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Communication

Laser-direct-writing of 3D self-supported NiS₂/MoS₂ heterostructures as an efficient electrocatalyst for hydrogen evolution reaction in alkaline and neutral electrolytes

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ABSTRACT

Searching for low-cost widely applicable electrocatalysts for hydrogen production is very important. Here, 3D self-supported NiS₂/MoS₂ heterostructures were synthesized via a one-step millisecond-laser-direct-writing method; these structures exhibited excellent hydrogen evolution reaction activities over a wide pH range. The current density of 10 mA cm⁻² could be reached at low overpotentials of 98 and 159 mV in alkaline and neutral electrolytes, respectively. Such an outstanding electrocatalytic performance should be attributed to the integration of the 3D self-supported nanostructures, the high conductivity of the framework, and particularly, the incalculable heterointerfaces formed between NiS₂ and MoS₂. This work provides a new strategy to study interfacial engineering and the mechanism of interface enhancement.

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As we know, electrocatalytic water splitting through hydrogen evolution reaction (HER) is a promising and sustainable pathway for H₂ production [1–4]. Up to now, the high-performance catalysts reported could only achieve high HER activities in acidic or alkaline conditions; these catalysts are based on Pt and other noble metals, which are rare and precious [5,6]. However, considering the demands on electrolysis equipment and the need for environmental protection, it is better to find efficient electrocatalysts for the HER in neutral media, which suffer from a large ohmic loss and low electron density of the neutral electrolyte [7]. Therefore, it is necessary to develop low-cost and widely applicable electrocatalysts for industrialization of hydrogen production in the near future.

To date, bimetal sulfide hybrids with diverse structures have exhibited attractive HER activities because of the reliability and plenitude of the active redox sites provided by both the

metal sulfide components [8,9]. Moreover, the interface between the two components brings about synergistic effects, which, owing to enrichment of the active sites and reconfiguration of the electronic structures, further enhance the HER activity, compared with those of their single-component counterparts [10–12]. For example, Zhang et al. [13] engineered the interface of MoS₂/Ni₃S₂ heterostructures with excellent water-splitting electrocatalytic properties in alkaline solutions. It has been confirmed that the lattice interfaces of NiS₂/MoS₂ heterojunctions are propitious to the dissociation of H₂O as part of all-pH HER [14]. Therefore, engineering of the interfacial structure between NiS₂ and MoS₂ is the key to further enhancing the HER activity in a wide pH electrolyte, particularly in alkaline and neutral conditions.

Here, we synthesized three-dimensional (3D) self-supported NiS₂/MoS₂ heterostructures on nickel foams by

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a facile method, namely, millisecond-laser-direct-writing; these structures can be directly used as an electrode for electrocatalyzing water splitting to produce H_2 , and exhibited outstanding HER activities in both alkaline and neutral electrolytes. In this work, we provide a new strategy for interface control. Thanks to the high instantaneous temperature and rapid cooling in this method, the heterostructures easily constitute highly dispersed minor-sized NiS_2 nanoparticles and MoS_2 nanosheets that exhibit large specific surface areas and abundant heterointerfaces between NiS_2 and MoS_2 , which ensure a larger amount of catalytically active sites compared to those obtained in other works. Additionally, the 3D porous micro/nanostructure is propitious to electrolyte permeation as well as H_2 diffusion, which further guarantees a distinguished electrocatalytic performance.

The synthetic method of catalysts, namely millisecond-

laser-direct-writing [15], is illustrated in Scheme S1. The 3D NiS_2/MoS_2 heterostructures were formed by the ablation of the millisecond laser and the rapid quenching of plasma comprising elements from the nickel foam and $(NH_4)_2MoS_4$ solution. As shown in Fig. 1a, the products were grown in-situ on the nickel foam at locations that were laser treated. The X-ray diffraction (XRD) pattern has been provided in Fig. S1, and it indicates the existence of two metal sulfides, instead of doping. We can see nanospheres piled on the nickel foam surface (Fig. 1b), and the size of the nanospheres is about 100 nm, with the surface appearing rough or wrinkled (Fig. 1c). It is obvious that MoS_2 nanosheets with a thickness of about 5 nm interweaved in NiS_2 nanoparticles of sizes below 30 nm, and the two mixed irregularly in the nanospheres (Fig. 1d). As a result, a massive heterointerface developed in the nanospheres between NiS_2

Fig. 1. (a) SEM images of NiS_2/MoS_2 heterostructures on nickel foam. (b, c) SEM, (d) TEM, and (e) HRTEM images of the NiS_2/MoS_2 heterostructures. (f) Enlarged view of the heterointerface formed between NiS_2 and MoS_2 lattice fringes. (g) HAADF and (h–j) EDS mapping images of the NiS_2/MoS_2 heterostructures. High-resolution X-ray photoelectron spectroscopy (XPS) spectra of (k) Ni 2p and (l) Mo 3d.

and MoS₂ (Fig. 1e and S2). Lattice fringes with lattice distances of approximately 0.25 and 0.61 nm well corresponded to the (210) lattice plane of NiS₂ and the (002) lattice plane of MoS₂ (Fig. 1f), respectively. The fast Fourier transform patterns of MoS₂ and NiS₂ reveal their high crystallinities (inset of Fig. 1f), which match well with the XRD results. Energy dispersive X-ray spectroscopy (EDS) reveals the elemental composition of the sample (Fig. S2d). Moreover, scanning transmission electron microscopy results and the corresponding EDS mapping images show that nickel, molybdenum, and sulfur are well distributed in the NiS₂/MoS₂ heterostructures (Fig. 1g–j), which in turn indicates that NiS₂ and MoS₂ are well dispersed in the heterostructures.

XPS measurements were used to examine the chemical states of the elements in the NiS₂/MoS₂ heterostructures (Fig. S3). The Mo 3d spectrum of the NiS₂/MoS₂ heterostructures shows two significant peaks located at 229.5 and 232.7 eV, which are ascribed to Mo 3d_{5/2} and Mo 3d_{3/2}, respectively, which indicate the dominance of Mo⁴⁺ in NiS₂/MoS₂ [16]. However, in the spectrum of pure MoS₂ nanosheets, these peaks appear at 229.2 and 232.5 eV (Fig. 1h). In the Ni 2p spectrum of the NiS₂/MoS₂ heterostructures, the Ni 2p_{3/2} and 2p_{1/2} peaks are observed at 855.4 and 872.9 eV, along with two satellite peaks, that represent Ni²⁺ [17]. Obviously, compared with the peaks of pure NiS₂, these peaks display a positive shift of nearly 0.4 eV (Fig. 1i). The positive shift in the Mo 3d and Ni 2p spectra of the NiS₂/MoS₂ heterostructures suggests the existence of strong electronic interactions between NiS₂ and MoS₂, which indicates the establishment of coupling interfaces [13], more precisely named as a heterointerface. Moreover, the XPS pattern of physically mixed NiS₂ and MoS₂ provides further

support to the above conclusion (Fig. S4) because no peak shifts are observed.

To evaluate the HER catalytic activity of the NiS₂/MoS₂ heterostructures in alkaline media, we established a three-electrode system in 1 mol L⁻¹ KOH electrolyte. As shown in Fig. 2a, the overpotential of the NiS₂/MoS₂ heterostructures is 98 mV, with 10 mA cm⁻² constant cathodic current density (η_{10}). On the other hand, nanostructured NiS₂ and MoS₂ both show lower HER electrocatalytic activities, with η_{10} of 221 and 320 mV, respectively, which reveal the necessity of the heterointerface. Besides, the curve of the nickel foam (η_{10} = 253 mV) indicates that although the substrate plays an important role in gas diffusion, it is not the main reason for the improvement in the HER performance. Fig. 2b reveals the Tafel slope of the NiS₂/MoS₂ heterostructures as 88 mV dec⁻¹, which suggests that the HER follows the Heyrovsky mechanism. Further, this Tafel slope is notably smaller than those of NiS₂, MoS₂, and nickel foam, which were calculated as 178, 154, and 227 mV dec⁻¹, respectively. The outstanding HER activity reported above indicated that these heterostructures outperformed many transition metal sulfides in basic solutions (Table S1). Cyclic voltammograms were recorded at different scan rates in the range of non-Faradaic potentials (Fig. S6), and the capacitive currents were plotted against the scan rates, the slopes of which corresponded to the electrochemical double-layer capacitance (Cdl; Fig. 2c). In line with the low Tafel slope, the NiS₂/MoS₂ heterostructures exhibit the highest electrochemical active surface area (ECSA), based on the Cdl, which suggests the existence of more active sites in the NiS₂/MoS₂ heterostructures and smaller η_{10} (Fig. 2d).

The EIS results of the NiS₂/MoS₂ heterostructures are

Fig. 2. (a) Polarization curves and (b) the corresponding Tafel plots of NiS₂/MoS₂, NiS₂, MoS₂, and Pt/C electrodes obtained at a scan rate of 5 mV s⁻¹ in 1.0 mol L⁻¹ KOH. (c) Current densities (j) of NiS₂/MoS₂, NiS₂, MoS₂, and nickel foam plotted against the scan rate at -0.55 V vs Hg/HgO. (d) Electrochemical double-layer capacitance and η_{10} of NiS₂/MoS₂, NiS₂, and MoS₂. Results of (e) electrochemical impedance spectroscopy (EIS) and (f) chronoamperometric measurements of the samples.

shown in Fig. 2e. Obviously, compared with those of NiS₂, MoS₂, and nickel foam, the Nyquist plot of the NiS₂/MoS₂ heterostructures suggests a smaller charge transfer resistance (*R*_{ct}), which is advantageous in improving the HER activity. As shown in Fig. 2f, a long-term test based on galvanostatic measurement at about 10 mA cm⁻² in 1 mol L⁻¹ KOH solution was carried out for 10 h to evaluate the stability of the NiS₂/MoS₂ heterostructures. Only 12% reduction from the original current density is observed for the NiS₂/MoS₂ heterostructures, and the polarization curves reveal no obvious changes after the long-term test (inset of Fig. 2f); on the other hand, evident decreases are observed for the other materials (Fig. S7). Besides, the XRD, SEM, TEM, and XPS results presented in Fig. S8–10 indicate that after the long-term test, the NiS₂/MoS₂ heterostructures still remain, though the content has reduced.

It is particularly noted that not only in an alkaline electrolyte, but also in 1 mol L⁻¹ PBS solution (as a neutral electrolyte), the NiS₂/MoS₂ heterostructures display excellent HER performances. As shown in Fig. 3a, the η_{10} of the NiS₂/MoS₂ heterostructures is 157 mV, which is optimum when comparing with those reported for other transition metal sulfides (Table S2). Meanwhile, the η_{10} of NiS₂, MoS₂, and nickel foam as electrodes are 224, 261, and 406 mV, respectively. As for the Tafel plots (Fig. 3b), the NiS₂/MoS₂ heterostructures exhibit a Tafel slope of 109 mV dec⁻¹, which is lower than those of NiS₂ and MoS₂, which suggests facile electron transfer for the HER. The superior HER activity and promoted charge transfer should be ascribed to the higher ECSA of the NiS₂/MoS₂ heterostructures, which is further confirmed by the Cdl investigations (Figs. 3c, 3d and S11). The improved charge transfer was also verified by

EIS measurements (Fig. 3e), with the NiS₂/MoS₂ heterostructures displaying the smallest charge transfer resistance, compared to those of the other samples. In addition, the NiS₂/MoS₂ heterostructures also present excellent stability under neutral conditions, and no noticeable change in the polarization curve is observed after long-term electrolysis (Figs. 3f and S12).

According to the literature, Kuang and coworkers [14] performed DFT calculations to obtain the chemisorption free energies of hydroxide (ΔE_{OH}) and hydrogen (ΔE_{H}) on the nickel and sulfur sites on the (210) plane of NiS₂ and molybdenum, and on the sulfur and Mo-S edge sites on the (002) plane of MoS₂. It was concluded that the nickel and molybdenum sites at the heterointerface offered the best locations for OH and hydrogen adsorption. Furthermore, Zhang and coworkers [13] calculated the chemisorption free energies based on a more accurate model of MoS₂/Ni₃S₂ heterostructures, and deduced that the nickel site on the (101) plane of molybdenum-doped Ni₃S₂ and the molybdenum-sulfur edge site on the (002) plane of nickel-doped MoS₂ should be the sites where the HER proceeds. As shown in Fig. 4, based on the above findings, it is not difficult to conclude that the heterointerface of NiS₂/MoS₂, where the chemisorption free energies of the intermediate are obviously reduced, is the key factor for improving the catalytic activity; while the nickel sites act as centers where the dissociation of H₂O occurs, the molybdenum sites favor the absorption of hydrogen-containing groups.

In summary, based on previous work, we have prepared a non-noble-metal and efficient catalyst, namely, NiS₂/MoS₂ heterostructures, composed of highly dispersed NiS₂ nanoparticles and MoS₂ nanosheets that were in-situ grown on a nickel foam

Fig. 3. (a) Polarization curves and (b) the corresponding Tafel plots of NiS₂/MoS₂, NiS₂, MoS₂, and Pt/C electrodes obtained at a scan rate of 5 mV s⁻¹ in 1.0 mol L⁻¹ PBS. (c) Current densities (*j*) of NiS₂/MoS₂, NiS₂, MoS₂, and nickel foam plotted against the scan rate at -0.55 V vs Hg/HgO. (d) Electrochemical double-layer capacitance and η_{10} of NiS₂/MoS₂, NiS₂, and MoS₂. Results of (e) electrochemical impedance spectroscopy and (f) chronoamperometric measurements of the samples.

Fig. 4. Proposed mechanism of the dissociation of H_2O within the $\text{NiS}_2/\text{MoS}_2$ heterointerface.

by using a one-step millisecond-laser-direct-writing method. This technique is not only simple, but also reduces the sizes of the two phases, so that the unit volume contains more heterointerfaces that are exposed. The combined advantages of a 3D porous structure, highly conductive self-supporting electrode, high specific surface area, and most importantly, synergistic effect at the heterointerface have led to greatly enhanced HER performances in both alkaline and neutral electrolytes, which suggest high promise for applications related to industrialized electrochemical H_2 production. Though the acidity properties require further improvement, this work provides a new pathway of engineering the interfaces of composites for developing low-cost and highly efficient electrocatalysts for water splitting.

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Graphical Abstract

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Laser-direct-writing of 3D self-supported $\text{NiS}_2/\text{MoS}_2$ heterostructures as an efficient electrocatalyst for hydrogen evolution reaction in alkaline and neutral electrolytes

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Mechanisms have been proposed for the dissociation of H_2O , and the HER performance of $\text{NiS}_2/\text{MoS}_2$ heterostructures in different electrolytes was evaluated.

激光直写制备三维自支撑NiS₂/MoS₂复合电催化剂应用于碱性和中性电解水制氢

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摘要: 电催化析氢反应(HER)是一种有前途和可持续的制氢途径。到目前为止, 所报道的高性能催化剂如铂和其他贵金属基催化剂大多只能在酸性或碱性条件下展现出优异的HER催化活性, 而且这些贵金属储量稀少, 催化剂制备成本高昂。此外, 考虑到电解设备和环境保护的要求, 在中性介质中寻找高效的HER电催化剂是潜在的发展方向, 但也需要克服中性电解质中欧姆损失较大、电子密度较低等问题。因此, 开发低成本、应用广泛的电催化剂是今后实现制氢产业化的必然选择。根据已有研究, 具有不同结构的双金属硫化物杂化物由于两种金属硫化物成分所提供的可靠且充分的氧化还原活性位点, 显示出其具有吸引力的活性。此外, 由于丰富的活性位点和重新配置的电子结构, 复合材料两组分之间的界面产生协同效应会进一步增强催化剂的HER催化活性。之前的工作已经在同样材料体系中获得了较好的催化性能, 但是在宽pH条件下的HER催化性能却不如意。因此, NiS₂与MoS₂界面结构的优化是进一步提高其在宽酸碱度电解质中活性的关键。

本文使用毫秒激光直写法在镍泡沫上合成了三维(3D)自支撑的NiS₂/MoS₂异质结构, 并将其直接用作电解水析氢反应电极, 后者在碱性和中性电解质中都表现出了优异的HER活性。毫秒激光直写法具有瞬时高温和快速冷却的特点, 常用于纳米材料的制备。毫秒激光作用于溶液中的泡沫镍时, 由于瞬间高温使其气化, 与溶液中的离子、分子等组成了等离子体, 随后借助液体环境的急速冷却限制效应, 这团高温混合物在靶材表面原位生长出NiS₂/MoS₂纳米复合催化剂。通过物相表征, 发现NiS₂/MoS₂异质结构是由高度分散的小尺寸NiS₂纳米粒子和MoS₂纳米片组成, 这些纳米片具有较大的比表面积以及大量NiS₂与MoS₂之间的界面。借助宏观XPS表征, 我们可以确认在NiS₂/MoS₂异质结构的界面处存在强烈的电子相互作用, 说明复合材料两相之间存在异质界面。而异质界面可以作为HER反应过程中的催化位点, 有利于水分子的裂解吸附, 从而提升复合材料的催化性能。我们对NiS₂/MoS₂复合催化剂在碱性(1 mol L⁻¹ KOH)和中性(1 mol L⁻¹ K₂SO₄)条件下分别进行了HER性能测试。结果表明, 在10 mA cm⁻²的电流密度下, 催化剂在碱性和中性电解质中的过电势分别为98和159 mV, Tafel斜率分别为88和130 mV dec⁻¹, 并且催化剂具有高效的电荷转移和大的电催化活性表面积, 性能优于同体系的其他催化剂。

关键词: 异质结构; 电解水制氢; 激光直写

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