



Novel three-dimensional flower-like porous Al₂O₃ nanosheets anchoring NiS₂ nanoparticles for high-efficiency hydrogen evolution



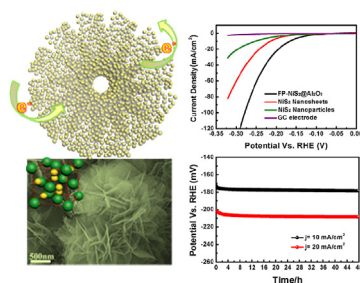
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HIGHLIGHTS

- Unique 3D flower-like NiS₂@Al₂O₃ is fabricated for the first time.
- The 3D morphology can efficiently disperse active nanoparticles.
- The anchored structure can effectively improve the structural stability.
- The porous structure facilitates ion transfer and enlarge specific surface area.
- The flower-like composite exhibits superior performances for HER.

GRAPHICAL ABSTRACT



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ABSTRACT

In this contribution, we report unique flower-like porous γ -Al₂O₃ nanosheets anchoring uniform NiS₂ nanoparticles, which are firstly fabricated through a common hydrothermal process and two-step calcinations. Different from the general strategy, the flower-like NiS₂@Al₂O₃ are directly prepared by the precursor of Ni₂Al(CO₃)₂(OH)₃ nanosheets rather than adding Al₂O₃ coating later. This novel nano-architecture can efficiently disperse and confine the active nanoparticles, which can not only offer large specific surface area, but also hinder aggregation and peeling off from the substrates, thus to demonstrate superior HER activities, especially the long-time stability. In this work, the as-synthesized composite exhibits an onset potential of –126 mV and excellent durability of 3% decrease in potential at constant current of 10 mA/cm² for 48 h.

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1. Introduction

With the growing energy crisis and increasing energy demand, great attention has been paid on clean, high efficiency and sustainable energy sources [1,2]. Hydrogen has been considered as one of the attractive candidates for sustainable energy carrier due to its

low-cost, high specific energy and environmentally friendly [3,4]. Recently, hydrogen is primarily generated by natural gas, fossil fuels and water splitting [5,6]. When considering the purity, cost and environment, water splitting by sunlight or electricity seems to be the most efficient and renewable means [7,8]. Hydrogen evolution reaction (HER), as one of the water splitting reaction ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$), requires low overpotential and good stability to consequently enhance the efficiency of this vital process [9–12]. In the past few years, numerous inorganic materials, considered as the potential HER electrocatalysis, have been attracted great attention, but the

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state-of-the-art HER catalysts are precious metals, especially Pt or Pt-based materials due to their near-zero overpotential and electrochemical stability [13–15]. However, the scarcity and high price of Pt promote the researchers to exchange their concentration from noble metals to non-noble metals. Recently, a large number of earth-abundant solid-state electrocatalysts, such as carbides [16], borides [17], chalcogenides [18] and alloys [18], are emerged to our attention. Within the electric catalytic materials, the cubic transition metal dichalcogenides (denoted as MX_2 , where $\text{M} = \text{Co}, \text{Fe}, \text{Ni}$; $\text{X} = \text{S}, \text{Se}$) have been explored as promising candidates of HER catalysis owing to their long-term stability and low cost [19–21].

Among the transition metal pyrites, nickel disulfide (NiS_2) has drawn great research attention because of its promising applications, such as Li-S batteries and supercapacitors. Meanwhile, it can be also regarded as potential HER catalyst because of its interesting electrical, magnetic and optical properties [22,23]. In recent years, extensive efforts have been devoted to enhance the HER activities, mainly through enlarging exposed active sites by dispersing active materials [24] and improving electron conduction by size reduction [25], shape control [26] and hybridization [28]. To our knowledge, nanosized materials have drawn a great deal of attention due to their large specific surface, enriched active sites and short electron diffusion pathways, which can indeed enhance the catalytic performances. So far, a various of nanostructured NiS_2 catalysts have been reported, including nanoparticles [27], nanosheets [28] and nanocubes [29]. Unfortunately, there remains the common but serious issue that the nanosized materials would easily get aggregation and agglomeration during long-time operation and also induce further structural defects, leading to poor stability, which severely hampers the further applications [30,31]. Therefore, it is urgent to fabricate and design sophisticated nanomaterials, especially with novel nanostructures. Among the devised morphologies, combining two materials seems the feasible solution to solve the mentioned problems. To date, nanoscale materials are always combined with conductive substrate coating, such as carbon and metal oxides. As reported, ZnO , MgO , Al_2O_3 , AlF_3 and Al_2O_3 have been discovered as efficient substrates in electrochemical reactions [32–35]. Significantly, among various coatings, Al_2O_3 is investigated to deliver distinct electro-chemical properties especially stability owing to its high thermal stability and large surface area [36–38]. Nevertheless, fabricating Al_2O_3 coating through an easy and facile way still faces a big challenge as most of the Al_2O_3 coating are synthesized by a complex method of atomic layer deposition.

Herein, we report unique three-dimensional flower-like porous Al_2O_3 nanosheets anchoring NiS_2 nanoparticles ($\text{FP-NiS}_2@/\text{Al}_2\text{O}_3$) by a facile and general method. In the process, the flower-like $\text{Ni}_2\text{Al}(\text{CO}_3)_2(\text{OH})_3$ nanosheets were uniformly fabricated through a hydrothermal process. In contrast to the previous methods, our novel $\text{FP-NiS}_2@/\text{Al}_2\text{O}_3$ can be directly synthesized through two-step calcinations, including one step in H_2 atmosphere to obtain flower-like $\text{Ni}@\text{Al}_2\text{O}_3$ and the second step in Ar atmosphere reacted with sulfur. This special three-dimensional (3D) architecture, consisting of large quantities of ultrathin nanosheets, possesses numerous advantages. To our knowledge, the nanoscaled structure can effectively shorten the ion/electron diffusion pathways, which can accelerate ion/electron exchange between electrolyte and catalyst [39,40]. Moreover, the nanoarchitecture can enlarge the specific surface area and may enrich the active sites for electrocatalysis. In addition, the nanopores, derived from plenty of substances loss, can further increase the specific surface area of the catalyst and promote the electrons' fast and easily exchange. Importantly, the Al_2O_3 nanosheets can tightly fix the active materials, fully maintaining the structural integrity, which can efficiently improve the cyclic stability. Therefore, our novel $\text{FP-NiS}_2@/\text{Al}_2\text{O}_3$ can no doubt exhibit enhanced electrocatalytic performances.

2. Experimental

2.1. Materials

Ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28–30 wt%, J. T. Baker), ethylene glycol (99.99%, Fisher Chemical), sodium carbonate (Na_2CO_3 , 99.9%, Aldrich), aluminium nitrate ($\text{Al}(\text{NO}_3)_3$, 99.9%, Aldrich), nickel nitrate ($\text{Ni}(\text{NO}_3)_2$, 99.9%, Aldrich).

2.2. Preparation of flower-like $\text{Ni}_2\text{Al}(\text{CO}_3)_2(\text{OH})_3$ nanosheets

15 mL $\text{NH}_3 \cdot \text{H}_2\text{O}$, 10 mL ethylene glycol, 5 mL $\text{Ni}(\text{NO}_3)_2$ (2 M), 2 mL $\text{Al}(\text{NO}_3)_3$ (2 M) and 7 mL Na_2CO_3 (1 M) were gradually added into beaker. Then stirred for 25 min until the mixture was turned into sapphire blue. And next, the mixture was poured into autoclave of 50 mL and put into an oven at 180 °C for 18 h. After reaction, the precursor was precipitated in the bottle and then washed several times separately by DI water and ethanol. Finally, the precursor was dried in oven overnight.

2.3. Preparation of $\text{FP-NiS}_2@/\text{Al}_2\text{O}_3$

At first, the flower-like $\text{Ni}_2\text{Al}(\text{CO}_3)_2(\text{OH})_3$ nanoplates were put into the tube furnace and annealed at 750 °C for 200 min under H_2 atmosphere. After that, the $\text{Ni}@\text{Al}_2\text{O}_3$ and sulfur with the mass ratio of 1:10 were placed in one glass tube with the interval distance of 3 cm. Under Ar atmosphere, $\text{Ni}@\text{Al}_2\text{O}_3$ could be transformed into $\text{NiS}_2@/\text{Al}_2\text{O}_3$ by further calcination at 400 °C for 200 min. In order to reduce the proportion of Al_2O_3 , the $\text{FP-NiS}_2@/\text{Al}_2\text{O}_3$ was further treated by weak base solution of dilute ammonia solution (~6 wt%).

2.4. Preparation of NiS_2 nanosheets and NiS_2 nanoparticles

Firstly, to synthesize $\text{Ni}(\text{OH})_2$ nanosheets, 10 mL ethylene glycol, 12 mL $\text{NH}_3 \cdot \text{H}_2\text{O}$, Na_2CO_3 aqueous solution 4 mL (1 M) and $\text{Ni}(\text{NO}_3)_2$ 4 mL (1 M) were gradually mixed in the beaker and then transferred into autoclave. Then the autoclave was put into electric dry oven and reacted for 16 h at 170 °C. The NiS_2 nanosheets were fabricated through the further calcined of $\text{Ni}(\text{OH})_2$ nanosheets with sulfur in Ar atmosphere at 400 °C.

As for synthesis of NiS_2 nanoparticles, $\text{Ni}(\text{OH})_2$ nanosheets were calcinated by two-step calcinations, including one in H_2 atmosphere to obtain Ni nanoparticles and another in Ar atmosphere with sulfur.

2.5. Characterization of the samples

Powder X-ray diffraction with $\text{CuK}\alpha$ radiation (XRD, Bruker D8 Advance), field-emission scanning electron microscope (SEM) along with an EDX analyzer (JSM-7800F, JEOL, 5 kV), transmission electron microscopy (TEM, F30, Philips, Tecnai, 300 kV), Raman Microscope (RENISHAW Invia, UK, voltage: 100–240 V, Power: 150 W), BET surface-area measurement of surface-area and pore-size analyzer (Quantachrome Autosorb-6B).

2.6. Composition of $\text{FP-NiS}_2@/\text{Al}_2\text{O}_3$

200 mg final composite was dissolved in 30 mL 1 M hydrochloric acid for 24 h. The NiS_2 nanoparticles was totally dissolved as Al_2O_3 is pretty stable in acid. Finally weigh the left sample. The content of Al_2O_3 is calculated [37].

$$\text{Al}_2\text{O}_3\% = \text{M}(\text{Al}_2\text{O}_3) / \text{M}(\text{NiS}_2@/\text{Al}_2\text{O}_3) \times 100\% \quad (1)$$

where $\text{M}(\text{Al}_2\text{O}_3)$ and $\text{M}(\text{NiS}_2@/\text{Al}_2\text{O}_3)$ are the weight of Al_2O_3 and $\text{FP-NiS}_2@/\text{Al}_2\text{O}_3$, separately.

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