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# Facile synthesis of free-standing nickel chalcogenide electrodes for overall water splitting

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## ABSTRACT

Developing high-performance noble metal-free and free-standing catalytic electrodes are crucial for overall water splitting. Here, nickel sulfide ( $\text{Ni}_3\text{S}_2$ ) and nickel selenide ( $\text{NiSe}$ ) are synthesized on nickel foam (NF) with a one-pot solvothermal method and directly used as free-standing electrodes for efficiently catalyzing hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in alkaline solution. In virtue of abundant active sites, the  $\text{Ni}_3\text{S}_2/\text{NF}$  and the  $\text{NiSe}/\text{NF}$  electrodes can deliver a current density of  $10 \text{ mA cm}^{-2}$  at only 123 mV, 137 mV for HER and 222 mV, 271 mV for OER. Both of the hierarchical  $\text{Ni}_3\text{S}_2/\text{NF}$  and  $\text{NiSe}/\text{NF}$  electrodes can serve as anodes and cathodes in electrocatalytic overall water-splitting and can achieve a current density of  $10 \text{ mA cm}^{-2}$  with an applied voltage of  $\sim 1.59 \text{ V}$  and  $1.69 \text{ V}$ , respectively. The performance of as-obtained  $\text{Ni}_3\text{S}_2/\text{NF}||\text{Ni}_3\text{S}_2/\text{NF}$  is even close to that of the noble metal-based  $\text{Pt}/\text{C}/\text{NF}||\text{IrO}_2/\text{NF}$  system.

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## 1. Introduction

Due to the high combustion heat and clean combustion product, hydrogen has been regarded as an ideal energy carrier for future renewable energy systems [1,2]. Electrochemical water splitting is a promising and sustainable strategy for hydrogen production with zero carbon emission, especially if the electrical energy can be supplied by renewable resources, such as solar or wind energy [3,4]. Water splitting usually involves two half reactions, including hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). The theoretical reversible potential to drive overall water splitting is 1.23 V, while the commercial electrolyzers often operate at a much higher value of 1.80–2.00 V in the practical applications [5]. Thus, electrocatalysts for HER and OER are usually needed to decrease the overpotential and make the hydrogen production less energy intensive. At present, Pt-based and Ir or Ru oxide-based electrocatalysts are the most active catalysts

for HER and OER, respectively. However, the very limited resources and high costs of the noble metal-based materials remarkably restrict their scalable applications [6]. Therefore, it is crucial to develop low-cost and highly active non-noble metal-based electrocatalysts for overall water splitting.

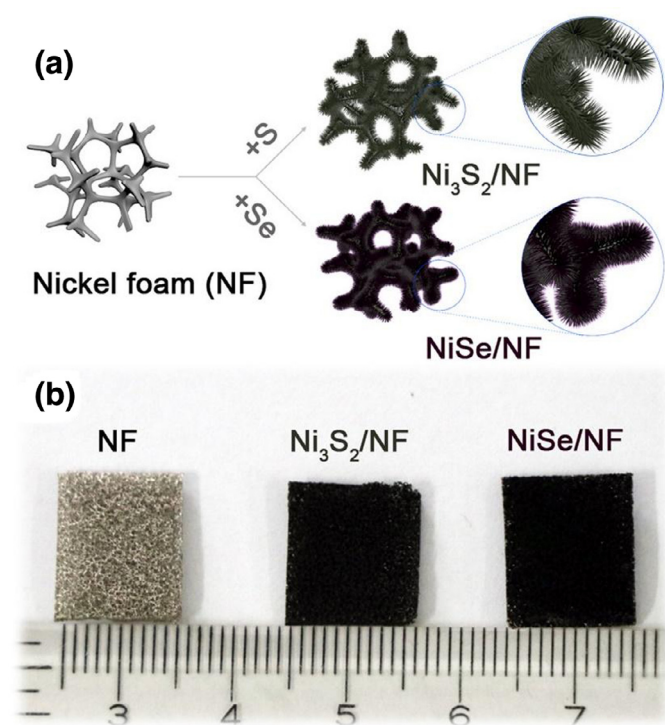
In the past few years, significant efforts have been made toward developing non-noble metal-based catalysts, such as transition metal carbide [7], boride [8], phosphide [9], sulfide [10], selenide [11] for HER catalysis and perovskite [12,13], metal oxide [14–17], hydroxide [18,19], chalcogenide [20] for OER catalysis. However, in order to minimize the overpotential and simplify the device design, electrocatalysts for overall water splitting are highly desirable to catalyze HER and OER directly in the same solution [21]. Recently, metal chalcogenides, especially nickel chalcogenides are attracting increasing attention due to their catalytic activity for HER or OER in alkaline solution [22,23]. However, it is still very challenging to effectively increase the number of active sites of the electrodes for highly efficient HER and OER catalysis with a facile synthesis [24–26]. In addition, many state-of-the-art HER and OER catalysts are in powder form, which needs binders to form a good contact with current collectors [26,27]. It is crucial to develop binder-free and highly efficient non-noble metal-based catalysts for the future practical applications of overall water splitting.

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**Fig. 1.** (a) One-pot synthesis of  $\text{Ni}_3\text{S}_2/\text{NF}$ ,  $\text{NiSe}/\text{NF}$  by solvothermal reaction, here NF denotes nickel foam; (b) optical photographs of original nickel foam,  $\text{Ni}_3\text{S}_2/\text{NF}$  and  $\text{NiSe}/\text{NF}$  samples.

homogeneous catalyst ink (2 mL) was obtained by adding 20 mg Pt/C or  $\text{IrO}_2$  into 500  $\mu\text{L}$  water, 100  $\mu\text{L}$  5% nafion solution, and 1.4 mL ethanol solution and sonicating for 30 min. All catalyst ink was dropped on the surface of a nickel foam (surface area:  $1\text{ cm}^2$ ). Consequently, the loading amount of the noble-metal catalysts on nickel foam electrode is about  $20\text{ mg cm}^{-2}$ . As control samples,  $\text{Ni}_3\text{S}_2$  and  $\text{NiSe}$  powders on graphite paper (GP) were also synthesized. The  $\text{Ni}_3\text{S}_2$  or  $\text{NiSe}$  powders were obtained by peeling them off from nickel foam with ultrasonic treatment. Then, a homogeneous catalyst ink (2 mL) was obtained by adding 6  $\text{cm}^2$   $\text{Ni}_3\text{S}_2/\text{NF}$  or  $\text{NiSe}/\text{NF}$  electrodes (about 120 mg of catalysts) into 500  $\mu\text{L}$  water, 100  $\mu\text{L}$  5% nafion solution, and 1.4 mL ethanol solution and sonicating for 30 min. Then 335  $\mu\text{L}$  of the catalyst ink is loaded onto a graphite paper (GP) of  $1\text{ cm}^2$ , on which loading amount of the catalysts is about  $20\text{ mg cm}^{-2}$ . The  $\text{Ni}_3\text{S}_2$  and  $\text{NiSe}$  powders on graphite paper (GP) are denoted as  $\text{Ni}_3\text{S}_2/\text{GP}$  and  $\text{NiSe}/\text{GP}$ .

## 2.2. Sample characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku 2500 V diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.542\text{ \AA}$ ). The X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALABMK 250 Xi. Scanning electron microscopy (SEM) images were taken on a MERLIN Compact. Transmission electron microscopy (TEM) measurements and energy-dispersive X-ray spectroscopy (EDS) elemental mappings were performed on a JEM-2100F electron microscopy with an accelerating voltage of 200 kV.

## 2.3. Electrochemical tests

All electrochemical experiments were performed at room temperature with a Bio-logic Science EC-LAB. For the electrocatalytic HER and OER in alkaline media (1 M KOH), the as-prepared  $\text{Ni}_3\text{S}_2/\text{NF}$  and  $\text{NiSe}/\text{NF}$  were used as working electrodes directly, while an  $\text{Ag}/\text{AgCl}$  electrode (3 M KCl) and a graphite rod were used as the reference electrode and the counter electrode, respectively. All potentials were converted to the reversible hydrogen electrode (RHE) reference scale, using  $E(\text{RHE}) = E(\text{Ag}/\text{AgCl}) + 0.059\text{ pH} + 0.210\text{ V}$ . Linear sweep voltammetry (LSV) measurement was used to obtain the polarization curves with a scan rate of  $2\text{ mV s}^{-1}$ , from which Tafel plots were derived. The potentials in all the polarization curves and Tafel plots were IR corrected. Chronoamperometry (CA) tests were used for evaluating the catalytic stability. Cyclic voltammetry (CV) was carried out at various scan rates (5, 10, 20, 50, 100,  $200\text{ mV s}^{-1}$ ) to probe the electrochemical double layer capacitance at non-Faradaic potentials, estimating the electrochemical surface area (ECSA). As for electrochemical impedance spectroscopy (EIS), potential EIS measurements were performed at  $-1.3\text{ V}$  and  $0.7\text{ V}$  versus  $\text{Ag}/\text{AgCl}$  electrode for all the materials prepared, with scanning frequency ranging from 200 kHz to 50 mHz. Overall water splitting catalytic performance was performed in an alkaline electrolyzer in a two-electrode system with the  $\text{Ni}_3\text{S}_2/\text{NF}$  or  $\text{NiSe}/\text{NF}$  directly as cathode and anode.

## 3. Results and discussion

$\text{Ni}_3\text{S}_2/\text{NF}$  or  $\text{NiSe}/\text{NF}$  is synthesized by direct sulfurization or selenization of NF with sulfur or selenium powders through a solvothermal reaction (Fig. 1(a)). The nickel foam serves as the Ni source as well as the current collector. The photograph of the synthesized  $\text{Ni}_3\text{S}_2/\text{NF}$ ,  $\text{NiSe}/\text{NF}$  and the blank NF are shown in Fig. 1(b). After solvothermal reaction, the color of NF changes from argente to dark green for  $\text{Ni}_3\text{S}_2/\text{NF}$  or dark gray for  $\text{NiSe}/\text{NF}$  sample.

In this contribution, we report our efforts in developing binder-free hierarchical structures of nickel sulfide ( $\text{Ni}_3\text{S}_2$ ) or nickel selenide ( $\text{NiSe}$ ) on nickel foam (NF) with a one-pot solvothermal method. NF serves as both the current collector and nickel source, while  $\text{Ni}_3\text{S}_2$  or  $\text{NiSe}$  nanowires can directly grow on it. This procedure leads to an intimate contact between the catalysts and current collectors, thus facilitates a fast charge transfer. Consequently, both of the materials can serve as free-standing catalytic electrodes for highly efficient HER and OER catalysis. The  $\text{Ni}_3\text{S}_2/\text{NF}$  could deliver a current density of  $10\text{ mA cm}^{-2}$  at 123 mV for HER and 222 mV for OER, while the  $\text{NiSe}/\text{NF}$  could deliver a current density of  $10\text{ mA cm}^{-2}$  at 137 mV for HER and 271 mV for OER. Alkaline electrolyzers are assembled using  $\text{Ni}_3\text{S}_2$  and  $\text{NiSe}$  as both cathode and anode respectively. The hierarchical  $\text{Ni}_3\text{S}_2/\text{NF}$  and  $\text{NiSe}/\text{NF}$  electrodes can achieve a current density of  $10\text{ mA cm}^{-2}$  at a cell voltage of about 1.59 V and 1.69 V and show a good long-term durability.

## 2. Experimental

### 2.1. Sample synthesis

$\text{Ni}_3\text{S}_2/\text{NF}$  and  $\text{NiSe}/\text{NF}$  were synthesized by a one-pot solvothermal method, which is illustrated in Fig. 1(a). Typically, ethylene glycol (35 mL) and ethylenediamine (35 mL) were added into 100 mL Teflon-lined stainless-steel autoclave. Then, after stirring vigorously for 30 min, nickel foam (350 mg), sulfur powder (287.6 mg) for  $\text{Ni}_3\text{S}_2/\text{NF}$  or selenium powder (424.5 mg) for  $\text{NiSe}/\text{NF}$  were added into the autoclave, respectively. The autoclave was maintained at  $160\text{ }^\circ\text{C}$  for 4 h. After it was cooled down to room temperature, the final samples were taken out and washed with deionized water for further characterizations and electrochemical tests. Based on the mass increment of the nickel foam, the loading amounts of  $\text{Ni}_3\text{S}_2/\text{NF}$  and  $\text{NiSe}/\text{NF}$  catalysts are determined to be  $\sim 19.3$  and  $\sim 21.5\text{ mg cm}^{-2}$ , respectively. For comparison, a ho-

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