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MoS_2 nanoparticles coupled to SnS_2 nanosheets: The structural and electronic modulation for synergetic electrocatalytic hydrogen evolution

Lin Hu[a], Xiu-Feng Song[a,*], Sheng-Li Zhang[a], Hai-Bo Zeng[a], Xue-Ji Zhang[a], Robert Marks[b], Dan Shan[a,*]

[a] MIIT Key Laboratory of Advanced Display Materials and Devices, School of Environmental and Biological Engineering, Nanjing University of Science and Technology, Nanjing 210094, China
[b] Department of Biotechnology Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel

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ABSTRACT

The electrocatalytic hydrogen evolution reaction (HER) is one of the core components of energy conversions. The chemical-physical properties and morphological structures of electrocatalysts are the main factors that determine the HER performance. Thus, the rational design of efficient electrocatalysts is essentially required. A new heteronanostructured system is proposed, which comprises MoS_2 nanoparticles (MoS_2 NPs) coupled to SnS_2 ultrathin nanosheets (SnS_2 NS) and operates as an efficient HER electrocatalyst. Advanced spectroscopic techniques are applied to confirm formation of heteronanostructure and occurred electron modulation of MoS_2 NPs/SnS_2 NS. Surprisingly, the MoS_2 NPs/SnS_2 NS electrocatalyst is highly efficient for HER with a low overpotential (~0.249 V at the current density of 10 mA cm^{-2}), small Tafel slope (~42.1 mV $decade^{-1}$) and excellent electrocatalytical stability.

1. Introduction

Clean and sustainable hydrogen generation renders a magnificent prospect to fulfil the human's dream of rebuilding energy supplying systems that work eternally without pollution [1,2]. Water electrolysis driven by a renewable resource of energy, such as wind and solar, is a promising pathway to achieve this goal, which requires highly active and cost-effective electrocatalysts to be developed. Electrode catalytic materials for water electrolysis have complicated chemical composition and multi-level structure, of which the chemical-physical properties and morphology structure are the main factors that determine the performance of electrolysis of water [3,4].

Owing to the earth-abundant nature and high electrochemical activity, as one of transition metal dichalcogenides, MoS_2 has been regarded as promising electrocatalyst for hydrogen evolution reaction (HER) [5–7]. Computational and experimental results demonstrated that the basal planes of MoS_2 were perfect and catalytically inert, while the active sites derived from the sulfur edges of MoS_2. Layer [8–10]. The limited surface area, poor electrical conductivity, and especially, the lack exposure of active edges of MoS_2 nanostructures still remain a challenge in using MoS_2-based electrocatalysts for HER [11].

For the further improvement of HER performance of MoS_2, many strategies have focused on the increasing the density of active sites by exploring the high catalytic behavior of nanostructured MoS_2, such as nanoflakes [12,13], amorphous structures [14–18], clusters [19], vertically aligned layers [20,21], and quantum dots [22–25]. Considerable efforts have been also devoted into enhancing the conductivity. Generally, MoS_2 NPs were anchored on conductive surface such as carbon nanotube, g-C_3N_4, or graphene [26–34]. The conductivity and catalysis can be adjusted through the chemical composition. For instance, cationic doping with a small fraction of cobalt or nickel is well-known [35,36]. Moreover, the "defect design" of basal plane of MoS_2 by creating the special heterostructure, resulting in the more metallic phase of MoS_2 [37,38].

Most recently, the development of catalytic activity was obtained by $MoSe_2$-NiSe vertical heteronanostructure due to the injection of electrons from NiSe onto the $MoSe_2$ nanosheets [39]. It indicates that electrocatalytic ability of MoS_2 based materials can be further enhanced by promoting the electronic injection from one semiconductor to MoS_2. Encouraged by the synergistic effect of electronic injection, the design of MoS_2 NPs-Metal sulfide hybrids could be a good strategy to enhance the electrocatalytic performance of MoS_2. Because the similar material structure, the different band structure of the composite materials and the

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* Corresponding authors.
E-mail addresses: xiufengsoong@njust.edu.cn (X.-F. Song), danshan@njust.edu.cn (D. Shan).

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alignment of the energy levels at the interface can facilitate the separation of electrons and holes, as well as efficient and fast interfacial charge transfer, which could enhance the electrocatalytic performance of MoS_2 catalysts for HER.

Based on the above assumption, tin disulfide (SnS_2) ultrathin nanosheet was initially synthesized by liquid exfoliation, which has the similar hexagonal layered structure with MoS_2. As a result, we proposed a novel heteronanostructure based on MoS_2 NPs/SnS_2 NS to investigate the effect of structural and electronic modulation for synergetic electrocatalytic HER. The coupling of MoS_2 NPs to SnS_2 Ns was achieved by controlling MoS_2 NPs growth on SnS_2 NS via solvothermal method. SnS_2 NS worked as substrate and prevented efficiently the agglomeration of in-situ formed MoS_2 nanocrystallites, resulting in as-formed MoS_2 of low-dimensionality with more exposure active sites. Besides, the fine distribution of MoS_2 NPs on SnS_2 NS ensure the formation of high-quality heterointerfaces. The occurred electronic modulation was confirmed by computational calculations as well as advanced spectroscopic experiments.

2. Experimental section

2.1. Chemicals

All the reagents were purchased from Aladdin without further purification.

2.2. Instruments

The SEM and TEM measurements were performed on FEI Quanta 250F scanning electron microscopy and TEM, FEI Tecnai G20 transmission electron microscopy. AFM measurements were carried out on Bruker MultiMode 8 atomic force microscopy. The electronic structures were performed with ultraviolet photoemission spectroscopy (UPS, PHI 5000 VersaProbe III) with a monochromatic He I light source (21.2 eV) and a VG Scienta R4000 analyzer. A sample bias of −5 V was applied to observe the secondary electron cutoff.

2.3. Synthesis of SnS_2 NS

SnS_2 NS used in this work was synthesized easily by liquid exfoliation as described below: 100 mg SnS_2 powder was dispersed in 100 mL deionized water and then bubbled with argon (Ar) for 30 min. After that, the solution was sonicated in an ice-bath for 2 h at a power of 250 W in an Ar atmosphere. The resulting dispersion was centrifuged at 6000 rpm for 10 min to remove the residual unexfoliated particles. The collected supernatant with SnS_2 NS was subjected to Ar bubbles and characterized.

2.4. Synthesis of MoS_2 NPs/SnS_2 NS

MoS_2 NPs/SnS_2 NS was synthesized by controlling MoS_2 NPs growth on as-prepared SnS_2 NS via solvothermal method. The optimal protocol was as follow: 20 mg $(NH_4)_2MoS_4$ and 10 mg SnS_2 were dispersed in 10 mL DMF, followed by sonication for 30 min at room temperature until an homogeneous solution was achieved. Then, the $N_2H_4{\cdot}H_2O$ with 0.1 mL was added into the solution. After that, the solution mixture was sonicated for 10 min before transferred to a 40 mL Telflon-lined autoclave. The reaction solution was heated at 200 °C for 10 h in the oven and cooled down until reaching room temperature. The resulting precipitate was collected by centrifugation and washed by DI water for at least 5 times. Finally, the product was freeze-dried to obtain the MoS_2 NPs/SnS_2 NS.

2.5. Electrochemical measurements

1 mg of catalyst (Pt/C, MoS_2 NPs, SnS_2 NS or MoS_2 NPs/SnS_2 NS) was dispersed in 1 mL DI water with sonication at least 30 min to form colloidal solution (1 mg mL^{-1}). 5 L of catalyst solution was spread on the surface of bare glass carbon electrode (GCE) (3 mm in diameter) and dried in air. 5 L of 0.5 wt% Nafion solution was then finally covered on the surface of above-modified electrode and dried in air.

All electrochemical studies were carried out with a conventional three-electrode cell, in which the Ag/AgCl electrode was used as reference electrode and a platinum wire was used as counter electrode, as well as the 0.5 M H_2SO_4 as electrolyte. In all electrochemical studies, the reference electrode was calibrated with respect to reversible hydrogen electrode (RHE). The scan rate of linear sweep voltammetry (LSV) was set at 10 mV s^{-1}. Before electrochemical testing, the electrolyte was bubbled with N_2 for 15 min. The electrochemical impedance spectroscopy (EIS) measurements were carried out at an overpotential of 250 mV over a frequency range from 0.01 Hz to 100 kHz with an amplitude of 10 mV. The frequency was fixed at 1 kHz for the Mott-Schottky measurements.

2.6. Calculation method

The structural optimizations and electronic structure calculations were conducted in the context of the density functional theory as implemented by VASP code. We employed the hybrid Heyd-Scuseria-Ernzerhof functional to obtain accurate electronic properties of both MoS_2 NPs and SnS_2 NS, respectively. The wave functions were constructed using a projected augmented wave approach with a plane wave cutoff energy of 520 eV. The convergence threshold was set as 10^{-4} eV in energy and 10^{-3} eV $Å^{-1}$ in force. The Brillouin zone integration was sampled using a set of 13′13′1 Monkhorst-Pack k-points.

3. Results and discussion

The proposed MoS_2 NPs/SnS_2 NS was tentatively designed based on electronic injection from SnS_2 NS to MoS_2 NPs. To address this issue, computational calculations on the electronic structure monolayer of MoS_2 and SnS_2, and the structural optimization of MoS_2 NPs/SnS_2 NS were initially performed. The band structures of SnS_2 and MoS_2 were analyzed according to density functional theory. The corresponding computational results are illustrated in Fig. 1A. MoS_2 appeared to be a direct band-gap semiconductor with band gap of 1.80 eV at the HSE06 level, and its conduction band maximum (CBM) and the valence band minimum (VBM) are located at K high-symmetry point. Differently, SnS_2 is an indirect band-gap semiconductor with band gap of 2.60 eV at the HSE06 level, its CBM is located at M high-symmetry point, whereas VBM is between G and M high-symmetry point in the Brillouin zone. Generally, structural optimization is highly relative to character of chemical bonding, which can be evaluated by the deformation electronic density. Fig. 1B displays the deformation electronic density of the MoS_2 NPs/SnS_2 NS. Inspection reveals that there is remarkable electron transfer (about 0.1 e^-) from SnS_2 ($\sqrt{2} \times \sqrt{2}$) to MoS_2 ($\sqrt{7} \times \sqrt{7}$), clearly indicating the charge separation in the MoS_2 NPs/SnS_2 NS heterostructure. This theoretical confirmation on occurred electron injection encouraged us to synthesize MoS_2 NPs/SnS_2 NS and experimentally investigate its synergistic effect on enhanced HER performance.

The SnS_2 NS used in this work were synthesized by liquid exfoliation, and the thickness of the as-prepared nanosheets was further determined to be approximately 27 nm by AFM (Fig. S1).