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Surface Modulation of Hierarchical MoS₂ Nanosheets by Ni Single Atoms for Enhanced Electrocatalytic Hydrogen Evolution

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Abstract

Surface modulation at the atomic level has been an important approach for tuning surface chemistry and boosting the catalytic performance. Here, we demonstrate a surface modulation strategy through the decoration of isolated Ni atoms onto the basal plane of hierarchical MoS₂ nanosheets supported on multichannel carbon nanofibers for boosted hydrogen evolution activity. X-ray absorption fine structure investigation and density functional theory (DFT) calculation reveal that the MoS₂ surface decorated with isolated Ni atoms displays highly strengthened H binding. Benefiting from the unique tubular structure and basal plane modulation, the newly developed MoS₂ catalyst exhibits excellent hydrogen evolution activity and stability. This single-atom modification strategy opens up new avenues for tuning the intrinsic catalytic activity towards electrocatalytic water splitting and other energy-related processes.

Keywords: surface modulation, single atom, MoS₂, hydrogen evolution reaction

As one of the most promising candidates for replacing traditional fossil fuels, hydrogen has drawn extensive attention in the past decades. Electrocatalytic hydrogen evolution reaction (HER) driven by renewable energy input is believed as one efficient strategy to develop this clean-energy carrier.^[1, 2] Currently, Pt-based materials exhibit unrivaled catalytic performance for HER. However, the practical application of Pt-based electrocatalysts is greatly limited by their scarcity and high cost.^[3-5] Developing highly active and cost-efficient alternatives is considered as one ideal approach to enable the hydrogen economy. Among those newly developed electrocatalytic materials, molybdenum disulfide (MoS_2) has been identified as a promising candidate due to its layered structure and unique electronic configuration.^[6-8]

As proved by the theoretical calculation and experimental investigation, the HER activity of MoS_2 mainly comes from the S atoms on edge sites.^[9-11] However, the high proportion of electrochemically inactive basal plane greatly limits its electrocatalytic activity.^[12] Moreover, the low electron transfer capability of MoS_2 can hamper electron transport pathways and thus generate sluggish electrocatalytic kinetics.^[13, 14] Improving the intrinsic activity and increasing the number of active sites are two effective strategies to improve the electrocatalytic efficiency of MoS_2 .^[15] Amongst, introducing the promoter cations has proved its strength to trigger the inert S atoms in the basal plane.^[16-18] However, it is hard to separate the involved factors for the enhancement such as the structural phase transitions and changes in H binding energy.^[19, 20] Recent studies about single-atom modification have provided an opportunity to investigate the chemical environment between the single foreign atoms and the host crystal at the atomic level.^[21-23] Therefore, deeper understanding of the promotional effects could be established for developing high-performance HER electrocatalysts at low cost. Moreover, the configuration of MoS_2 should be delicately designed to ensure good

electronic conductivity and maximize the exposed active sites for HER.

Here, we report the decoration of isolated Ni atoms onto hierarchical MoS₂ nanosheets supported on multichannel carbon matrix (MCM) nanofibers (designated as MCM@MoS₂-Ni) through a wet-impregnation technique and a subsequent annealing treatment under reducing atmosphere. Theoretical and experimental investigations demonstrate that the isolated Ni atoms can be effectively decorated into the lattice structure of MoS₂. The single-atom Ni modification creates a large quantity of activated S atoms in the basal plane with greatly modified electronic structure for facilitating water dissociation and subsequent catalytic process. Apart from tuning the electronic structure of catalysts, the HER performance is also optimized through the manipulation of the architecture. The hybrid MCM@MoS₂-Ni nanofibers facilitate the electron transfer for electrocatalytic hydrogen production.

The synthetic process for the MCM@MoS₂-Ni is depicted in **Figure 1**. First, MCM is obtained by annealing the electrospun polystyrene-polyacrylonitrile (PS-PAN) nanofibers at 800 °C in N₂ atmosphere (Figure S1, Supporting Information).^[24] Here, PS, acting as the sacrificial channel-forming agent, is removed during the thermal treatment. Meanwhile, PAN is carbonized into conductive carbonaceous matrix, resulting in the formation of MCM nanofibers. Field-emission scanning electron microscopy (FESEM) images show that the as-synthesized MCM nanofibers possess smooth surface with an average diameter of 1 μm (Figure S2a,b, Supporting Information). Transmission electron microscope (TEM) image reveals that carbonized nanofibers have parallel channels inside to form a lotus root-like porous structure (Figure S2c, Supporting Information). Subsequently, ultrathin MoS₂ nanosheets are grown on the surface of MCM (MCM@MoS₂) through a solvothermal reaction (Figure S3, Supporting Information). Afterward, isolated Ni atoms are decorated into the as-synthesized MCM@MoS₂ through a wet-impregnating method in Ni(NO₃)₂

solution. An annealing process at 600 °C is followed to increase the crystallinity of MoS₂ and strengthen the mutual interaction between the decorated Ni atoms and in-plane S atoms.

The MCM@MoS₂-Ni retains the original morphology of MCM@MoS₂ and no noticeable change can be observed after the decoration of isolated Ni atoms (**Figure 2a,b**). Magnified FESEM image clearly shows that the hierarchical shell is composed of randomly assembled ultrathin nanosheets (**Figure 2c**). The multichannel structure of the MCM@MoS₂-Ni can be directly observed through the cross-section view (**Figure 2d**). TEM observation reveals the same hierarchical structural features, although the core-shell structure could be hardly identified due to the intimate contact between the MoS₂-Ni nanosheets and the MCM nanofibers (**Figure 2e**). The high-resolution TEM (HRTEM) image of some interconnected MoS₂ nanosheets show some visible lattice fringes (**Figure 2f**). The interplanar distance is confirmed as 0.62 nm, which corresponds to the (002) plane of hexagonal MoS₂ (**Figure 2g**).^[25] The atomic resolution picture and the fast Fourier transform (FFT) filtered image clearly demonstrate the hexagonal structure of Ni decorated MoS₂ basal plane with obvious defects (**Figure 2h,i**). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) confirms the smooth surface of the nanosheet without any obvious nanoparticle or cluster (**Figure 2j**). The energy dispersive X-ray (EDX) spectra demonstrate the successful decoration of Ni species into the hybrid (**Figure S4**, Supporting Information). As confirmed by the inductively coupled plasma optical emission spectroscopy (ICP-OES), the content of decorated Ni in MCM@MoS₂-Ni is about 2.7 wt.%. The electron energy loss spectroscopy (EELS) mapping combined with the related energy loss peaks reveals the uniform distribution of the elements over the entire architecture (**Figure 2k,l**, and **Figure S5**, Supporting Information).^[26] The decorated Ni atoms have also been characterized by the linear EDX scanning with varied signal intensities (**Figure S6**,

Supporting Information). Different from the cases of Mo and S species that are distributed over the entire scanning area, Ni species are located on the specific sites. These results indicate that the decorated Ni species are isolated over the MoS₂ nanosheets.^[27] X-ray powder diffraction (XRD) patterns of the as-synthesized MCM@MoS₂-Ni and MCM@MoS₂ verify that the decoration of Ni atoms does not change the crystal structure of the hexagonal MoS₂ (Figure S7, Supporting Information). For comparison, pristine MoS₂ microflowers with an average diameter of about 500 nm are also synthesized via the similar route except for the addition of MCM (Figure S8, Supporting Information).

The coordination environment of Ni centers is investigated by the extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectroscopies. The EXAFS spectra demonstrate that there is no Ni-Ni bonding in MCM@MoS₂-Ni, thus ruling out the existence of Ni particles or clusters (**Figure 3a**). Instead, a dominant peak centered at 1.63 Å is clearly observed, and should be attributed to the Ni-S bonding (Figure S9 and S10, Supporting Information).^[16] A radial distance resolution in the *K* space is provided by Wavelet transform (WT) simulation. The WT intensity maximum near 5.25 Å⁻¹ arising from the Ni-S coordination is well resolved at 1.0 to 3.0 Å for MCM@MoS₂-Ni, whereas an intensity maximum at ~7.96 Å⁻¹ associated with the Ni-Ni connection is not observed (Figure 3c,d). These results further illustrate that the Ni species in MCM@MoS₂-Ni are atomically dispersed without aggregation.^[28] The coordination sphere of the atomically dispersed centers is further quantified by least-squares EXAFS curve-fitting analysis. The best-fitted results clearly confirm that the bond length of Ni-S is 2.19 Å, much shorter than the Mo-S bonding (2.37 Å) in MoS₂ (Figure 3b,e, and Table S1, Supporting Information). As shown in the XANES spectra, the intensity of the Ni L₃-edge in MCM@MoS₂-Ni is much higher than that of

Ni foil (Figure 3f). This phenomenon indicates the electron transfer from Ni to S in the MCM@MoS₂-Ni hybrid via the Ni-S bonding, resulting in the formation of positively charged Ni centers.^[29] We further carry out XANES simulation of the MoS₂-Ni moiety, which is built by the Ni substitution of Mo atom in the distorted coordination configuration. The three features (denoted as a, b, c) of the experimental XANES spectrum for MCM@MoS₂-Ni are all satisfactorily reproduced, thus fully corroborating the structure of the isolated Ni atom decorated MoS₂ (Figure S11, Supporting Information).^[30]

X-ray photoelectron spectroscopy (XPS) spectrum clearly confirms the decoration of Ni atoms into the MCM@MoS₂-Ni material. The high-resolution XPS spectrum for Ni 2p reveals the direct Ni-S bonding with chemically distinct species (Figure S12a, Supporting Information).^[31] The peak fittings for the Mo 3d spectra of the MCM@MoS₂-Ni and MCM@MoS₂ catalysts confirm that there are two oxidation states (Mo⁴⁺ and Mo⁶⁺) in the hybrids.^[32] The content of Mo species in high valence state is obviously increased after the Ni decoration, demonstrating the electron transfer between the decorated Ni species and MoS₂ nanosheet (Figure S12b,c, Supporting Information).^[33] Two distinct peaks at 377.5 cm⁻¹ and 401.1 cm⁻¹ are observed in the Raman spectra, corresponding to the in-plane Mo-S phonon mode (E¹_{2g}) and the out-of-plane Mo-S mode (A_{1g}) of typical MoS₂-layered structure, respectively (Figure S13a, Supporting Information). The relative intensities of A_{1g}/E¹_{2g} increase from 1.39 (in MCM@MoS₂) to 1.58 (in MCM@MoS₂-Ni), indicating that the Ni decoration might induce lattice strain into the in-plane Mo-S phonon mode and decrease its vibration intensity.^[34] The high graphitic order of the carbon substrate has also been confirmed by the intensity ratios of D band to G band (I_D/I_G) for MCM@MoS₂ (1.12) and MCM@MoS₂-Ni (1.06) (Figure S13b, Supporting Information).^[35, 36] The single-atom modification process causes little changes to the porous structure,

as both samples of MCM@MoS₂-Ni and MCM@MoS₂ exhibit similar Brunauer-Emmett-Teller surface areas of 50 m² g⁻¹ (Figure S14, Supporting Information).

We then investigate their electrocatalytic HER performance to explore the contribution from the well-resolved atomistic structure with impressive surface modulations. Density functional theory (DFT) calculations are performed for gaining further insights into the electronic nature and the consequent HER energetics.^[37] The calculated distributions of charge density indicate the remarkable changes after the Ni decoration (Figure S15, Supporting Information). The calculated densities of states (DOS) confirm that the surface modulation generates some new hybridized electronic states (Figure S16, Supporting Information). According to the Kohn-Sham orbitals for the new bands in the gap near the Fermi level (**Figure 4a,b**), these states are localized around the Ni-activated S sites to control the corresponding H adsorption.^[10, 38] These results clearly demonstrate the highly strengthened H binding after the decoration of Ni atoms, which could cast significant influence on the catalytic performance. We further conduct DFT calculation to investigate the changes in the H adsorption free energy (ΔG_{H}^*) after the single-atom Ni modification process.^[39, 40] A moderate ΔG_{H}^* (close to zero) is necessary for a good electrocatalyst to overcome the adsorption and desorption barriers. For the inert basal plane of MoS₂, ΔG_{H}^* is confirmed as 1.75 eV. Activating the S sites with the decorated Ni atoms results in a much-reduced ΔG_{H}^* of 0.15 eV, which is much closer to that of S atoms from the edge sites (0.08 eV) (Figure S17, Supporting Information).^[41] The ΔG_{H}^* of the isolated Ni sites is confirmed as 1.43 eV, indicating its little contribution to the overall catalytic performance.

To confirm the DFT predictions, steady-state linear sweep voltammetry (LSV) is applied to investigate the electrocatalytic HER performances in 0.5 M H₂SO₄. As shown in Figure 4c,

MCM@MoS₂ exhibits obviously enhanced performance with a positively shifted overpotential at 10 mA cm⁻² (263 mV) compared with pristine MoS₂ (297 mV). The integration of MoS₂ and MCM can effectively promote the electrocatalytic kinetics and thus improve the catalytic performance. Moreover, the hydrogen evolution is considerably accelerated by the MCM@MoS₂-Ni catalyst, as evidenced by the smaller onset overpotential (53 mV) with a higher current increase rate. Particularly, the overpotential required to achieve the current density of 10 mA cm⁻² is significantly decreased from 263 to 161 mV. These results suggest that MCM@MoS₂-Ni is among the most active nonprecious HER electrocatalysts in acidic solution (Table S2, Supporting Information). By decreasing the decoration content of Ni to 1.3 wt.%, the obtained catalyst MCM@MoS₂-Ni-1.3 exhibits greatly reduced catalytic performance, revealing that the decoration contents of Ni species influence the HER activity obviously (Figure S18, Supporting Information).

The HER kinetics, as well as the rate-determining step (RDS) can be revealed by the Tafel plots calculated from LSV curves (Figure 4d).^[42] MCM@MoS₂-Ni shows a Tafel slope of -81 mV dec⁻¹, whereas MCM@MoS₂ and MoS₂ exhibit the Tafel slopes of -136 and -179 mV dec⁻¹, respectively. These results indicate the HER on MCM@MoS₂-Ni occurs via the Volmer-Heyrovsky mechanism and the single-atom modification together with the structural design could change the RDS from the H adsorption to electrochemical desorption step.^[43] Durability is an important criterion for evaluating the performance of electrocatalysts. To study the stability of the MCM@MoS₂-Ni and MCM@MoS₂ catalysts, long-term electrolyses at a constant potential have been operated. The current densities of MCM@MoS₂-Ni and MCM@MoS₂ remain stable over 24 h with small degradation (Figure 4e and Figure S19a, Supporting Information). To further evaluate the stability of the catalysts, consecutive LSV scans are carried out. After 1000 cycles, the LSV curves show very small shifts, further

demonstrating the high stability of the electrocatalysts (Figure 4f and Figure S19b, Supporting Information). The MCM@MoS₂-Ni catalyst after the electrocatalytic test is further characterized. No obvious change of the morphology is observed. Besides, XRD pattern, Raman and XPS investigations further demonstrate the nearly unchanged framework and surface composition of MCM@MoS₂-Ni (Figure S20, Supporting Information).

The electrochemically active surface area (ECSA) has also been evaluated by investigating the double-layer capacitance (C_{dl}).^[44] The C_{dl} of MCM@MoS₂-Ni is calculated to be 4.78 mF cm⁻². This value is higher than that of MCM@MoS₂ (4.28 mF cm⁻²) and pristine MoS₂ (1.57 mF cm⁻²) (Figure 4g,h, and Figure S21, Supporting Information).^[45] The roughness factor (R_f) and specific HER current density ($j_{specific}$) of various catalysts are also evaluated. Although Ni decorated MCM@MoS₂-Ni contributes to its increased R_f in comparison to MCM@MoS₂ and pristine MoS₂, MCM@MoS₂-Ni exhibits the highest $j_{specific}$ by decoupling the geometric effect (Figure S22, Supporting Information).^[46-48] To further elucidate the sources of the apparent activities, the intrinsic activities of the catalysts have been evaluated by dividing the $j_{specific}$ by the corresponding R_f . As observed from these results, the significant enhancement in the activity of MCM@MoS₂-Ni is most likely associated with its high intrinsic activity originating from the surface modification, while the increase in the apparent activity of MCM@MoS₂ should be attributed to the geometric effect (Table S3, Supporting Information).^[49] The charge transfer kinetics are also characterized by the electrochemical impedance spectroscopy (EIS). The fitted results prove that MCM@MoS₂-Ni exhibits much smaller charge-transfer resistance than MCM@MoS₂ and pristine MoS₂ (Figure 4i, Figure S23 and Table S4, Supporting Information).^[18, 50-52] Furthermore, apart from MCM@MoS₂-Ni, such surface modulation improved HER catalysis could also be observed in carbon cloth (CC) substrated CC@MoS₂-Ni,

suggesting the generality of this strategy (Figure S24-S26, Supporting Information).

In summary, a surface modulation strategy has been developed for the effective decoration of isolated Ni atoms on hierarchical MoS₂ nanosheets supported on MCM nanofibers. X-ray absorption fine structure analyses unambiguously reveal that the decorated Ni atoms produce shortened Ni-S bonding and distorted configuration over the basal plane of MoS₂. DFT calculations reveal that the decoration of isolated Ni atoms could form new electronic states to tune the adsorption behavior of H atoms on the coordinated S atoms. The synthesized MCM@MoS₂-Ni electrocatalyst is found to be a highly active and stable for HER. The present work might represent a good strategy to trigger the electrocatalytic activity of inert basal plane of MoS₂ for HER and other energy-related catalytic processes.

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Figures and Captions

Figure 1. Schematic illustration of the synthetic process for MCM@MoS₂-Ni: (I) growth of MoS₂ nanosheets, (II) surface decoration of isolated Ni atoms.

Figure 2. (a-d) FESEM images, and (e-f) TEM images of the hierarchical MCM@MoS₂-Ni nanofibers. (g) HRTEM image of the Ni decorated MoS₂ nanosheets. (h) atomic resolution picture of the Ni decorated MoS₂ nanosheet, and (i) related FFT-filtered atomic resolution image. (j) HAADF-STEM image of MCM@MoS₂-Ni, and its corresponding (k) EELS image and (l) EELS mapping for the rectangle area.

Figure 3. (a) Ni K-edge EXAFS spectra of MCM@MoS₂-Ni and Ni foil. (b) Experimental and best-fitted EXAFS spectra in R space for MCM@MoS₂-Ni. WT for the k^3 -weighted EXAFS signals for (c) MCM@MoS₂-Ni and (d) Ni foil. (e) Experimental and best-fitted EXAFS spectra in K space for MCM@MoS₂-Ni. (f) Experimental XANES spectra for MCM@MoS₂-Ni and Ni foil.

Figure 4. Band structures of (a) MoS₂ and (b) Ni decorated MoS₂. (c) LSV curves and (d) corresponding Tafel plots for different catalysts in 0.5 M H₂SO₄. (e) Time dependence of the current density for MCM@MoS₂-Ni at a constant overpotential of 0.25 V. (f) LSV curves of the MCM@MoS₂-Ni for the initial and 1000th cycles. (g) CV curves at different scan rates (mV s⁻¹) for the MCM@MoS₂-Ni. (h) Capacitive $\Delta j/2 = (j_a - j_c)/2$ as a function of the scan rate for MCM@MoS₂-Ni, MCM@MoS₂ and MoS₂ catalysts. j_a represents the anodic current density; j_c represents the cathodic current density. (i) Nyquist plots of MCM@MoS₂-Ni, MCM@MoS₂ and pristine MoS₂, the fitted curves and experimental points are presented as solid lines and symbols, respectively.

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Tailoring the surface chemistry at the atomic level has been an important approach for boosting the catalytic performance of electrocatalysts. Here, we present a combined theoretical and experimental study on Ni atom decorated hierarchical MoS₂ nanosheets supported on the multichannel carbon matrix. Owing to the unique structural design and surface modulation in the inert basal plane, the obtained hybrid MoS₂-Ni electrocatalyst with activated S sites exhibits high performance for electrocatalytic hydrogen evolution.