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Controllable synthesis of ultrathin Co_9S_8 nanosheets as a highly efficient electrocatalyst for overall water splitting

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ABSTRACT

A facile and convenient hydrothermal method was employed to synthesize cobalt sulfides with different controllable morphologies by varying the filling factor, and ultrathin Co_9S_8 nanosheets (~3 nm) were obtained with the autoclave filled up to 60%. For the first time the electrocatalytic performance of the ultrathin Co_9S_8 nanosheets for both oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) was investigated. Benefiting from the larger electrochemical active surface area and more exposed accessible active sites, the ultrathin Co_9S_8 nanosheets, meanwhile, presented a remarkable performance towards OER and excellent catalytic activity for the HER process. To reach a current density of 10 mA cm^{-2}, the overpotential is only 206 mV for OER in 1.0 M KOH, which is very close to RuO_2 (200 mV). For HER, a low overpotential of only 178 mV is needed to reach 10 mA cm^{-2} in 0.5 M H_2SO_4. This work may inspire the development of low-cost, efficient electrocatalysts for energy conversion with ultrathin Co_9S_8 nanosheets.

1. Introduction

With the increasing demand for clean and long-term sustainable energy, alternative energy conversion and storage systems are being researched intensively. Electrocatalytic water splitting into hydrogen and oxygen is an appealing and promising way to renewable energy storage [1,2]. However, the half-reactions of water-splitting, namely the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), are energy intensive with high overpotentials. The most efficient catalysts for OER are IrO_2 and RuO_2 at present. In the meantime, the noble metal catalysts, Pt, is known as the state-of-the-art HER catalysts exhibiting high activities [3]. The large-scale availability of noble metals, however, cannot be expected due to their high cost and earth scarcity [4]. On the other hand, although the latest achievements have displayed large numbers of high performance catalysts with an overpotential approaching zero, there is still a great scientific challenge that the OER catalysts usually have poor HER activity, and the HER electrocatalysts possess unattractive activity for the OER process. Hence, research and development of low-cost and effective electrocatalysts with satisfactory properties for both HER and OER is one of the currently important topics.

To resolve the aforementioned two problems, extensive research efforts on developing cost-saving electrocatalysts that can replace the precious metals efficiently have been carried out over the past several decades. Among them, non-noble metal catalysts, like transition metal based compounds, such as oxides [5,6], layered double hydroxides [7–9], carbides [10,11], sulfides [12–15] have attracted enormous interest owing to their low cost and excellent catalytic activities. Especially transition-metal sulfides as electrocatalysts have shown preeminent electrocatalytic activities for potential value in energy technologies because of their earth abundant, inexpensive, efficiently catalytic properties [16–20]. In addition, in contrast to metal oxide counterparts, the covalent bonding sulfide host in the transition metal sulfides may have preferable conductivity, and inhibit their corrosion in catalytic process, resulting in good stability for the catalysts [1,21]. Co_9S_8, as one of the transition-metal sulfides, has been widespreadly reported to be quite active for HER [22,23]/OER [24–26] and been successfully prepared with a diversity of morphologies to promote

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its electroactivity, including hollowing microplates [27], nanoparticles [28], core–shell nanostructures [26]. Not only that, but more strategies remain to be proposed to further enhance their catalytic activity. Both theoretical [29] and experimental studies [30–32] proved that ultrathin 2D nanostructures had larger catalytic area, more exposed active sites and improved charge transport, which resulted in superior electrocatalytic performance for OER and HER in relation to their bulk counterparts [33–35].

Despite enormous attempts have been made focusing on the development of electrocatalytic activity of the ultrathin Co_9S_8 nanostructures, there is only one report about Co_9S_8 nanosheets as efficient electrocatalyst for the HER process [36]. The electroactivity for both HER and OER of Co_9S_8 nanosheets, however, to our best knowledge, has not yet been reported. Based on the above considerations, in this work, a series of Co_9S_8 samples are controllably synthesized with different morphologies, from hexagon to ultrathin nanosheets, by changing the filling factor in a facile hydrothermal process. For the first time the electrocatalytic performance of the ultrathin Co_9S_8 nanosheets for both OER and HER is investigated. As expected, the as-prepared ultrathin Co_9S_8 nanosheets exhibit excellent catalytic performance toward both OER and HER with lower overpotentials of 206 and 178 mV at a current density of 10 mA cm^{-2} for OER and HER, respectively, which is significantly superior to the activities of other kinds of morphologies derived from the same simple synthetic route but different filling factor in this work. These interesting results, recording one of the distinguished performances among non-noble metal electrocatalysts reported so far [11,16,26], may inspire the development of low-cost, efficient electrocatalysts for energy conversion with ultrathin Co_9S_8 nanosheets.

2. Experimental

2.1. Chemicals and materials

Cobalt sulfate heptahydrate ($CoSO_4{\cdot}7H_2O$, Tianjin Damao Chemical Reagent Co., Ltd., 99.5%), sodium sulfite (Na_2SO_3, Beijing Chemical Reagent Co., Ltd, 97.0%), hydrazine hydrate ($N_2H_4{\cdot}H_2O$, Xilong Chemical Co., Ltd, 80%), potassium hydroxide (KOH, Beijing Chemical Reagent Co., Ltd, 82.0%), Nafion solution (Sigma-Aldrich Co., 5 wt%), Pt/C (Shanghai Macklin Biochemical Co., Ltd, 20 wt%) and RuO_2 (Shanghai Macklin Biochemical Co., Ltd, 99.9%). All the materials in this experiment were used directly without any purification.

2.2. Synthesis of Co_9S_8 electrocatalysts

4 mmol $CoSO_4{\cdot}7H_2O$ and 3.7 mmol Na_2SO_3 were dissolved in 44 mL deionized water (DI water), then 20 mL $N_2H_4{\cdot}H_2O$ was added to the solution with vigorous stirring continuously for 30 min at room temperature. Next, the well mixed solution was transferred into an 80 mL Teflon-lined stainless steel autoclave filled up to 80% of the total volume. The autoclave was sealed and maintained at 180 °C for 72 h. After naturally cooling down to room temperature, the hexagon Co_9S_8 (Co_9S_8-80) was obtained by centrifugation, then washed with DI water and absolute ethanol for three times, respectively, and dried at 50 °C under vacuum for 4 h. To prepare ultrathin Co_9S_8 nanosheets (Co_9S_8-60), we followed by the same route as mentioned above but adjusted filling factor to 60% by reducing the amount of chemicals and materials proportionally. For comparison, other Co_9S_8 samples with different morphologies are also synthesized with the autoclave filled up to 70% (Co_9S_8-70) and 50% (Co_9S_8-50).

2.3. Characterizations

X-ray powder diffraction (XRD) patterns were performed on a Phillips X'pert ProMPD diffractometer (CuKα, λ = 1.54056 Å). The morphologies of the products were measured using field emission scanning electronic microscope (FESEM, an acceleration voltage of 10 kV, S-8010, Hitachi) and a high-resolution transmission electronmicroscope (HRTEM, an acceleration voltage of 200 kV, JEM-2010, JEOL and FEI Technai G2 F20). Raman spectra were analyzed using Renishaw at an excitation wavelength of 532 nm. The specific surface area was calculated from the adsorption branches in the relative pressure range of 0.09–1.00 by the Brunauer–Emmett–Teller (BET) method. The pore size distribution was derived from the desorption branch using the Barrett-Joyner-Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS) measurements were performed on ESCALAB 250Xi spectrometer (Thermo Fisher) with Al Kα radiation as the X-ray source for excitation.

2.4. Electrochemical measurements

Electrochemical measurements were conducted on an electrochemical workstation (Zennium IM6 station, Germany) using a conventional three-electrode setup, a platinum foil as the counter electrode, a Hg/HgO electrode as the reference electrode, and a glassy carbon electrode as the working electrode with the diameter of 3 mm and geometric area of 0.07 cm^{-2}. The working electrode was prepared as follows: 2 mg of catalyst sample was dispersed in 1 mL of a mixed water-alcohol (3:1 v/v) solution, then 40 μL of 5 wt % Nafion solution was added as the binder. After sonication for 30 min, 20 μL of the suspension was loaded onto the surface of glassy carbon electrode and air-dried naturally at room temperature. The active loadings of catalyst were 0.55 mg cm^{-2}. The OER performances were tested in 1.0 M KOH using linear sweep voltammetry (LSV) with a scan rate of 2 mV s^{-1}. The HER performances of the as-prepared catalysts were tested in N_2-saturated 0.5 M H_2SO_4 by LSV with a scan rate of 5 mV s^{-1}. The measured potentials were converted to the reversible hydrogen electrode (RHE) and the overpotentials (η) for OER are calculated based on the following formula:

$$E_{RHE} = E_{Hg/HgO} + 0.095 + 0.0591\,pH \quad (1)$$

$$\eta = E_{RHE} - 1.23\ V \quad (2)$$

Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range of 100 kHz to 0.01 Hz at the applied potential of 1.58 V with AC amplitude of 5 mV. To estimate the catalytically active sites of the materials, the electrochemical double layer capacitance (Cdl) was measured by cyclic voltammetry curves at a potential range of 1.2–1.3 V (vs. RHE) with scanning rates of 1, 2, 5, 10, 15, and 20 mV s^{-1}. The obtained Cdl can be converted into an electrochemically active surface area (ECSA) using the formula: $ECSA = C_{dl}/C_S$, where the specific capacitance value was 40 μF cm^{-2} [37].

3. Results and discussion

A series of Co_9S_8 with different morphologies, from hexagon to ultrathin 2D nanosheets, were controllably synthesized by changing the filling factor in a facile hydrothermal process. The illustration of controllable synthesis of Co_9S_8 was schematically shown in Fig. 1. Because the boiling point of $N_2H_4{\cdot}H_2O$ (118.5 °C) and water (100 °C) were lower than the reaction temperature (180 °C), a high vapor pressure was produced inside the enclosed system. With