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Flower-like CoS₂/MoS₂ nanocomposite with enhanced electrocatalytic activity for hydrogen evolution reaction

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ABSTRACT

Molybdenum sulfide (MoS₂) has received tremendous attracts for its promising performance in the aspects of hydrogen evolution reaction (HER). To improve the HER activity of MoS₂, we designed a flower-shaped CoS₂/MoS₂ nanocomposite with enhanced HER electroactivity compared with MoS₂ nanosheets by a simple one-step hydrothermal method. The facile approach brings about distinct transformation of the morphology from nanosheets to nanoflower structures. The introduction of Co element into MoS₂ results in the larger active surface area, more edge-terminated structures, and higher conductivity of the CoS₂/MoS₂ nanocomposite, which are good for improving the HER electroactivity. In brief, the optimized catalyst exhibits the low overpotential of 154 mV at 10 mA cm⁻², small Tafel slope of 61 mV dec⁻¹, and excellent stability in acidic solution.

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Introduction

Hydrogen, as a kind of environmentally friendly burgeoning resource, has stimulated extensive interests in multitudinous research fields [1–4]. Taking into account environmental pollution and the increasingly severe energy crisis, it is urgent to explore promising and appealing pathways which can generate sustainable and clean energy [5–10]. However, as the most effective catalyst for hydrogen evolution reaction (HER) in the aspects of electrochemical technology, platinum has been hindered by its intrinsic insufficiency (high cost and low reserves) in its broaden application [7,11]. Thus, exploring

highly efficient non-precious metal catalysts as a substitute for platinum has already become a significant subject for scientific researchers [12,13].

Molybdenum sulfide (MoS₂) is one of the most promising non-noble HER catalysts among various alternatives for its intriguing structure and property characteristics, which is concluded by both theoretical and experimental research [14–16]. As a typical semiconductor material, the poor intrinsic conductivity of MoS₂ limits electron transfer in the catalytic reaction and consequently HER activity [17]. Although the 2D layered structure of MoS₂ indeed makes it have a large surface area, the active sites for HER are mainly existed in the edges of the layers instead of the basal plane of

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2D MoS₂ [14]. Thus, the trouble is that bulk MoS₂ cannot act as an efficient HER catalyst itself for its poor conductivity and the worse exposure of electroactive sites [18,19]. Numerous attempts have been made to address this critical problem [20–23]. Engineering the surface structure of MoS₂ to expose more active sites for HER is an effective way, such as doping with other element [24–28], functional design of the structure [29], and controlling the growth of MoS₂ to form double-gyroid morphology [30]. To accelerate electron transfer between the catalyst and electrolyte in HER, supporting MoS₂ on Au [31], graphene [32,33] or carbon nanotubes [34] has been extensively proceeded. Among these efforts, doping with other element particularly Co may increase the HER performance by tuning the electron characteristic of MoS₂. For example, Bao et al. validated single Co atom doped MoS₂ can provide moderate adsorption free energy of H* (ΔG_{H}) and exhibit good stability in HER [27]. Hu et al. synthesized Co-MoS₃ films with a low overpotential of 188 mV at 10 mA cm⁻² for HER, originating from the strengthened effects of Co²⁺ ions [35]. Especially, CoS₂, with the superiority of metal-like conductivity [36], may favor the electron transfer of MoS₂ in HER if it integrated with MoS₂. For example, CoS₂/MoS₂ on carbon fiber cloth [37], CoS₂-MoS₂ supported on carbon nanotubes [38], and MoS₂-CoS₂ nanowire arrays on carbon cloth [39] were produced as efficient electrochemical catalysts for HER. However, these catalysts still suffered from the complicated synthesis process or the low electrocatalytic activity for HER.

Herein, we designed a flower-like nanocomposite of CoS₂ and MoS₂ with enhanced HER electroactivity by a facile one-step hydrothermal method without noble metal. On one hand, the irregular arranged MoS₂ nanosheets can be self-assembled into nanoflower structures after the introduction of Co, which may increase the effective electrochemical area with more HER active sites. On the other hand, the incorporation of CoS₂ promotes the conductivity of the composite, resulting in enhanced catalytic activity for HER. Under the optimized conditions, the composite (180-CoS₂/MoS₂-2) exhibits the best HER performance with low overpotential, small Tafel slope, and excellent stability in acidic medium.

Experimental section

Materials

Co(NO₃)₂·6H₂O, (NH₄)₆Mo₇O₂₄·4H₂O, and Pt/C (20 wt %) were obtained from Sinopharm Chemical Reagent Co. Ltd., Xilonghuagong Co. Ltd., and Johnson Matthey, respectively. Thiourea (CS(NH₂)₂), CH₃CH₂OH (~99 wt %), and H₂SO₄ (~98 wt %) were purchased from Beijing Chemical Reagent Co. Ltd. Nafion (5 wt %) was purchased from Sigma–Aldrich. All the reagents were of A. R. grade and used as received without further purification. All aqueous solutions were prepared with ultrapure water from a Water Purifier System (Sichuan Water Purifier Co. Ltd., China).

Catalysts preparation

The x-CoS₂/MoS₂-y, in which x means the synthesis temperature and y means the molar ratio of (NH₄)₆Mo₇O₂₄·4H₂O to Co(NO₃)₂·6H₂O, was synthesized by the following typical

process. (NH₄)₆Mo₇O₂₄·4H₂O (1.0 mmol), (CS(NH₂)₂) (30 mmol), and Co(NO₃)₂·6H₂O (0.50 mmol) were dissolved into distilled water (35 mL) under vigorous stirring. After forming a homogeneous solution, the solution was transferred into a 50 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 24 h. After cooling to room temperature naturally, the obtained products were collected by centrifugation, washed with distilled water and ethanol for several times to remove any impurities, and then dried at 60 °C under vacuum. The final product was named as 180-CoS₂/MoS₂-2. For comparison, MoS₂ was synthesized under the same conditions without Co(NO₃)₂·6H₂O. CoS₂ was synthesized with Co(Cl)₂·6H₂O (1.0 mmol) and (CS(NH₂)₂) (5.0 mmol) as reactants for 12 h under the same conditions. The as-prepared catalysts with various molar ratios of (NH₄)₆Mo₇O₂₄·4H₂O to Co(NO₃)₂·6H₂O (10:1, 50:1, and 100:1) were prepared under the same conditions, and denoted as 180-CoS₂/MoS₂-10, 180-CoS₂/MoS₂-50, and 180-CoS₂/MoS₂-100, respectively. The catalysts synthesized at 150 and 200 °C were named as 150-CoS₂/MoS₂ and 200-CoS₂/MoS₂, respectively.

Instruments

Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDS) analysis were obtained from an XL 30 ESEM FEG SEM (Philips, Netherlands). Transmission electron microscopy (TEM) images, high-resolution TEM (HRTEM) image, high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image, and corresponding energy-dispersive X-ray (EDX) elemental mapping were carried out on a FEI TECNAI G² F20 STWIN TEM (FEI, Holland) operated at 200 kV. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE (Bruker AXS, Germany) X-ray diffractometer (Cu K_α radiation) in the 2θ range of 5° to 65°. X-Ray photoelectron spectroscopy (XPS) analysis was carried out on an ESCALAB MKII X-ray photoelectron spectrometer (VG Scientific, UK) with Al K_α X-ray radiation as the X-ray source for excitation. Raman spectra were obtained from the LabRAM HR Evolution Raman Spectrometer (HORIBA Scientific, France).

Electrochemical measurements

All electrochemical experiments were performed in 0.50 M H₂SO₄ with a three-electrode system. It consists of a catalyst modified glassy carbon electrode (GCE) as working electrode, an Ag/AgCl (saturated KCl) electrode as reference electrode, and a graphite rod as counter electrode, respectively. The potential, measured against the Ag/AgCl electrode, was converted to reversible hydrogen electrode (RHE) according to $E(\text{vs RHE}) = E(\text{vs Ag/AgCl}) + 0.059 \text{ pH} + 0.197$. For the electrode modification, 6 mg of catalyst powder was dissolved in a mixture (3.0 mL) of water, isopropyl alcohol, and Nafion (5.0 wt%) with a ratio of 20:1:0.075 (v/v/v). Then the mixture was ultrasonicated for 2 h to generate a homogeneous ink, which was transferred onto the GCE surface with a loading of 0.285 mg cm⁻². For comparison, the Pt/C modified GCE was prepared according to the same method with optimal amount of catalyst (25 μg Pt cm⁻²). Linear sweep voltammetry (LSV) was measured at a scan rate of 5 mV s⁻¹ without activation

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