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Activating MoS₂ by interface engineering for efficient hydrogen

evolution catalysis

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Graphical abstract



Herein, we proposed a facile strategy for the design of Au-MoS₂ nanoparticles with abundant edge sites and regular core-shell structure through the interface engineering.

Highlights

- 1. Activating the pristine MoS_2 by introducing MoS_2 into core shell heterostructures through the interface engineering.
- 2. CNFs served as reactor and support to control the heterostructures of Au and MoS₂.
- **3.** The Au-MoS₂/CNFs exhibits the overpotential of 92 mV (10 mA cm⁻²) and a Tafel slope of 126 mV dec⁻¹.

Abstract

Transition metal sulfides have been widely investigated and used as efficient catalysts for hydrogen evolution reactions (HER). However, the trade-off between catalytic activity and long-term stability represents a formidable challenge and has not been extensively addressed. Herein, we proposed a facile strategy for the design of Au-MoS₂ nanoparticles with abundant edge sites and regular core-shell structure through the interface engineering. The electrospun carbon nanofibers (CNFs) served as reactors and supports to control the preparation of core-shell heterostructures. Core-shell heterostructure exhibits more excellent catalytic than single component resulting from the synergistic effects at nano-interface. The obtained Au-MoS₂/CNFs

catalyst yield a current density of 10 mA cm⁻² at the overpotential of 92 mV and a Tafel slope of 126 mV dec⁻¹. Particularly, the durability of catalyst is relatively stable at the 50 h. The successful synthesis of core-shell nanocrystals provides a new path for designing advanced electrocatalysts.

Keywords: hydrogen evolution reaction; transition metal sulfides; electrocatalysis; electrospinning; core shell

Introduction

With the increasing global warming and critical energy shortage, developing clean and renewable energy is an urgent task. Hydrogen is considered as the one of the most promising sustainable energy sources, due to its high energy density and environmentally friendly combustion products.^[1-3] Nowadays, electrocatalytic water splitting including hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) is an effective way to produce hydrogen gas.^[4] However, HER and OER process both require appropriate catalysts to reduce the overpotential.^[5,6] Noble metal such as Pt, Pd and Ru are the best catalysts for water splitting, however, the scarcity and instability limit their further application. Hence, developing efficient HER electrocatalysts is an emergency task to produce hydrogen gas efficiently. Due to the unique d electron configurations, high corrosion resistance, and earth-abundant nature, transition metals-based sulfides,^[7] phosphides,^[8] nitrides,^[9] selenides,^[10] and oxides,^[11] are promising candidates for efficient electrocatalysts toward water splitting.

Recently, earth-abundant MoS₂ is considered as a promising catalyst for the HER.

However, the highly catalytic performance of MoS₂ still remains challenges due to the poor conductivity of pristine MoS₂.^[12] Recently, our group reported an effective strategy to improve the pristine electrocatalytic activity of MoS₂ by introducing the Co₉S₈ phase into heterostructures through the interface engineering. The synergetic effects between Co and Mo at the proposed localized interface region between the MoS₂ and Co₉S₈ phases improved the catalytic activities stem from a large reduction of the kinetic energy barrier of H₂ molecule desorption on the nanointerfaces.^[13,14] In addition, Metal particle-modified molybdenum disulfide can effectively improve the electron transport from metal to molybdenum disulfide, thereby low the Fermi level of molybdenum disulfide.^[15] However it is a huge challenge to build an efficient electronic transmission interface. Core-shell heterostructure can create a great nano-interface to improve the catalytic performance. The core can provide a stable and effective electron transport path and the shell can increase the specific surface area which provides more active sites.^[16] Therefore, the formed core-shell heterostructure can shorten the proton diffusion path and form more efficient electron transport.

In this work, we proposed a facile approach to synthesize metal- transition metal sulfide core-shell heterostructure. The electrospun carbon nanofibers (CNFs) served as reactors and supports to control the preparation of core-shell heterostructures of Au and MoS₂. It can also further increase the conductivity of hybrid materials which possess abundant edge sites and regular hexagonal structure. Core-shell heterostructure exhibits more excellent catalytic than single component

resulting from the synergistic effects at nano-interface.^[17] The obtained Au-MoS₂ electrocatalyst exhibit the superior catalytic performance with an overpotential of 92 mV at current density of 10 mA cm⁻² and a relatively low Tafel slope of 126 mV dec⁻¹ as well as the remarkable durability. This work indicated that the synergetic effects of the nanointerfaces generated by metal-transition metal sulfide lead to promising promoted electrocatalytic activity.

Experimental section

1. Materials

Chloroauric acid (HAuCl₄·4H₂O, 99.9%) was acquired from Shanghai Civi Chemical Technology Co., Ltd. Epigallocatechin gallate (EGCG) was purchased from Cool Seoul Chemical Technology Co., Ltd. N, N-dimethylformamide (DMF) was purchased from Hangzhou Gaojing Fine Chemical Co., Ltd. (China). Ammonium tetrasulfide molybdate ((NH₄)₂MoS₄) was purchased from Beijing Bai Ling Wei Technology Co., Ltd. Polyacrylonitrile (PAN, M_w=1.5×10⁵, copolymerized with 10wt % acrylate) was purchased from Sinopec Shanghai Petrochemical Co., Ltd.)

2. Synthesis of the Au-MoS₂/CNFs, MoS₂/CNF and Au/CNF

1.7 g PAN was added to 15 mL DMF solution to form a uniform transparent solution under magnetic stirring for 8 h, then 0.45 g HAuCl₄·4H₂O and 0.05 g EGCG were added to the homogeneous solution, and a uniform solution was formed under heating and stirring at 65 °C for 4 hours. After the solution was cooled to room temperature, 0.15 g (NH₄)₂MoS₄ was added to the solution, the precursor solution was obtained after stirring at room temperature for 12 hours. The precursor solution

was then transferred to a 10 mL syringe with an inner diameter of 0.7 mm stainless steel needle. The needle was positively pressurized at 15 kV, negative high pressure 0.6 kV, receiving distance 15 cm, and propulsion speed 0.5 mL/h. The ambient temperature was stable at around 38 °C. After 15 hours, the Au-Mo-PAN nanofibers membranes were obtained.

The collected Au-Mo-PAN nanofibers membranes were placed in an alumina ceramic boat for direct growth, which in the middle of the chemical vapor deposition furnace. Another alumina ceramic boat containing 0.6 g of sulfur powder was placed in front of the relative gas flow direction. Next, the nanofiber membrane was heated to 230 °C in air and kept at this temperature for 3 hours. During the continuous heating of the furnace, the nanofiber membrane was protected by an argon gas flow rate of 150 cc. When the temperature reached 400 °C, Another separate heater for heating the sulfur boat is turned on and raised to 250 °C holding two hours. After two hours of heating, the temperature of the furnace reached 900 °C. After maintaining the heat for three hours, the furnace was turned off. Moreover, the heating rate of the furnace and the separate heater is 5 °C per minute, and the cooling phase is naturally cooled to room temperature.

The synthesis process of MoS₂/CNF and Au/CNF is similar to the Au-MoS₂/CNFs. 1.7 g PAN, 0.15 g (NH₄)₂MoS₄ and 15 mL DMF solution were formed into uniform solution under magnetic stirring for 8 h. The homogeneous solution was used as the precursor solution for electrospinning. For the synthesis process of Au/CNFs, 1.7 g PAN, 0.45 g HAuCl₄.4H₂O and 0.05 g EGCG was added to 15 mL DMF solution and

then the mixture stirred at 65 °C for 4 h. After the solution was cooled to room temperature, the mixture was used as the precursor solution for electrospinning. The electrospun parameter and the graphitization parameter were same to the Au-MoS₂/CNFs.

3. Materials characterizations

The high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images, STEM mapping, and line-scan energy dispersive X-ray spectroscopy (EDX) were recorded using a STEM (Tecnai G2 F30S-Twin,Philips-FEI) at an acceleration volt-age of 300 kV. Transmission electron microscopy (TEM) images were taken using a JEM-2100 transmission electron microscope (JEOL, Japan) at an acceleration voltage of 200 kV. Field emission scanning electron microscopy (FE-SEM) images were characterized using a JSM-6700F FE-SEM (JEOL, Japan) at an acceleration voltage of 3 kV. X-ray diffraction (XRD) were analyzed using a Bruker AXSD8 Advance X-ray diffractometer with Cu K_a radiation (λ = 1.5406 Å) at a scanning rate of 0.02 2 θ s⁻¹ in the 2 θ range of 5-90°. X-ray photoelectron spectroscopy (Kratos Axis Ultra DLD) with an Al (mono) K_a source (1486.6 eV). The Al K_a source was operated at 15 kV and 10 mA.

4. Electrochemical characterization

All electrochemical tests use a traditional three-electrode system in 0.5 M H_2SO_4 . For the preparation of working electrode, the membranes after calcination in the tube vacuum furnace were cut into 1 x 1 cm² squares, which were fixed on the Teflon motor clip. Carbon rods and saturated calomel electrodes are used as counter

and reference electrodes, respectively. Then, the cyclic voltammetry (CV) test for the working electrode in 0.5 M H₂SO₄ at a scan rate of 100 mV s⁻¹ using the CHI660E electrochemical workstation. After that, to characterize the HER performance of the working electrode, and the linear sweep voltammetry (LSV) was obtained at a scan rate of 5 mV s⁻¹. The electrochemical impedance spectra (EIS) ranged from 100 kHz to 0.001 Hz. Meanwhile, the stability test for the working electrode was carried out at a voltage of -0.6 V for 50 hours, and argon gas was introduced to remove the bubbles generated on the electrode surface. Moreover, all measurements were taken at room temperature without IR correction.

Result and discussion

To investigate the morphology and structure, Fig. 1a and b show the field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) images of the Au-MoS₂ core–shell. As shown in Figure 1a, small and large amounts of Au-MoS₂ core shell nanocrystals are evenly distributed on the surface of CNFs. Fig. 1c indicates that the nanocrystals possess a regular hexagonal structure and grown on the CNFs. In order to further reveal the elemental distribution of nanocrystals, the scanning TEM energy dispersive X-ray (STEM-EDX) elemental mapping of Au-MoS₂ were performed and shown in Fig. 1d-g. It is indicated that the Au, Mo and S elements were uniformly dispersed over the whole nanocrystal, suggesting that the Au nanoparticles were completely encapsulated in the MoS₂ shells.

In order to investigate the core-shell structure, Fig. 1h-i exhibit the resolution

transmission electron microscopy (HR-TEM) images. It is demonstrated that the hexagonal Au nanoparticles were surrounded by several MoS₂ shells, forming the unique core shell structures. For the core region of the Au nanocrystals, the inter-planar distance is measured to be 2.3 Å, corresponding to the (111) plane of the Au crystals. For the outer MoS₂ shells, the lattice spacing is about 6.5 Å, corresponding to the (002) plane of the MoS₂. Due to the formation of Au-MoS₂ core shell structures, the Au-S-Mo nano-interfaces could accelerate the electron transfers and further improve the hydrogen evolution performance. As shown in Fig.1j, the selected area electron diffraction (SAED) pattern shows a series of diffraction rings, revealing the polycrystalline property of Au-MoS₂ nanocrystals.



Fig.1 (a) FE-SEM image, (b-c) TEM image of Au-MoS₂/CNFs hybrid. (d-g) STEM and the corresponding EDS mapping images of the Au-MoS₂/CNFs hybrid (h-i) HR-TEM image of Au-MoS₂/CNFs hybrid. (j) the corresponding of SAED pattern. (k) The line-scan EDX spectra of the Au-MoS₂/CNFs hybrid.

As shown in the Fig. 1k, the Au molar exits the inner of the nanocrystal, the S and Mo molar signals appear outside the nanocrystal, which formed the shell of nanocrystal. The line-scan energy-dispersive X-ray spectroscopy (EDX) spectra of the Au-MoS₂ nanocrystal also demonstrate a 3.1:1:2.2 Au: Mo: S atomic ratios, and the mass fraction of the Au-MoS₂ nanocrystals is \approx 8%, which is shown in Fig. S1. In addition, the supported CNFs could improve the conductivity of the material and further enhancing HER performance.



Fig.2 (a) SEM image of MoS₂/CNFs hybrid and inset is the corresponding TEM image, (b) SEM image of Au/CNFs hybrid and inset is the corresponding TEM image.

In order to better understand the excellent synergy between the Au core and the MoS₂ shell, the MoS₂/CNFs and Au/CNFs hybrid materials were prepared as control. The field-emission scanning electron microscopy (FE-SEM) and TEM images of MoS₂/CNFs and Au/CNFs were shown in the Fig. 2. From Fig. 2a, the MoS₂ nanocrystal exhibits two-dimensional nanosheet morphology and there are evenly distributed on the CNFs. And the corresponding TEM image indicates the formation of (002) planes of MoS₂ nanosheets. Meanwhile, the Au nanoparticles on CNFs display some distinct (111) planes, as shown in Fig. 2b. The results indicate that the

Au-MoS₂ core shell structures only obtained when the Au nanoparticles meet the MoS₂ nanosheets.

X-ray diffraction (XRD) patterns were used to investigate the crystal structure of Au-MoS₂ nanocrystal, as shown in Fig. 3a. For the individual MoS₂/CNFs samples, it is clear that the diffraction peak located at about 14.4° corresponds to the (002) planes of MoS₂ crystals.^[18] Meanwhile, the XRD pattern of individual Au/CNFs exhibits five sharp peaks locating at 38.2°, 44.4°, 64.6°, 77.6° and 81.8°, which are attributing to the (111), (200), (220), (311) and (222) planes of the cubic Au crystals (JCPDS No. 65–2870), respectively. Focusing on the Au-MoS₂/CNFs, the XRD pattern exhibit both the characteristic peaks of Au and MoS₂, confirming the co-existence of Au and MoS₂.



Fig.3 (a) The XRD patterns of the MoS₂/CNFs hybrid (black line), Au/CNFs hybrid (blue line) and Au-MoS₂/CNFs hybrid (red line). (b) The Raman spectra of the Au-MoS₂/CNFs hybrid and MoS₂/CNFs hybrid.

Raman spectroscopy can be used to analyze the crystallinity and the number of layers of molybdenum disulfide in nanocrystals by analyzing the position and frequency of two typical vibration modes, E_{2g} and A_{1g} . Fig. 3b shows the Raman spectra of the Au-MoS₂/CNFs and MoS₂/CNFs. The MoS₂ layer exhibits two Raman

characteristic bands at 377.4 and 402.2 cm⁻¹, corresponding to the E_{2g} and A_{1g} modes respectively, while the Au-MoS₂/CNFs hybrid shows the modes at the 378.7 and 403.2 cm⁻¹. The E_{2g} mode corresponds two S atoms vibrate in a plane opposite to the direction of the Mo atom, while the A_{1g} mode is related to the opposite outer planes of the two S atoms.^[19] The difference between the frequencies of these two modes is very close to 25 cm⁻¹, which is smaller than the bulk molybdenum disulfide, confirming the multilayer structure of molybdenum disulfide, corresponding to the HR-TEM results. At the same time, it can be seen that the intensity of the peak of the Au-MoS₂/CNFs hybrid is significantly increased, which is caused by the plasmon resonance of the gold surface after the formation of nanocrystals of gold and molybdenum disulfide.^[20] Moreover the degree of graphitization is quiet high of the Au-MoS₂/CNFs hybrid and MoS₂/CNFs hybrid materials. Thus, the electrical conductivity of the material is also improved.



Fig. 4 The XPS spectra of (a) the survey, (b) Au 4f, (c) Mo 3d, and (d) S 2p of the Au-MoS₂/CNFs hybrid.

To further investigate the surface electronic states and the electronic interaction between Au, Mo and S, X-ray photoelectron spectroscope (XPS) was obtained in Fig. 4. It is clear that the Au, Mo, S, C, N and O elements appear in the XPS survey spectra of Au-MoS₂/CNFs as shown in Fig. 4a, corresponding to the results of mapping. Fig. 4b displays the Au 4f XPS spectra of Au-MoS₂/CNFs, and two distinct peaks emerged at the 87.2 and 83.5 eV, corresponding to the 4f_{5/2} and 4f_{7/2} doublet of metallic Au⁰.^[21] Meanwhile, the Mo 3d peak can be deconvoluted into two peaks at 232.2 and 228.9 eV in the Fig. 4c. It can be found that the characteristic peak at 228.9 eV of Mo 3d_{5/2} belongs to the hexagonal 2H phase Mo⁴⁺ oxidation

state, which is corresponding the result of TEM.^[22] Moreover, the peaks observed at 162.9 eV belongs to S 2p_{1/2} while the peaks at 161.5 eV can be assigned to S 2P_{3/2}, which is consistent with the previously reported binding energy of MoS₂.^[18] Meanwhile, it is calculated that the atomic ratio of molybdenum to sulfur is close to 1:2, which is in agreement with the EDX data. However, it is can be seen that the molybdenum disulfide shell completely encapsulates the gold particles, resulting in the two peaks of Au are much weaker than Mo and S, and it is also confirmed that the core-shell nanocrystals are successfully prepared.^[23,24]

The electrochemical HER performance of all samples were investigated by using a simple three-electrode setup in 0.5 M H₂SO₄ solution. In our experiment, we compared the HER activities between MoS₂/CNFs, Au/CNFs, Au-MoS₂/CNFs and the blank sample of Pt/C are tested in the three-electrode system in 0.5 M H₂SO₄ in the Fig. 5a. The MoS₂/CNFs with 2D morphology showed poor HER characteristics even at a high current density, could not delivering a current density of 10 mA cm⁻². This poor HER performance can be attributed to the lack of electronic coupling between the substrates and active sites in aggregated layered morphology that limits the exposure of activated basal plane toward HER. Meanwhile, the Au/CNFs could deliver an overpotential of 300 mV at 10 mA cm⁻². In contrast, the Au-MoS₂/CNFs electrode possess the impressive catalytic activity for HER in 0.5 M H₂SO₄ with the lowest overpotentials (92 mV at the current density of 10 mA cm⁻²).



Fig. 5 (a) polarization cures obtained for the $MoS_2/CNFs$ hybrid, Au/CNFs hybrid, Au-MoS_2/CNFs hybrid and Pt/C as indicated. (b) The corresponding Tafel plots and (c) the electrochemical impedance spectra of $MoS_2/CNFs$ hybrid, Au/CNFs hybrid, Au-MoS_2/CNFs hybrid, and (d) the time dependence of the current density under the static overpotential of -0.6 V.

The overpotential could be also used to evaluate the performance of the electrocatalysts. It is shown that the Au-MoS₂/CNFs possess the overpotential of 92 mV at a current density of 10 mA cm⁻², which is lower than the Au/CNFs (300 mV) and MoS₂/CNFs. The Tafel slope suggests the rate-determining step in the HER mechanism. Generally, a smaller Tafel slope means a smaller overpotential required for a faster HER rate by an orders of magnitude increment in current density. Therefore we obtain the Tafel plot of various electrocatalysts in Fig. 5b. It is indicated

that the Tafel splope of the Au-MoS₂/CNFs is 126 mV dec⁻¹, which is smaller than the Au/CNFs (203 mVdec⁻¹) and MoS₂/CNFs (321 mVdec⁻¹). Moreover, the HER catalysis active sites, the enhanced charge transfer kinetics also contribute to the improved HER efficiency of a catalyst. Electrochemical surface area (ECSA) was investigated by cyclic voltammetry test based on the linear relationship between ECSA and double-layer capacitance (C_{dl}).^[25] We estimate the double layer capacitance of the catalysts by plotting the ΔJ at 0.2 V as a function of scan rate. As shown in Figure S3, the Cdl value of Au-MoS₂/CNFs was calculated to be 14.4 mF cm⁻², which is higher than the MoS₂/CNF (0.9 mF cm⁻²) and Au/CNF (12.1 mF cm⁻²). The ECSA results demonstrate the relative activity of Au-MoS₂/CNFs is higher than the MoS₂/CNFs and Au/CNFs hybrids. We also evaluated the AC impedance at an overpotential of 260 mV as shown in Fig. 5c. The Au-MoS₂/CNFs hybrid exhibits a smaller charge transfer impendence at ~10 Ohm than that of the Au/CNFs hybrid (~30 Ohm) and $MoS_2/CNFs$ hybrid (~100 Ohm), suggesting the faster HER kinetics with Au-MoS₂/CNFs. In addition, the durability is also an important criterion to evaluate HER electrocatalyst. Therefore the catalytic durability of the Au-MoS₂/CNFs composite catalyst is evaluated by chronopotentiometry measurements under the static overpotential of -0.6 V for 50 h in the Fig. 5d. It can be found that the current density curves of the catalyts is relatively stable, and only exhibit a small degredation.



Fig.6 TEM and HRTEM images of Au-MoS₂/CNFs hybrid prepared at (a, b) 900 °C, (c, d) 800 °C and (e, f) 700 °C.

The Au-MoS₂/CNFs prepared at different graphitization temperature (700-900 °C) were also investigated. As shown in Figure 6a and 6b, the average size of the Au-MoS₂/CNFs prepared at 900 °C was about 90 nm. Similarly, from Figure 6c to 6f, the average size of Au-MoS₂/CNFs prepared at 800 °C and 700 700 °C were about 65 nm and 56 nm, respectively. The Au-MoS₂ nanocrystals prepared at different temperatures all exhibit distinct core/shell structures, indicating that the temperature could not affect the core/shell structures. Through tuning the heating condition, the size of Au-MoS₂ core-shell nanocrystals became larger with the increased temperatures. The higher temperatures would provide better condition for the growth of Au-MoS₂ nanocrystals towards the larger sizes.



Fig.7 (a) Polarization cures and the (b) corresponding Tafel plots of the Au-MoS₂/CNFs hybrid prepared at 700 °C, 800 °C and 900 °C, respectively.

The electrochemical HER performance of all samples were also obtained. It can be seen that the Au-MoS₂/CNFs of 800 °C possess the overpotential of 178 mV at a current density of 20 mA cm⁻², which is lower than the Au-MoS₂/CNFs of 900 °C (202 mV) and Au-MoS₂/CNFs of 700 °C (218 mV), as shown in the Fig.7a. The corresponding Tafel splope of the Au-MoS₂/CNFs of 800 °C was smallest in the Fig.7b. In addition, it would also affect the conductivity of the substrate CNFs and lower graphitization temperature would lead to the worse conductivity. Therefore, 800 °C was the optimal growth temperature for Au-MoS₂ core-shell nanocrystals with best HER performance.

The unique core shell structures several key factors for the efficient HER activity. The formation of the core/shell heterostructures increased the contact area between the electrolyte and the catalyst and increases the active sites, as well as the strong electron coupling between the core and the shell greatly enhances the hydrogen evolution performance. The good HER performance are due to the electrocatalytic synergetic effects of the nanointerfaces generated by the directly

contacting regions between the Au core and the MoS₂ shell. These advantages generate strong electron transfer between Au and Mo through the intermediate sulfur atoms bonded to both metals, leading to promising promoted electrocatalytic activity.

Conclusions

In summary, we have successfully prepared the Au-MoS₂/CNFs core-shell structure with abundant active sites by combining the electrospinning and interface engineering. The CNFs served as reactors and supports to control the preparation of core-shell heterostructures. Core-shell heterostructure exhibits more excellent catalytic than single component resulting from the synergistic effects at nano-interface. The obtained Au-MoS₂/CNFs catalyst yield a current density of 10 mA cm⁻² at the overpotential of 92 mV and a Tafel slope of 126 mV dec⁻¹. Particularly, the durability of catalyst is relatively stable at the 50 h. The successful synthesis of core-shell nanocrystals provides a new path for designing advanced electrocatalysts.

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