first discovery of MoS₂ in 2005 by Nørskov and coworkers [5]. In the past decade, great efforts have been made to develop other TMD such as WS₂, NiS₂, TaS₂ and MoSe₂ [6–9]. Even though many TMD catalysts have been synthesized with superior HER activity, a deep understanding of catalytic mechanism and active sites could provide valuable insights for developing efficient catalysts. Taking the most well-studied MoS₂ as an example, in 2007, Chorkendorff et al. experimentally demonstrated that only the edges of MoS₂ are catalytically active, while the basal planes are inert [10]. This important finding guided researchers to prepare MoS₂ nanostructures with more exposed edge sites to improve the catalytic activity in acidic

electrolyte [11,12]. However, recent study revealed that the terminal disulfide ligands were eliminated with the exposure of Mo as actual catalytic centers in amorphous MoS_x catalyst under neutral HER conditions [13]. The finding may arise people's attention to reconsider the active site of other TMD catalysts under neutral or alkaline conditions.

It has been demonstrated that metal sulfides and selenides were unstable during OER and completely converted to corresponding metal oxides which were responsible for their catalytic activity [14,15]. Although the characterizations of catalysts after catalysis is important to reveal the structural or compositional changes, in situ approaches can reveal the actual active species and catalytic mechanism of the reaction. For instance, in situ studies have been successfully performed to directly detect catalytic active sites during OER [16–18]. However, using in situ approaches to disclose the catalytic sites of HER has rarely been reported since it is widely assumed that catalysts are stable under HER conditions compared with harsh OER conditions [19,20]. However, very recently, by applying in situ X-ray absorption spectroscopy (XAS), we demonstrated that Ni-thiolate coordination polymer were entirely converted into ultrathin metallic Ni (Ni⁰) during alkaline HER [21]. This knowledge encouraged us to further investigate the HER active sites of transitional metal chalcogenides under alkaline conditions.

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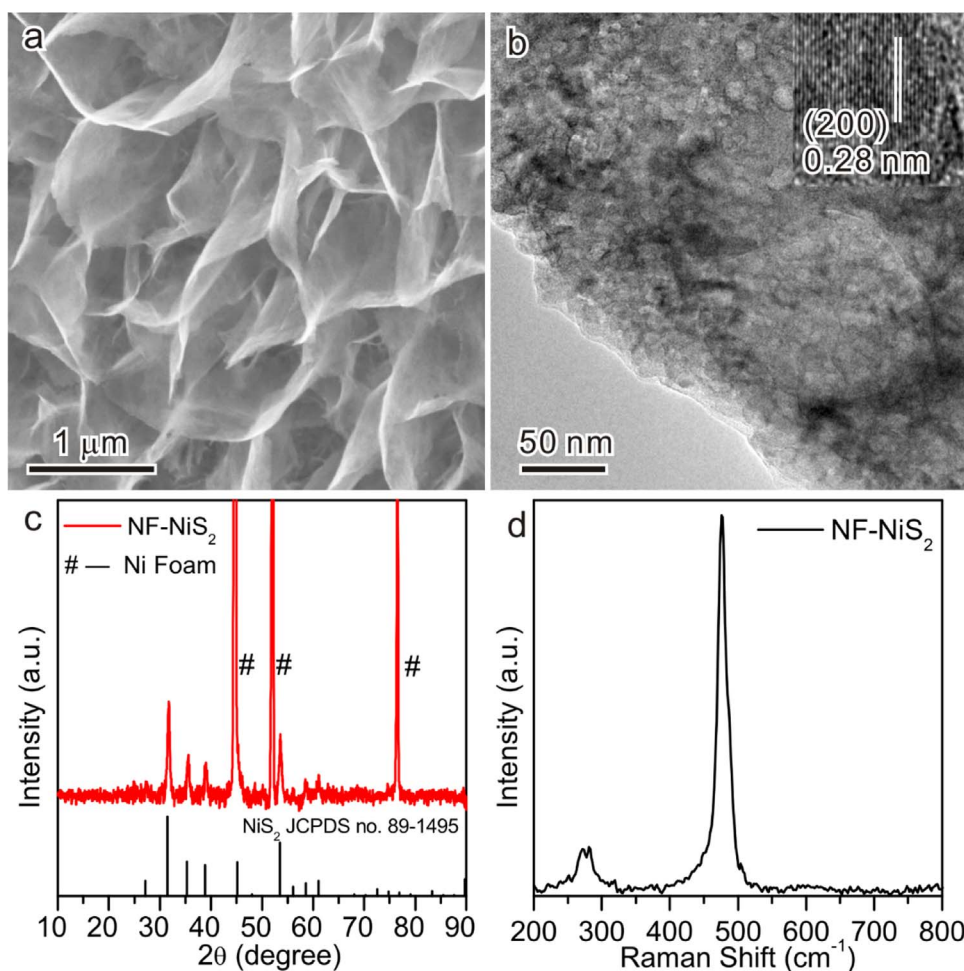


Fig. 1. Structural and compositional characterization of NF-NiS₂. (a) SEM (b) TEM images (inset: HRTEM image), (c) XRD pattern and (d) Raman spectrum of NF-NiS₂.

Herein, we demonstrate a facile method to prepare two-dimensional (2D) pyrite-type NiS₂ nanosheets (NSs) by using 2D Ni(OH)₂ as template. The as-synthesized NiS₂ displayed an activation period during the HER in alkaline electrolyte and finally reached an superior performance with an overpotential of 67 mV to reach 10 mA cm⁻². The electrochemical in situ XAS studies revealed that 2D NiS₂ were transformed into ultrathin Ni⁰ NSs which were responsible for the excellent HER activity. Moreover, the Ni⁰ NSs were easily oxidized to ultrathin Ni(OH)₂ upon exposing to air or applying anodic potentials with increased surface area and enhanced OER activity. The overall water splitting device was fabricated by using NiS₂-derived Ni⁰ and Fe doped NiS₂ (NiFeS₂)-derived hydroxide as HER and OER electrode with a potential of 1.52 V to reach 10 mA cm⁻².

2. Experimental section

2.1. Synthesis of Ni(OH)₂ on nickel foam

Ni Foam substrates were consecutively washed with HCl (1 M), and deionized water under sonication for 15 min in each solution to thoroughly remove nickel oxides and impurities on the surface. 2.9 g Ni(NO₃)₂, 2.8 g Hexamethylenetetramine were dissolved into 80 ml deionized water. After stirring, the mixture was poured into a 100 ml autoclave with a piece of Ni Foam (2*6 cm) leaned against the wall. The growth was carried out at 100 °C in an electric oven for 10 h. After allowing the autoclave to cool naturally to room temperature, the samples were removed, washed with deionized water, and then dried in vacuum oven under room temperature.

2.2. Synthesis of NiS₂ (NF-NiS₂) and NiFe sulfide (NF-NiFeS₂) on nickel foam

Ni-Ni(OH)₂ (2 cm*2 cm) and NF-NiFe hydroxide (2 cm*2 cm) were used as precursors and 0.5 g sublimed sulfur powder were heated in a tube furnace under nitrogen atmosphere at 250 °C for 2 h. After cooling to room temperature, the samples were washed with carbon disulfide, ethanol and deionized water for several times to remove the sulfur on the electrode surface, and then dried in vacuum oven under room temperature.

3. Materials characterizations

Transmission electron microscopy (TEM) studies were performed on a TECNAI F-30 high-resolution transmission electron microscope operating at 300 kV. SEM studies were carried out on ZEISS SIGMA field emission scanning electron microscope. Powder X-ray diffraction (XRD) measurements were performed with Rigaku Ultima IV instrument using Cu Kα (λ = 0.15418 nm) X-ray sources at room temperature. XPS measurements were carried out by using an Omicron Sphera II hemispherical electron energy analyzer (Monochromatic Al Kα with 1486.6 eV operating at 15 kV and 300 W). The samples were transferred into the chamber immediately after electrochemical activation with the protection of N₂ for the XPS measurements. Raman spectra were acquired using a confocal Raman system (Xplora, Horiba) using a 532 nm laser as the excitation light with the power around 0.15 mW.

The XAS at the Ni K-edge were recorded at beam line BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), China. The electrochemical in-situ XAS were recorded at SP8 (Japan) 12B2 Taiwan

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