



Hierarchical cobalt sulfide with vertical in-plane edge structure for enhanced electrocatalytic oxygen evolution reaction

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ABSTRACT

Transition metal-based sulfides are hopeful nonprecious electrocatalysts for enhanced oxygen evolution reaction (OER). Compared with noble-metal based materials, such transition metal-based sulfides have been widely investigated in catalysis and energy storage, which can be easily controlled into various morphology due to their various valences. However, it is still a challenge to engineer transition metal-based sulfides of 3D nanostructure with rich edges. In this work, hierarchical cobalt sulfide nanocomposites (HCSN), with the vertical growth of Co_9S_8 nanosheets on horizontal Co_{1-x}S nanoplates, were fabricated via simple one-pot synthesis. Due to adequate exposed-edge planes, the HCSN exhibited remarkably catalytic property for OER with low overpotential of 275 mV at a current density of 10 mA cm^{-2} , a low Tafel slope of 30 mV/decade and excellent stability. By investigating the chemical states before and after OER, the possible catalytic mechanism was provided. This work may provide a simple and efficient method to prepare hierarchical metal sulfides for electrocatalytic OER.

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1. Introduction

The world energy crisis is now driving the development to produce renewable and sustainable energy with high efficiency, low cost and environmental benignity. Water splitting is a promising approach to provide oxygen and hydrogen for rechargeable metal-air batteries and fuel cells [1,2]. In these devices, high efficient electrocatalysts with catalytic activities toward oxygen evolution reaction (OER) [3,4] or hydrogen evolution reaction (HER) [5] play an important role to generate oxygen and hydrogen. However, in the process of water splitting, the half reaction of the OER with a complex four-electron process is kinetically inert [6,7]. Therefore, Pt and other precious metal-based materials such as Ru and Ir have been explored to lower the overpotential and accelerate the OER catalysis [8,9]. However, obvious disadvantages can be still found including low earth abundance, high cost and poor stability. Thus, it is still challenging to develop an active and earth-abundant OER catalyst for the water oxidation reaction.

Recent OER catalysts are transition metal compounds including oxides such as Co_3O_4 [10], NiO [11] and MnO_2 [12], and sulfides such as CoS_2 [13] and NiS [14] due to their low cost and high

stability. Especially, cobalt sulfides (Co_mS_n) can exist in various phases including Co_9S_8 [15], CoS [16], Co_3S_4 [17], CoS_2 [18] and Co_{1-x}S [19]. By their electrical and catalytic properties, Co_mS_n compounds exhibit potential in energy storage and conversion devices, such as electrochemical capacitors, catalysts for fuel cells [20] and dye-sensitized solar cells [21], and cathode materials for lithium-rechargeable batteries [22]. The increasing attention has been attracted to fabricate Co_mS_n with different morphologies such as zero-dimensional sulfide nanoparticles [23], one-dimensional sulfide nanowires [24] or two-dimensional sulfide nanosheets [25]. Nevertheless, these materials still suffer from high overpotential, low catalytic activity and poor cycling stability, since they cannot supply enough catalytic active sites or high structural stability.

In order to improve the electrocatalytic ability, cobalt sulfide nanocomposites have been developed by decorating cobalt sulfide nanoparticles on carbon nanotube [26], Co foam [27], graphene [28] and $\text{Ni}_2\text{S}_3/\text{graphene}$ [29], but the activity remains unsatisfactory in relative to the target RuO_2 , since the interaction of such substrate and cobalt sulfide nanoparticles is too weak to disperse them from aggregation and to supply sufficient electrical contact between these phases. Therefore, a direct growth of hierarchical 3D nanostructure is proposed with following properties. (1) No additional junction between nanosheets and nanoflakes is needed, which can bring out fast interfacial charge transfer and electrochemical reaction; (2) the direct growth of nanosheets on

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nanoflakes can effectively prevent their aggregation, resulting in large surface area, and short diffusion pathway for electron and electrolyte ion. However, it is still difficult to fabricate such a hierarchical nanostructure with ultrathin nanosheets. Especially, due to the thermodynamic driving force, cobalt sulfides tend to overgrow into large size and aggregate [30].

In this work, by synthesizing cobalt sulfide nanoflakes with rich in-plane edged nanosheets, a nanosheet-nanoflake-assembled 3D architecture was formed, which exhibited remarkable OER activity with overpotential of 275 mV at a current density of 10 mA cm^{-2} and a Tafel slope as low as 30 mV/decade. The structure was characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and N_2 absorption, and then a possible formation mechanism was proposed.

2. Experimental

2.1. Instruments

X-ray diffraction (XRD) patterns were recorded on a Rigaku-Ultima IV diffractometer, using $\text{Cu-K}\alpha$ ($\lambda = 1.518 \text{ \AA}$) radiation at 40 kV and 40 mA. The morphology was investigated using a scanning electron microscope (SEM, Hitachi S-4800 and SU-70) and a transmission electron microscopy (TEM, JEM-2100 F). The chemical states in the sample were detected by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi) with $\text{Al K}\alpha$ ($h\nu = 1486.6 \text{ eV}$) radiation source. Nitrogen absorption/desorption isotherms were measured at 77 K on a Gemini VII 2390 analyzer after samples were degassed for 24 h at $150 \text{ }^\circ\text{C}$ under N_2 flow, while the specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method.

2.2. Synthesis of hierarchical cobalt sulfide nanocomposites (HCSN)

All chemicals were from Aladdin Company. Cobalt acetate tetrahydrate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 1.5 mmol) and thiourea ($\text{CS}(\text{NH}_2)_2$, 4 mmol) were dissolved into 30 mL mixture of ethylene glycol and water. The solution was stirred for 1 h, transferred into stainless steel autoclaves and kept at $160 \text{ }^\circ\text{C}$ for 12 h. Then, the precipitates were washed with water and ethanol triplicate, followed by drying at $60 \text{ }^\circ\text{C}$ under vacuum. During the synthesis, the solvent ratio of ethylene glycol and water was systematically adjusted as 3:0, 2:1, 1:1, 1:2 and 0:3, thus the product was named as the 30 EW, 21 EW, 11 EW, 12 EW and 03 EW sample, respectively. Whereas for the 21 EW material, at the same ratio of 1.5:4, the concentration of raw materials were synchronously increased or decreased, which were named as the 8 m, 4 m, 2 m and 1 m sample, according to the amount of thiourea.

2.3. Electrochemical measurement

The electrochemical measurements were carried out at room temperature with a standard three-electrode system on CHI660E workstation. Platinum plate ($2 \times 2 \text{ cm}^2$) and an Hg/HgO electrode with 1 M KOH filling solution were used as the counter and reference electrode, respectively. The glassy carbon (GC) electrode with a diameter of 2 mm was used as the working electrode, which was polished with $0.05 \text{ }\mu\text{m}$ alpha alumina, cleaned in ethanol and water by sonication for 10 s and rinsed with water. Then the electrode was electrochemically activated by 40 cycles between -0.5 – 0.9 V at a scan rate of 100 mV s^{-1} in 1 M KOH. The catalyst ink was prepared by dispersing catalyst powder (3 mg) into a mixture of water (0.8 mL) and ethanol (0.2 mL) via sonication for 30 min, followed by the addition of $10 \text{ }\mu\text{L}$ Nafion solution (5 wt%). After that, $2.0 \text{ }\mu\text{L}$ of catalyst ink with a loading density of 0.19 mg cm^{-2} was drop-casted

on the polished GC and dried overnight.

The fresh 1 M KOH electrolyte was bubbled by high-purity O_2 till saturation before electrochemistry measurements. Cyclic voltammogram (CV) was performed for 10 cycles between 0 and 0.75 V vs Hg/HgO at a scan rate of 50 mV s^{-1} . Then, linear scan voltammogram (LSV) was measured at a scan rate of 1 mV s^{-1} without IR compensation. The electrochemical impedance spectroscopy (EIS) was measured by applying an AC voltage with 5 mV amplitude in a frequency range from 0.1 Hz to 100 KHz. The high-purity O_2 was kept bubbling at all the process to prevent CO_2 into KOH. For comparison, commercial noble metal oxide, RuO_2 , was also investigated under the same condition. In 1 M KOH ($\text{pH} = 13.6$), $E_{\text{vs.RHE}} = E_{\text{vs.Hg/HgO}} + 0.90 \text{ V}$, while the overpotential (η) can be calculated from $\eta = E_{\text{vs.RHE}} - 1.23 \text{ V} = E_{\text{vs.Hg/HgO}} - 0.33 \text{ V}$.

3. Results and discussion

3.1. Characterization of the HCSN

The HCSN was synthesized by the facile one-pot hydrothermal reaction. By simply adjusting the ratio of ethylene glycol and water, HCSN can grow along certain planes with obvious morphology change, where the crystalline information of precipitates were characterized by XRD. As in Fig. 1A, HCSNs with different solvent ratios are composed of two materials with Co_{1-x}S and Co_9S_8 . The 2θ peaks at 30.6° , 35.3° , 46.9° and 54.4° are corresponded to the (100), (101), (102) and (110) planes of hexagonal Co_{1-x}S (JCPDS Card No. 42-0826), while the main peaks at 29.9° , 39.5° , 52.2° and 73.4° are corresponded to the (311), (331), (440) and (731) planes of Co_9S_8 (JCPDS Card No. 19-0364). By increasing the content of ethylene glycol, the peak strength of the plane (311) and (440) of Co_9S_8 is gradually enhanced. As in Table 1, compared with the accompanied peaks at (100) and (102) of Co_{1-x}S , the relative strength ratio of the characteristic peak between Co_9S_8 and Co_{1-x}S increases, implying that Co_9S_8 grows along the crystal planes (311) and (440). According to Fig. 1B, when the concentration decreases from 4 to 1 mmol, only Co_9S_8 is produced. However, if the concentration increases from 4 to 8 mmol, the peaks of Co_{1-x}S are remarkably strengthened, suggesting the high concentration of raw materials is contributed to generate Co_{1-x}S . In earlier work, high temperature and high concentration of raw materials were benefit to form Co_{1-x}S when the solvent was pure ethylene glycol [31]. However, here, the crystalline of Co_{1-x}S for the 30 EW sample from pure ethylene glycol is poor and the amorphous Co_9S_8 didn't diffract the peak, since the temperature here is only $160 \text{ }^\circ\text{C}$. Water can help to strengthen crystalline of HCSN, since it can lower the solvent viscosity [32]. Therefore, the content of ethylene glycol and the concentration of materials are decisive factors to promote the generation of Co_9S_8 .

The morphologies of HCSN were further monitored by SEM. In Fig. 2, the HCSN shows different structures at different ratios of ethylene glycol and water. With only water as the solvent, as for the 03 EW sample (Fig. 2A and B), irregular nanoplates composed of little nanorods with approximate width of 20 nm and length of 100 nm can be discovered. However, when the volume ratio of ethylene glycol reaches 33% (Fig. 2C and D) as the 12 EW sample, the nanoplates are gradually self-assembled to a flower-like structure with the diameter of $3 \text{ }\mu\text{m}$, while many nanosheets with width of 15 nm and length of 100 nm are dispersed on every petals. The further increase of ethylene glycol to 50% (Fig. 2E and F) can form the 11 EW sample, where an obvious 3D structure of vertical nanosheets on horizontal nanoplates can be found. In addition, the nanosheets seem to grow larger with sharper edges, meaning a high surface area is exposed. The EDS of the 11 EW sample (Fig. S1) suggests that the 60.5% of Co atoms and 32.2% of S atoms in the

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