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Hydrophilic cobalt sulfide nanosheets as a bifunctional catalyst for oxygen and hydrogen evolution in electrolysis of alkaline aqueous solution



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ABSTRACT

Hydrophilic medium and precursors were used to synthesize a hydrophilic electro-catalyst for overall water splitting. The cobalt sulfide (Co_3S_4) catalyst exhibits a layered nanosheet structure with a hydrophilic surface, which can facilitate the diffusion of aqueous substrates into the electrode pores and towards the active sites. The Co_3S_4 catalyst shows excellent bifunctional catalytic activity for both the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) in alkaline solution. The assembled water electrolyzer based on Co_3S_4 exhibits better performance and stability than that of Pt/C-RuO₂ catalyst. Therefore the hydrophilic Co_3S_4 is a highly promising bifunctional catalyst for the overall water splitting reaction.

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1. Introduction

Hydrogen is widely considered a clean, alternative energy resource to fossil fuel [1–4]. Water splitting provides a promising

and reliable method to generate hydrogen from renewable energy sources, such as solar, wind and hydropower. In the water-splitting process, the use of high-performance electrodes is critical for effective minimization of energy consumption [5–10]. The activation energy and overpotential at the electrodes have been shown to be significantly reduced by using Electro-catalysts, resulting in faster reaction rates and lower operating voltages. Hence, high-

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performance electro-catalysts are highly desirable for improving the efficiency of the water-splitting process [11–14].

Currently, IrO_2 and RuO_2 catalysts show the highest efficiency for the oxygen evolution reaction (OER), while, Pt is the best performing catalyst for the hydrogen evolution reaction (HER) [15]. However, these noble metal catalysts are expensive and are not compatible with each other in the same electrolyte system [16– 18]. Therefore, the development of bifunctional metal catalysts with excellent catalytic activities for both HER and OER can simplify the system and lower the cost [1,19–21]. However, only a few such catalysts have been realized so far. Among them, cobalt-based catalysts (e.g., Co_2B [22], CoP [23], CoO [24] and Ni Co_2S_4 nanowires [18]), constitute an important class that has attracted great attentions in recent years.

In particular, cobalt sulfide (Co_3S_4) is known to show excellent catalytic activity for both HER in acidic electrolytes [20] and OER in alkaline electrolytes [25]. Compared with phosphate cobalt [26], the synthesis of cobalt sulfide does not produce toxic phosphine gas. However, Co_3S_4 has not been reported to show bifunctional catalytic activity for both OER and HER in the same electrolyte system. In the OER and HER process, catalysts with hydrophilic sites often show higher reactivity by maximizing the contact between the catalyst and electrolyte. However, most synthetic processes of cobalt sulfides involve the use of hydrophobic long alkyl chain precursors or solvents, such as Oleyl amine and 1-Dodecanethiol [20]. These strategies inevitably lead to the long hydrophobic chains covering the surface of catalyst and consequently preventing the aqueous substrates (H₂O, OH⁻ or H⁺) from contact with the catalytic active sites.

To provide a hydrophilic catalytic surface, we used hydrophilic solvent and precursors to synthesize Co_3S_4 . The as-prepared Co_3S_4 exhibits a layered nanosheet structure with good water dispersibility. This 2D nanostructure is conductive and supports an enlarged catalytic interface that improves charge transfer efficiency. More importantly, the hydrophilic Co_3S_4 (Co_3S_4 -L) showed excellent bifunctional catalytic activity for both OER and HER, as well as good stability in alkaline solution in a water electrolyzer.

2. Experimental

2.1. Catalyst synthesis

2.1.1. 1Synthesis of hydrophilic Co_3S_4 (Co_3S_4 -L)

3 mmol C₄H₆CoO₄·4H₂O was dissolved in Triethylene glycol (30 mL) in a two-neck flask. After all the solid was dissolved, 8 mmol C₃H₈O₂S was added to the mixture. Then it was heated to 220 °C under argon atmosphere. The reaction was kept at that temperature for about 3 h under the magnetic stirring. Then, the generated black solution was cooled to room temperature and then 10 mL of ethanol was added. The formed precipitate was centrifuged (at 5000 rpm, for 5 min), washed with ethanol for several times, and vacuum-dried at 60 °C for 4 h to provide the purified product.

2.1.2. Synthesis of hydrophobic Co₃S₄ (Co₃S₄-B)

3 mmol C₄H₆CoO₄·4H₂O and 30 mL Oleyl amine were put in a two-neck flask and stirred magnetically under argon atmosphere. After all the solid was dissolved, 8 mmol CH₄N₂S was added to the reaction mixture, then it was heated to 220 °C and kept at this temperature for 3 h. After cooling to room temperature, a black precipitate was obtained by adding 30 mL methanol to the solution and separated by centrifugation (at 5000 rpm, for 5 min). Then the black precipitate was washed with a mixture of methanol and methylbenzene (volume ratio is 5:1) for three times. Finally, Co₃S₄-B were obtained by drying in vacuum at 60 °C for 4 h.

2.2. Characterization

Scanning electron microscope (SEM) images, Transmission electron microscopy (TEM) and energy dispersive spectra (EDS) were acquired using a Hitachi SU-8010, Hitachi HT-7700 fieldemission electron microscope. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurement were carried out using Bruker D8 Advance X-ray diffractometer and PHI Quantera X-ray Photoelectrometer Spectrometer, respectively. Contact angles were tested by Dataphysics OCA15 Pro. Infrared absorption spectrum was acquired using a Thermo Nicolet IR spectrophotometer model (IR 460).

2.3. Assembly of Water-splitting electrolyzer

A mixture of the prepared catalysts, 1-Methyl-2-pyrrolidone and PVDF (Polyvinylidene Fluoride) (5%) brushed as an ink onto the carbon cloth (1 cm \times 1 cm). After drying, the sample was vacuum dried at 60 °C for 1 h.

2.4. Electrochemical measurements

Electrochemical measurements were performed on CHI630e electrochemistry workstation. The working electrodes consisted of 5 mm glassy carbon stick, with surface area of 0.197 cm² Samples were prepared for analysis by dispersing 3 mg of catalyst in 50 µL Nafion solution with 950 µL of H₂O. 27.5 µL of the catalyst ink was deposited onto the glassy carbon electrodes (~0.42 mg cm⁻²). All measurements were performed in 1M KOH solution, at the scan rate of 5 mV/s with 95% *iR*-compensation (*iR*-corrected), using a three-electrode cell that contained an Ag/AgCl-3 M KCI (with a double junction) as the reference electrode and a platinum wire (isolated in a proton exchange membrane sealed tube) as the counter electrode. The potential could be easily converted to the one versus Reversible Hydrogen Electrode (RHE) by using the Nernst equation: ($E_{RHE} = E_{Ag/AgCl} + 0.059 \times pH + E^0_{Ag/AgCl}$).

Additionally, the catalytic stability test was carried out using graphite plate electrode as the counter electrode. Before analysis, the electrolyte solution was purged with O_2 for at least 15 min. A constant stream of bobbing O_2 was maintained for all further electrochemical experiments. All measurements were performed at room temperature.

3. Results and discussion

In order to achieve a hydrophilic surface, hydrophilic solvent and precursors was selected to synthesize the target catalyst (Co_3S_4 -L). Our previous research has showed that 1-Thioglycerol is a highly reactive sulfur precursor for the synthesis of metal sulfides [27]. Therefore, we chose 1-Thioglycerol as the sulfur precursor. Triethylene glycol was used as the solvent because of its high boiling point and hydrophilic nature. Catalyst with hydrophobic surface (Co_3S_4 -B) was also synthesized and studied to demonstrate the critical role of hydrophilic surface in the high bifunctional catalytic performance of Co_3S_4 -L.

3.1. Structure and morphology analysis

X-ray diffraction (XRD) was used to characterize the crystal structure of the cobalt sulfides synthesized following our protocol. Fig. 1a shows the XRD patterns of the Co₃S₄-L. All of the diffraction peaks matched well with the structure of Co₃S₄ (JCPDS#42-1448), with the diffraction peaks at $2\Theta = 31.4^{\circ}$, 38.1° and 55.0° attributed to (3 1 1), (4 0 0), and (4 4 0) crystal faces, respectively. Co₃S₄-B showed similar XRD patterns, suggesting that the catalysts synthe-

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