

Communication

Double-layer hybrid chainmail catalyst for high-performance hydrogen evolution

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ARTICLE INFO

Keywords:

Electrocatalysis
Electron traversing
Graphene-encapsulated metal
Hydrogen evolution reaction
Single-layer molybdenum disulfide

ABSTRACT

Developing highly catalytic active but stable MoS₂ catalyst for electrochemical hydrogen evolution reaction (HER) performance, requires atomic-level tailoring of the electronic structure, but is greatly challenging. Herein, via precisely growing a double-layer MoS₂/graphene hybrid structure encapsulating CoNi nanoalloy (MoS₂/CoNi@G), we report both significantly enhanced HER activity and stability by the electrons of the CoNi cores traversing through the graphene to the outmost MoS₂ layer. It achieves 10 mA cm⁻² at a significantly lower overpotential of 150 mV than that of 262 mV over pristine MoS₂ nanosheets, and runs stably for over 10000 cyclic voltammetry cycles. The electron traversing effect efficiently tunes the electronic structures of both edge S sites and in-plane S vacancies, resulting in more appropriate adsorption energy of hydrogen on these active centers. It also induces strong electronic interactions between the MoS₂ and CoNi@G, which stabilizes the outmost MoS₂ layer and thereby significantly improves its catalytic stability.

1. Introduction

Electrochemical hydrogen evolution reaction (HER) driven by renewable energy supply is a promising and sustainable pathway of producing hydrogen as clean energy [1], which is typically catalyzed by platinum-based precious metal catalysts [2,3]. Much effort has been devoted to developing non-noble metal electrocatalysts for the HER [4,5]. Molybdenum disulfide (MoS₂) as a potential candidate has attracted wide attention owing to its low cost, earth abundance, and unique catalytic activity of the edge S sites [6–9]. However, its catalytic performance is severely restricted by both low intrinsic activity and low stability. Although strategies of morphology [10–13] or defect engineering [14,15] to expose more edge sites are of importance for improving the HER activity, finely tuning the electronic structures at the atomic level toward the optimum hydrogen adsorption while simultaneously improving the robustness of MoS₂ is also critically significant to mitigate the activity gap between the MoS₂ and Pt-based catalysts. Graphene layers encapsulating non-precious transition metal cores can

be activated by the electrons transferred from the metal to the graphene surface [16–19]. Such a structure may serve as a promising electronic mediator for modifying the properties of MoS₂ and thus improving the HER activity, which, however, is greatly challenging due to the difficulty in atomic-scale precise assembling of the two materials.

Herein, via precisely growing single-layer MoS₂ on single-layer graphene shell encapsulating CoNi alloy (denoted as MoS₂/CoNi@G), which is vividly similar to a double-layer chainmail structure, we show that the electrons of CoNi cores can traverse through the graphene layer to the outmost MoS₂ layer and thereby tailor the electronic properties of MoS₂ towards a high HER activity. At 10 mA cm⁻², the hybrid structure drives HER with a significantly lower overpotential of 150 mV compared with that of 262 mV over the pristine MoS₂ nanosheets. Moreover, such an effect also induces strong electronic interactions between the MoS₂ and CoNi@G, which stabilizes the outmost MoS₂ layer and thereby significantly improves the reaction stability compared with the pristine MoS₂ nanosheets. Density functional theory (DFT) calculations indicate that the traversed electrons efficiently tune

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the electronic structures of both the edge S sites and in-plane S vacancies, resulting in more appropriate adsorption energy of hydrogen on these active centers for the HER. This study provides a novel strategy of effectively tuning the electronic structure and catalytic activity of a catalyst by traversed electrons from encapsulated metal cores.

2. Experimental section

2.1. Materials synthesis

2.1.1. Synthesis of (CoNi@G)/SiO₂

Co(NO₃)₃·6H₂O (524 mg), Ni(CH₃COO)₂·4H₂O (446 mg), urea (900 mg), citric acid (120 mg) and SiO₂ nanospheres (900 mg, 70 nm in diameter) were dispersed in deionized water (100 mL) by sonication. The suspension was placed in a round bottom flask with reflux, which was heated to 100 °C in an oil bath and maintained for 12 h under magnetic stirring. After the reaction, the light pink precipitate was collected via centrifugation and vacuum drying. Then the solid powder (CoNi(OH)_x/SiO₂) was transferred into a tube furnace and heated to 900 °C in 25 vol % H₂/Ar atmosphere, followed by bubbling CH₃CN with Ar for 15 min at 900 °C. After cooling down to room temperature, the sample was treated in 0.5 M H₂SO₄ aqueous solution at 80 °C for 8 h, followed by washing with distilled water and ethanol for several times and then vacuum dried. The product was denoted as (CoNi@G)/SiO₂.

2.1.2. Synthesis of MoS₂/(CoNi@G)

(CoNi@G)/SiO₂ (200 mg) and specified amount of (NH₄)₆Mo₇O₂₄·4H₂O were dispersed in deionized water (20 mL), followed by magnetic stirring at room temperature to remove the solvent and then was vacuum dried. Then, the obtained solid and CS₂ (10 mL) were transferred into a 40 mL stainless steel autoclave under Ar and maintained at 400 °C for 4 h. The final product was treated with 5% HF aqueous solution for 5 h, followed by washing with distilled water and ethanol for several times and then vacuum dried at 80 °C. The sample was denoted as MoS₂/(CoNi@G)-*m* (*m* represents the mass content of Mo in the final MoS₂/(CoNi@G) samples which was measured by ICP-OES, see Table S1).

2.1.3. Synthesis of MoS₂ and MoS₂/CNTs

MoS₂ nanosheets were synthesized according to the previous work [20]. Typically, (NH₄)₆Mo₇O₂₄·4H₂O (300 mg) was dissolved in deionized water (20 mL), then the solution and CS₂ (10 mL) were transferred into a 40 mL stainless steel autoclave under Ar and maintained at 400 °C for 4 h. The product was treated with saturated NaOH aqueous solution under stirring at 60 °C for 3 h, followed by washing with distilled water and ethanol for several times and then vacuum dried at 80 °C. For the MoS₂/CNTs sample, CNTs (100 mg) and specified amount of (NH₄)₆Mo₇O₂₄·4H₂O were firstly dispersed in deionized water (20 mL), then the suspension and CS₂ (10 mL) were enclosed into the autoclave under Ar, also following the same reaction and treatment process as MoS₂.

2.2. Materials characterization

Transmission electron microscopy (TEM) was carried out on a FEI Tecnai F30 microscope operated at an accelerating voltage of 300 kV. High angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) and energy dispersive X-ray (EDX) mapping were conducted on a JEOL ARM200F microscope equipped with a probe-forming aberration corrector which was operated at 200 kV. X-ray absorption near-edge spectra (XANES) and extended X-ray absorption fine structure (EXAFS) were measured at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF) recorded in transmission mode. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Fisher ESCALAB 250Xi spectroscope using Al K α X-rays as the excitation source. X-ray diffraction (XRD)

measurements were conducted on a Rigaku D/MAX 2500 diffractometer with Cu K α radiation at a voltage of 40 kV and a current of 200 mA. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was carried out in PerkinElmer Optima 7300DV.

2.3. Electrochemical measurement

The electrochemical measurements were carried out with a three-electrode cell using a potentiostat/galvanostat (CHI 760E). Graphite rod and Ag/AgCl (saturated KCl-filled) were used as the counter electrode and reference electrode, respectively. To prepare the working electrode, catalyst (4 mg) was dispersed in ethanol (1 mL) with 20 μ L of Nafion solution (5 wt%, Du Pont) by sonication to form a homogeneous ink. Then 25 μ L of the catalyst suspension was spread onto a glassy carbon rotating disk electrode with a diameter of 5 mm (loading amount: 0.5 mg cm⁻²). Linear sweep voltammetry (LSV) was conducted in Ar-saturated 0.5 M H₂SO₄ electrolyte at 25 °C with a sweep rate of 5 mV s⁻¹ and a rotation speed of 1600 rpm using *iR*-drop compensation. The polarization curves without *iR*-correction are shown in Fig. S9. The onset potential is defined as the potential required to achieve the current density of 0.1 mA cm⁻². For the electrochemical durability test, the polarization curves were recorded initially and after 10000 cyclic voltammetry (CV) sweeps from -0.17 to +0.33 V (vs. RHE) with a scan rate of 100 mV s⁻¹. All the potentials were referenced to a reversible hydrogen electrode (RHE, Fig. S14).

2.4. Theoretical calculations

Density functional theory (DFT) calculations were performed using the Vienna Ab-initio Simulation Package (VASP) with the projector augmented-wave pseudopotential method and Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [21–26]. A plane-wave cutoff energy of 400 eV and a Monkhorst-Pack k-point sampling of 1 $\times$ 1 $\times$ 1 were used [27]. Zero-damping DFT-D3 method of Grimme was used to calculate the van der Waals interaction [28,29]. The structure of MoS₂/(CoNi@G) was built in a rectangular supercell, in which the graphene is in a two-dimensionally periodic model and the MoS₂ and CoNi alloy are in nanoribbon models. The (111) surface of the CoNi nanoribbon was used for interacting with the graphene surface. The supercell along the axial direction of the nanoribbon is composed of 5 repeated units for the graphene and the CoNi alloy and 6 repeated units for the MoS₂ to minimize the lattice mismatch. The detailed structure is shown in Fig. S15. For the MoS₂ nanoribbon, the Mo edge was saturated with S monomers and the S edge was saturated with a combination of S monomers and dimers (Fig. S15b) [30,31]. In structural optimizations, all atoms were allowed to move and the residual forces between atoms were converged below 0.02 eV/Å. The adsorption free energy of hydrogen was calculated as $\Delta E_{\text{total}} + \Delta \text{ZPE} - T\Delta S$, where E_{total} is DFT calculated total energy, ZPE is the zero-point energy, T is temperature, S is the entropy.

3. Results and discussion

The synthetic procedure of the MoS₂/(CoNi@G) catalyst is illustrated in Fig. 1a. Briefly, CoNi hydroxides were firstly coated onto the SiO₂ nanospheres (CoNi(OH)_x/SiO₂) via a hydrothermal method. Then the precursor was annealed at 900 °C via a chemical vapor deposition (CVD) process to convert the CoNi(OH)_x into CoNi nanoparticles (NPs) encapsulated in graphene layer ((CoNi@G)/SiO₂). After impregnating molybdenum precursors onto the (CoNi@G)/SiO₂, MoS₂ layers were then formed by directly reacting with CS₂. Finally, the hybrid structure of double-layer MoS₂/graphene encapsulating CoNi alloy (MoS₂/(CoNi@G)) was obtained after removing the SiO₂ templates via a chemical etching (see Experimental section for details).

The successive morphology transformations in the synthetic procedure of MoS₂/(CoNi@G) were tracked by the transmission electron

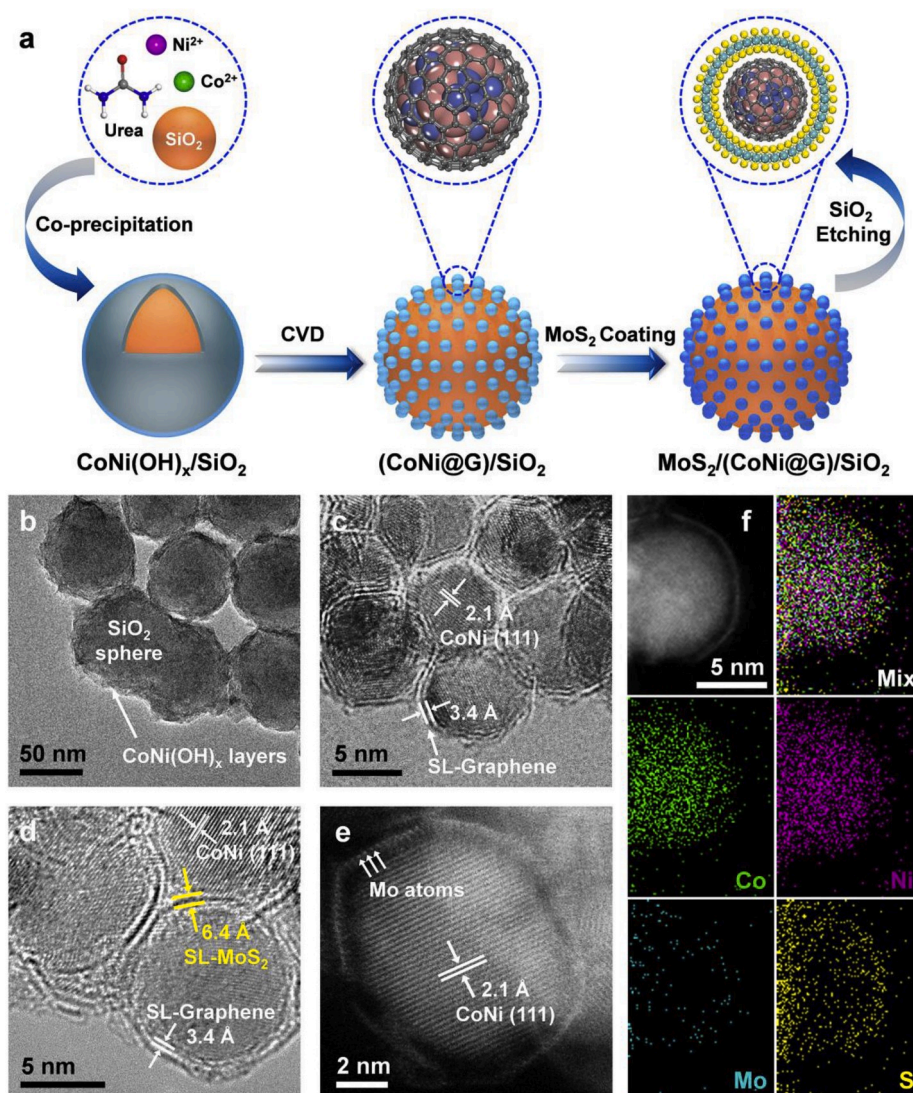


Fig. 1. Synthesis schematic and morphology characterizations of $\text{MoS}_2/(\text{CoNi@G})$. (a) Schematic illustration of the fabrication and structure of $\text{MoS}_2/(\text{CoNi@G})$. TEM images of (b) $\text{CoNi(OH)}_x/\text{SiO}_2$, (c) CoNi@G and (d) $\text{MoS}_2/(\text{CoNi@G})$. (e) HAADF-STEM image of $\text{MoS}_2/(\text{CoNi@G})$ showing the single layer of MoS_2 and the (111) crystal plane of the CoNi alloy. (f) HAADF-STEM and the corresponding EDX mapping images of $\text{MoS}_2/(\text{CoNi@G})$.

microscopy (TEM) (Fig. 1b–d). The CoNi(OH)_x layers were firstly wrapped onto the SiO_2 templates via hydrothermal process (Fig. 1b). Then through a CVD processing, the metallic CoNi NPs were encapsulated within graphene layer (CoNi@G), which were uniformly dispersed on the SiO_2 nanospheres with a metal size distribution of 5–7 nm (Fig. S1). To validate the intact feature of graphene layer on metal NPs, acid etching was adopted to remove the SiO_2 nanospheres and no significant structure variation of CoNi@G was observed before and after the template removal (Fig. 1c and S1). Further high-resolution transmission electron microscopy (HRTEM) image (Fig. 1c) shows that the layer thickness is around 3.4 Å, which corresponds to the single-layer graphene (SL-graphene). In addition, the *d*-spacing of the crystal lattice of 2.1 Å corresponds to the (111) plane of CoNi alloy (Fig. 1c). After a chemical synthesis using molybdenum precursors and CS_2 on the CoNi@G , a new layer around 6.4 Å corresponding to a single-layer MoS_2 (SL-MoS₂) appeared along the periphery of CoNi@G (Fig. 1d), confirming SL-MoS₂ was covered around the surface of CoNi@G . Such an architecture is further confirmed by the high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) image (Fig. 1e), showing a Mo-atoms layer surrounds the metal NPs, although not tightly bounds to the periphery of the CoNi NPs owing to the

separation by the graphene interlayer. Note that the S and C elements are not observable because of the comparatively low contrast. It is observed that a number of edges and defects of MoS_2 are exposed (Figs. S2–S4), since the MoS_2 with S–Mo–S atomic trilayer is more rigid than the graphene layer. Further energy dispersive X-ray (EDX) analysis of the spatial distribution of the elements in the $\text{MoS}_2/(\text{CoNi@G})$ (Fig. 1f) exhibits that the Co and Ni signals dominate the inner core and the S and Mo signals contribute mainly to the shell. These structural characterizations validate that SL-MoS₂ shell was successfully coated onto the surface of SL-graphene encapsulating a CoNi nanoalloy.

To validate the metallic state of the encapsulated CoNi cores, the electronic structure of the CoNi cores was studied using X-ray photoelectron spectroscopy (XPS) and X-ray absorption near-edge structure (XANES) characterizations. The Ni 2p peaks at 870.2 and 852.9 eV with their satellite peaks at 875.6 and 859.1 eV correspond to metallic Ni⁰ 2p_{1/2} and 2p_{3/2}, respectively [32,33]. Similarly, the Co 2p peaks at 793.5 and 778.4 eV correspond to Co⁰ 2p_{1/2} and 2p_{3/2} states, respectively (Fig. S5). Thus, the XPS spectra indicate that both the Ni and Co components are in metallic states. This is consistent with the results of XANES spectra, in which the near edge absorption energies of the Ni K-edge and Co K-edge of the $\text{MoS}_2/(\text{CoNi@G})$ are close to those of Ni

and Co foils as the references, respectively (Figs. S6a and S6c). Moreover, k^3 -weighted Fourier transformation of extended X-ray absorption fine structure (EXAFS) spectra in the R-space presents only the peak of metal-metal bond without metal-O bond for both the Co and Ni components (Figs. S6b and S6d). The crystal structure of CoNi alloy was also studied using X-ray diffraction (XRD, Fig. 2a and S7), showing the characteristic peaks at 44.5° , 51.8° and 76.3° corresponding to the (111), (200) and (220) plane of the CoNi alloy, respectively. These results demonstrate that the metallic state of CoNi alloy is maintained in the MoS₂/(CoNi@G) and no cobalt/nickel sulfide and oxide phases were formed in the synthetic procedure due to the protection of the integrated graphene layer.

The electronic structure of the SL-MoS₂ covering the CoNi@G was investigated to unravel the electronic interactions between them. The k^2 -weighted Fourier transformation of the Mo K-edge EXAFS spectra of the MoS₂/(CoNi@G) shows two peaks at around 1.9 and 2.9 Å in the R-space, which correspond to the Mo-S and Mo-Mo coordination, respectively, and are similar to those of the pure MoS₂ sample (Fig. 2b) [34,35]. However, a negative shift in the near-edge absorption energy was observed for the MoS₂ layer of the MoS₂/(CoNi@G) relative to that of the pure MoS₂ (Fig. 2c), indicating that the former possesses excessive electrons and thus has a relatively lower valance state. This is also reflected by the XPS characterization of the MoS₂/(CoNi@G), in which the doublet at 232.1 and 229.0 eV representing Mo⁴⁺ 3d_{3/2} and 3d_{5/2} states and the doublet at 163.1 and 161.9 eV representing S 2p states of terminal S²⁻ or S₂²⁻ ligands, all shift by about 0.4 eV toward lower binding energies relative to those of the pure MoS₂ nanosheets (Fig. 2d and S8) [36–39]. Therefore, these results indicate that the SL-MoS₂ of the MoS₂/(CoNi@G) hybrid structure is enriched with electrons owing to the electron traversing from the CoNi metallic cores through the SL-graphene.

The electrocatalytic HER activity of the MoS₂/(CoNi@G)

electrocatalyst was evaluated on a typical three-electrode configuration in 0.5 M H₂SO₄ solution, as shown in Fig. 3a. Compared with the separated parts, i.e. pure MoS₂ nanosheets and the CoNi@G, the MoS₂/(CoNi@G) electrocatalyst shows a significantly higher HER activity. Moreover, the HER activities of the MoS₂/(CoNi@G) samples with different amount of MoS₂ are also measured, in which the MoS₂/(CoNi@G) sample with Mo mass content of 13.9 wt% shows the highest HER activity with the largest current density of 10, 46 and 133 mA cm⁻² at the different overpotentials of 150, 200 and 250 mV, respectively (Fig. 3b and S10), possessing a high HER activity among the MoS₂- and CoNi-based HER catalysts (Table S2). For comparison, the physical mixture of pure MoS₂ nanosheets and the CoNi@G (denoted as MoS₂+CoNi@G) with a MoS₂ mass content close to that of the MoS₂/(CoNi@G) requires a higher overpotential of 264 mV to reach 10 mA cm⁻², exhibiting a similar HER performance with that of the pure MoS₂ nanosheets. MoS₂ layers supported on carbon nanotubes (MoS₂/CNTs) with different loading amount were also prepared as references. They all show obviously lower electrocatalytic activities with much higher overpotentials compared with those of the MoS₂/(CoNi@G) samples (Fig. S10). The Tafel slope of MoS₂/(CoNi@G) is 66 mV dec⁻¹ and smaller than those of the MoS₂/CNTs (77 mV dec⁻¹) and MoS₂ (81 mV dec⁻¹) (Fig. 3c). This suggests the HER proceed via the Volmer–Heyrovsky mechanism over the MoS₂/(CoNi@G) catalyst, in which electrochemical desorption of the chemisorbed hydrogen is the rate-limiting step [17,40]. With a lower Tafel slope, the reaction rate of MoS₂/(CoNi@G) increases rapidly with increasing overpotential, resulting in a superior HER activity. Therefore, the existence of the CoNi core and the electronic interactions between the MoS₂ and the CoNi@G can promote the catalytic activity of the MoS₂/(CoNi@G), which demonstrates a significant effect of improving the HER activity by the electrons traversed from the CoNi metal core through the graphene layer to the outer MoS₂ layer.

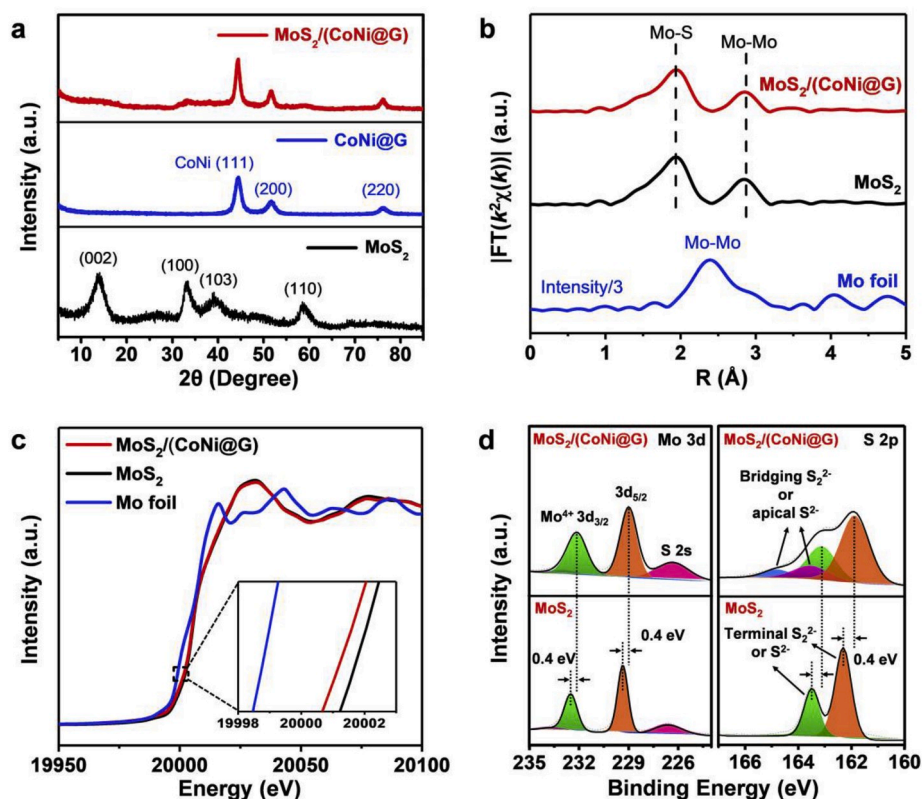


Fig. 2. Structural and electronic properties of MoS₂/(CoNi@G). (a) XRD patterns of MoS₂/(CoNi@G), CoNi@G and MoS₂. (b) The k^2 -weighted EXAFS spectra without phase correction and (c) Mo K-edge XANES spectra of MoS₂/(CoNi@G) in comparison with MoS₂ and Mo foil. (d) Mo 3d (left) and S 2p (right) XPS spectra for MoS₂/(CoNi@G) (upside) and MoS₂ (downside).

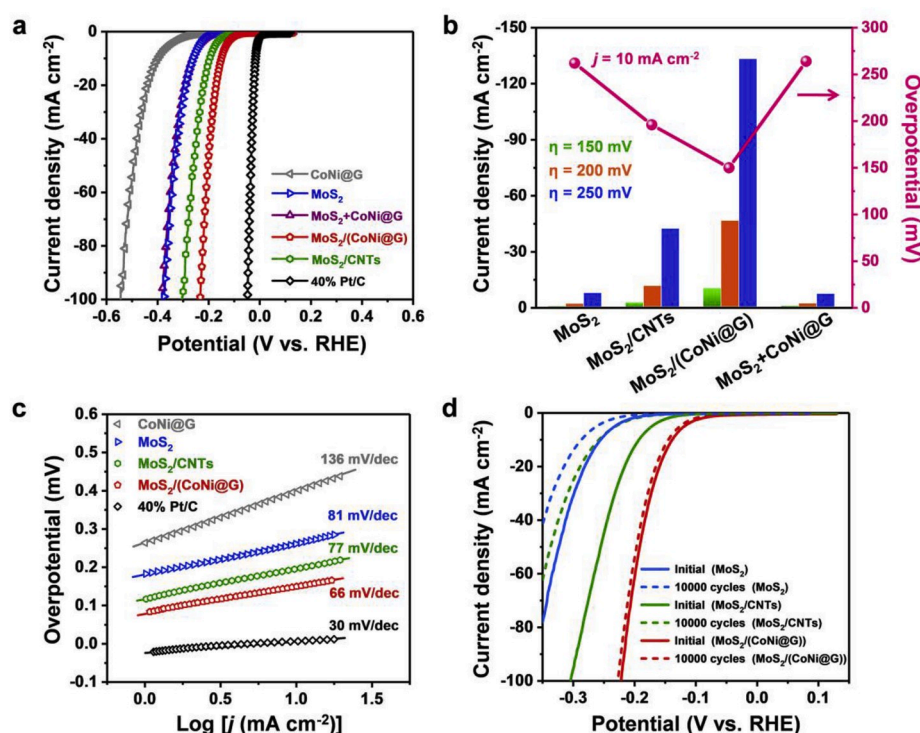


Fig. 3. Electrocatalytic HER activity and stability of MoS₂/(CoNi@G) at 25 °C in Ar-saturated 0.5 M H₂SO₄ solution. (a) HER polarization curves for MoS₂, CoNi@G, MoS₂/CNTs and MoS₂/(CoNi@G) in comparison with commercial 40% Pt/C on GCE with *iR* correction. Scan rate: 5 mV s⁻¹, rotation speed: 1600 rpm. (b) Current densities at the different overpotentials of 150, 200 and 250 mV, and the overpotentials at 10 mA cm⁻² of MoS₂/(CoNi@G), MoS₂/CNTs and MoS₂. (c) Tafel plots obtained from the polarization curves in (a). (d) Durability test of MoS₂/(CoNi@G) in comparison with MoS₂/CNTs and MoS₂.

The electrochemical durability of the MoS₂/(CoNi@G) was evaluated by continuous cyclic voltammetric (CV) scanning in 0.5 M H₂SO₄ solution. After 10,000 cycles, no obvious decay in the activity is observed (Fig. 3d), indicating the excellent electrochemical stability of the MoS₂/(CoNi@G) in acidic solution. In contrast, the HER activities of the MoS₂ and the MoS₂/CNTs catalysts decay obviously during the similar durability test. Additionally, the stability of MoS₂/(CoNi@G) is

also evaluated by chronopotentiometric and chronoamperometric tests, both of which can maintain the catalytic stability for 24 h in acid electrolytes (Fig. S11). The structure of the catalyst is well preserved after the HER durability test of 24 h, as confirmed by HRTEM (Fig. S12) and XPS analysis (Fig. S13), showing no observable change in both the morphology and the electronic structures. These results demonstrate that the HER stability of SL-MoS₂ can be significantly enhanced by the

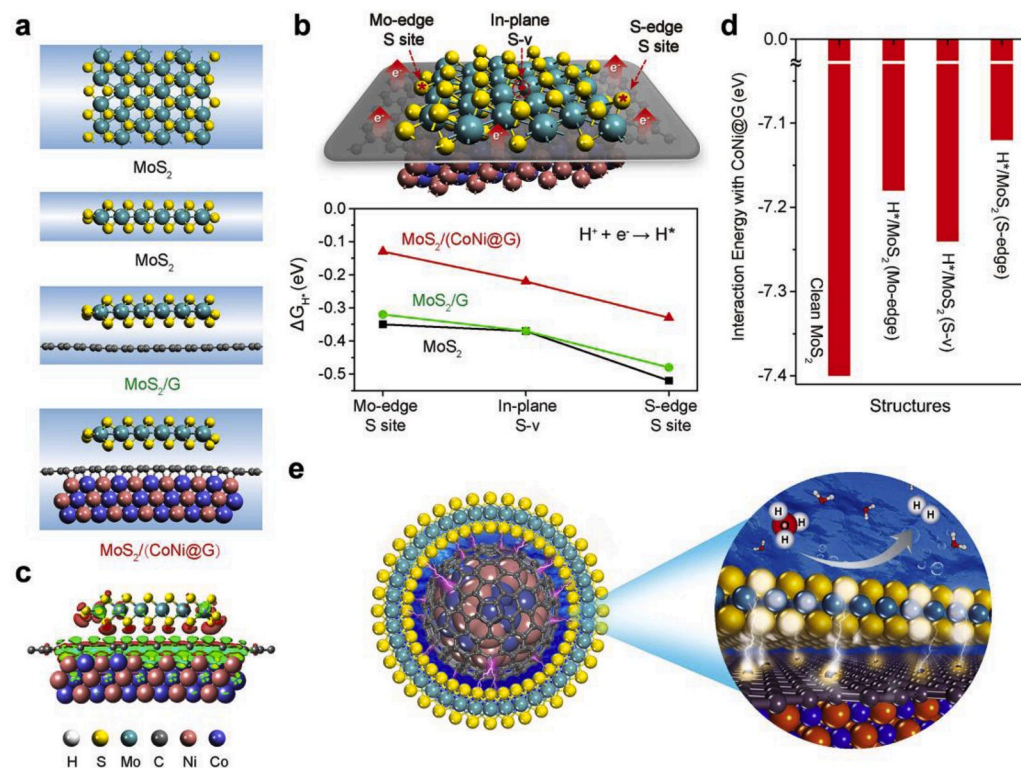


Fig. 4. Density functional theory study of the electron traversing effect in tuning the HER activity and stability of MoS₂/(CoNi@G). (a) Structures of pure MoS₂, MoS₂ supported on graphene (MoS₂/G), and MoS₂ supported on CoNi@G (MoS₂/(CoNi@G)) adopted for calculating the HER activity. The MoS₂ and CoNi parts are in nanoribbon models. (b) Illustration of the improved active centers including the Mo-edge and S-edge S sites and in-plane S vacancy (S-v) over MoS₂/(CoNi@G), and the corresponding adsorption free energies of H* at these sites of MoS₂, MoS₂/G, and MoS₂/(CoNi@G), respectively. (c) Differential charge density of MoS₂/(CoNi@G), obtained by using the charge densities of the entire structure subtracting those of the corresponding MoS₂, graphene, and CoNi parts. Red and green colors denote charge accumulation and depletion areas. (d) Binding energies of clean MoS₂ and the MoS₂ with H* adsorbed (H*/MoS₂) at different sites (Mo-edge, S-v, and S-edge) with the CoNi@G surface. (e) Schematic illustration of the HER on the MoS₂/(CoNi@G) catalyst.

electronic interaction between the MoS₂ and the CoNi@G surface induced by the traversed electrons.

To gain an atomic level understanding of the enhanced HER activity of the MoS₂/(CoNi@G) hybrid structure, density functional theory (DFT) calculations were performed to study the electron traversing effect in modulating the reactivity of the MoS₂ layers. Two-dimensional periodic graphene covering a nanoribbon model of CoNi alloy (CoNi@G) was adopted to simulate the SL-graphene encapsulating CoNi alloy (Fig. 4a). The adsorption free energies of H* (ΔG_{H^*}) on the Mo-edge, in-plane S vacancy, and S-edge sites of pure MoS₂ nanoribbon are −0.35, −0.37 and −0.52 eV, respectively. Supporting MoS₂ on bare graphene surface shows minor effect on the adsorption strength of H* (Fig. 4b). However, when introducing the CoNi alloy beneath the graphene, the ΔG_{H^*} is prominently reduced to −0.13, −0.22, and −0.33 eV at the corresponding Mo-edge, in-plane S vacancy, and S-edge sites of MoS₂/(CoNi@G), respectively, thus leading to notably enhanced HER activity of the MoS₂ shell (Fig. 4b). This denotes the significant role of metal cores in tailoring the HER activity of the MoS₂ shell via electron traversing from the metal to the outer MoS₂ layer, as shown in Fig. 4c. The weakened H* adsorption on the modulated MoS₂ sites originates from the different interaction energies of the clean MoS₂ and the MoS₂ with H* adsorbed on different sites (H*/MoS₂) with the graphene layer encapsulating CoNi metal (CoNi@G). The clean MoS₂ has a larger interaction energy with the CoNi@G compared with those of the H*/MoS₂ structures. Consequently, the clean active sites are more stabilized than the corresponding ones with H* adsorbed when supported on the CoNi@G and thereby the H adsorption activity is lowered (Fig. 4d). In view of the above results, the HER on MoS₂/(CoNi@G) is schematically depicted in Fig. 4e, in which the electrons derived from the CoNi metallic core can traverse through the SL-graphene to the outmost MoS₂ shell, leading to an enhanced HER performance on the MoS₂ shell.

4. Conclusions

In summary, via precisely growing double-layer MoS₂/graphene hybrid structure encapsulating CoNi alloy, we have experimentally and theoretically verified that the electrons derived from CoNi metallic cores, can traverse through the intermediate layer of graphene to the outmost MoS₂ shell. This is the first account of utilizing electron traversing effect to optimize the electronic structure of single-layer MoS₂. Such electron traversing effect induces a strong interaction between the MoS₂ and the CoNi@G surface, which optimizes the adsorption of hydrogen on both edge S sites and in-plane S vacancies of the MoS₂ shell toward a more favorable bonding strength for the HER. As a result, the optimized MoS₂/(CoNi@G) sample exhibits an enhanced HER activity and stability compared with pure MoS₂ nanosheets and MoS₂ coated on bare carbon. This work provides an innovative strategy of designing highly efficient and durable catalysts based on an electron traversing effect of graphene-encapsulated metal core.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Yunchuan Tu: Writing - original draft, Data curation, Investigation, Methodology. **Jiao Deng:** Writing - original draft, Investigation, Methodology. **Chao Ma:** Investigation, Methodology. **Liang Yu:** Methodology, Investigation, Software, Writing - review & editing. **Xinhe Bao:** Conceptualization, Supervision. **Dehui Deng:** Conceptualization, Supervision, Funding acquisition, Writing - review & editing.

Acknowledgements

We thank the staff at the BL14W1 beamline of Shanghai Synchrotron Radiation Facilities (SSRF) for assistance with the XAS measurements. This work was supported by the financial support from the National Key R&D Program of China (No. 2016YFA0204100 and 2016YFA0200200), the National Natural Science Foundation of China (No. 21890753, 21988101 and 21872140), the Key Research Program of Frontier Sciences of the Chinese Academy of Sciences (No. QYZDB-SSW-JSC020), the DNL Cooperation Fund, Chinese Academy of Sciences (No. DNL180201), and the China Postdoctoral Science Foundation (No. 2019M651156).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.nanoen.2020.104700>.

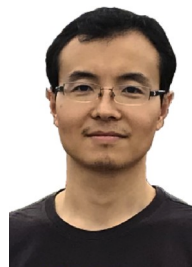
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