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Energy Level Engineering of MoS_2 by Transition-Metal Doping for Accelerating Hydrogen Evolution Reaction

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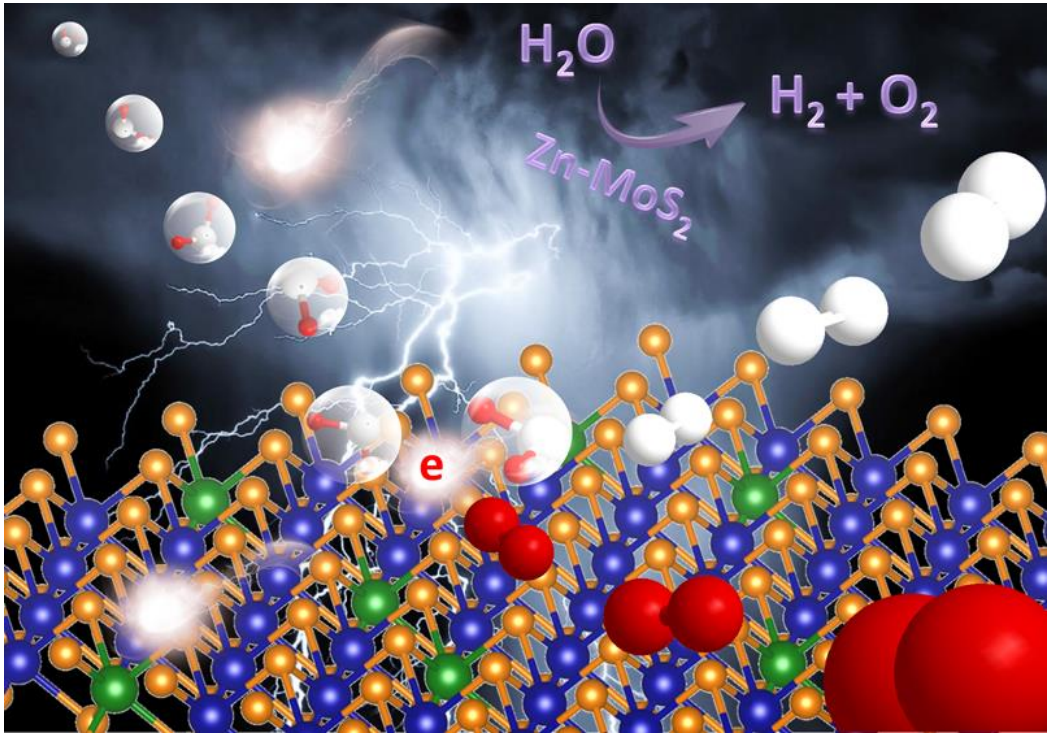

By
Biswajit
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Introduction

- In the modern industry of energy conversion, hydrogen holds great promise as the green energy carrier of the future due to its high energy density and zero effect of combustion product on environments.

- One of the most efficient pathway to produce hydrogen fuel is to electrolyze water in acidic media (hydrogen evolution reaction (HER), $2H^+ + 2e^- \longrightarrow H_2$).

- Up to date, promising alternatives of precise metals (Pt, Pd, and Rh) electrocatalyst have been exploited, including various combinations of metals (core−shell metals, metal alloys, single-atom metal-support nanostructures), 3d transition- metal (3d-TM) sulfides, 3d-TM phosphides, 3d-TM nitrides, along with molecular catalysts.

- Among these alternatives, molybdenum sulfide (MoS_2) has been recently considered as a promising and efficient nonprecise metal catalyst for HER.

- Unfortunately, nanostructured MoS_2 with large bandgap still suffers from sluggish kinetics of HER, which dramatically limits the overall electrocatalytic HER rate.

In this paper…

- In this paper, they have synthesized different transition metals doped MoS_2 (M-MoS_2, M = Zn, Cu, Fe, Ni, and Co) using solvothermal method.

- They have shown the easy pathway to engineer the electronic density of MoS_2 for accelerating HER via doing the semiconductor with different transition-metals.

Results and Discussion

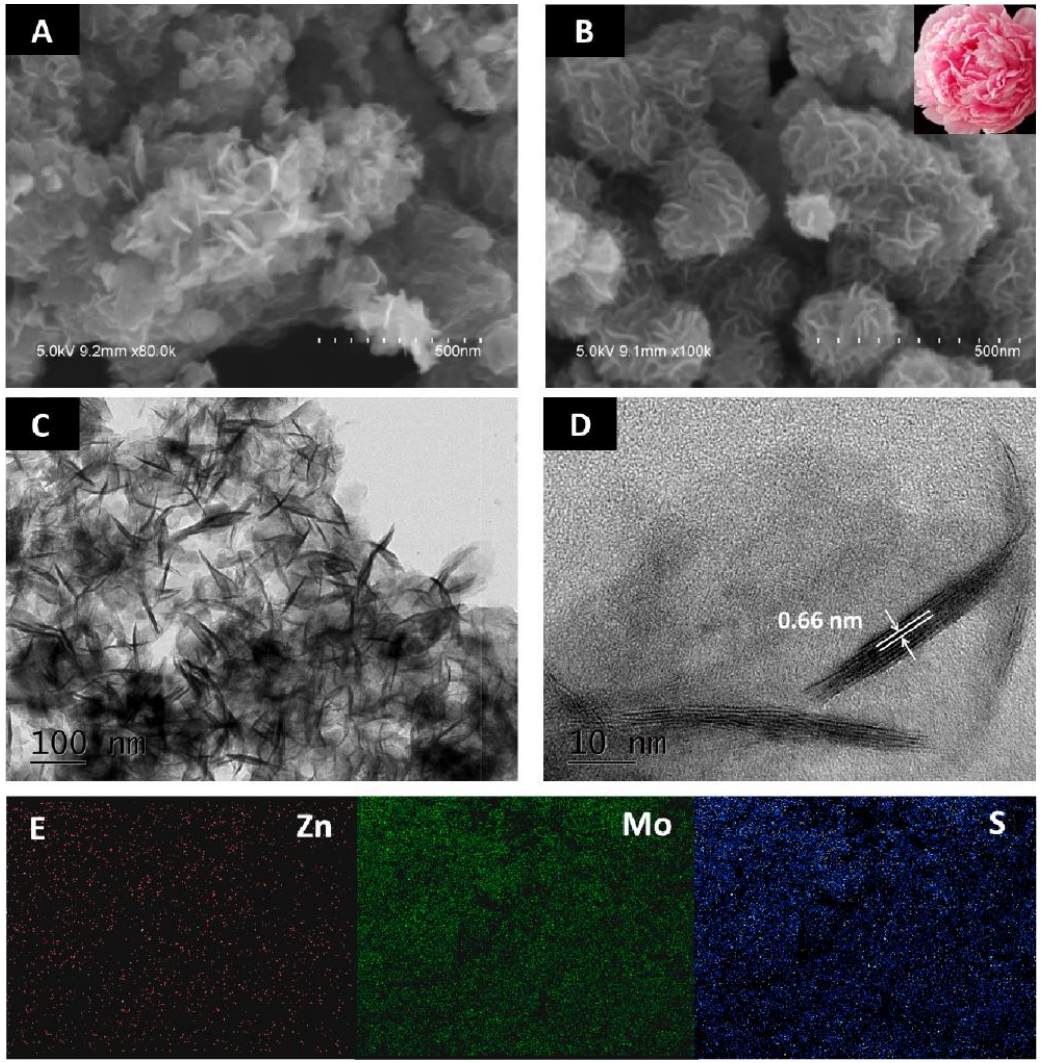


Figure 1. Morphologic characterizations of the catalysts. SEM images of pure MoS_2 (A) and Zn-MoS_2 (B). TEM (C) and HRTEM images (D) of Zn-MoS_2. Down panel shows the element mapping images of Zn, Mo, and S of Zn-MoS_2 (E).

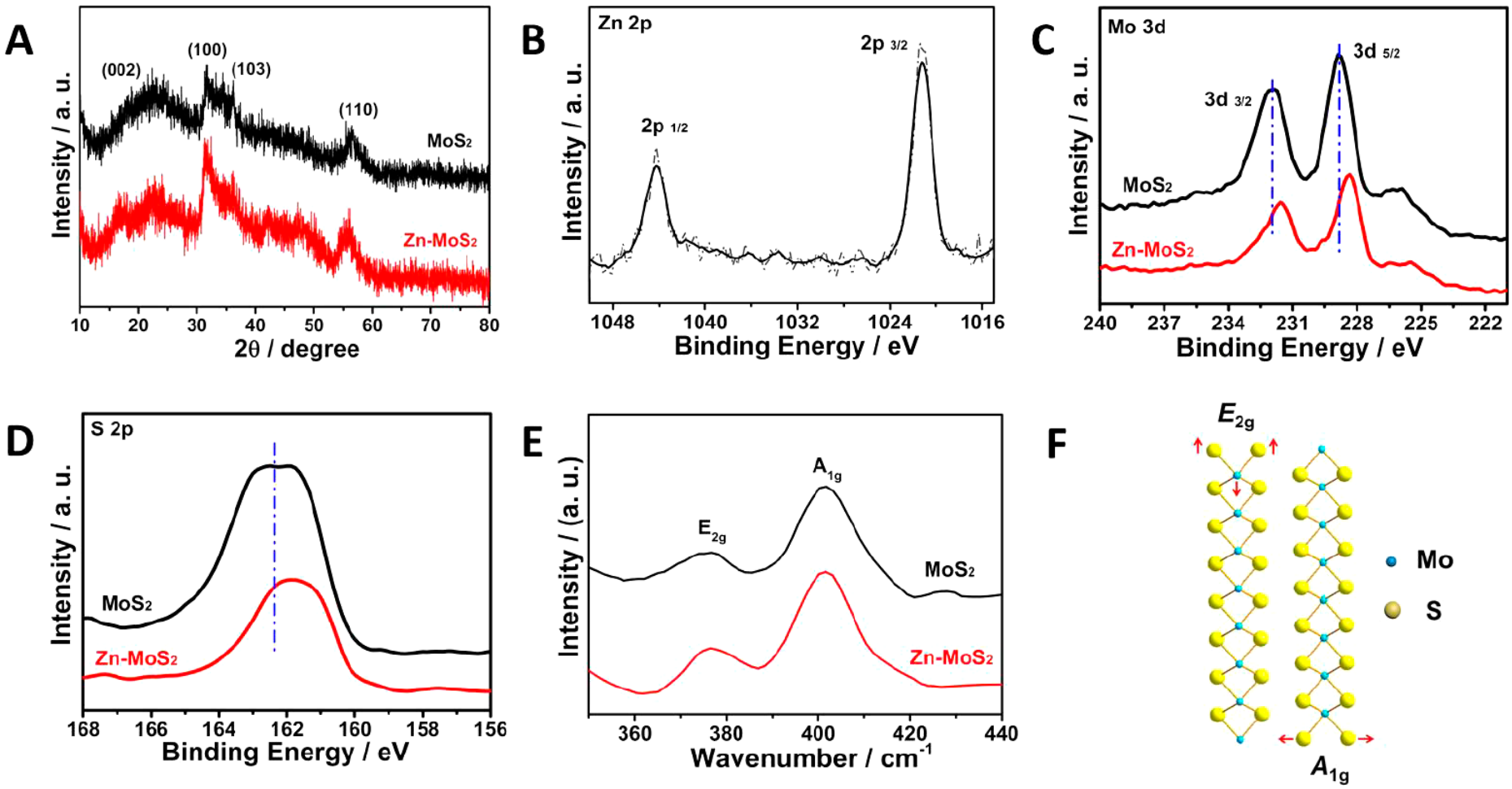


Figure 2. Spectral characterizations of the catalysts. (A) XRD patterns of pure MoS_2 and Zn-MoS_2. XPS spectra of Zn-MoS_2 as indicated in the Zn 2p (B), Mo 3d (C), and S2p (D) regions. (E) Raman spectra of pure MoS_2 and Zn-MoS_2. (F) Schematic diagram of different vibration modes of MoS_2. The E_{2g} and A_{1g} modes represent the in-plane (two S atoms moving in same direction, opposite to Mo atom) and out-of-plane (two S atoms moving in opposite directions) vibrations for MoS_2, respectively.

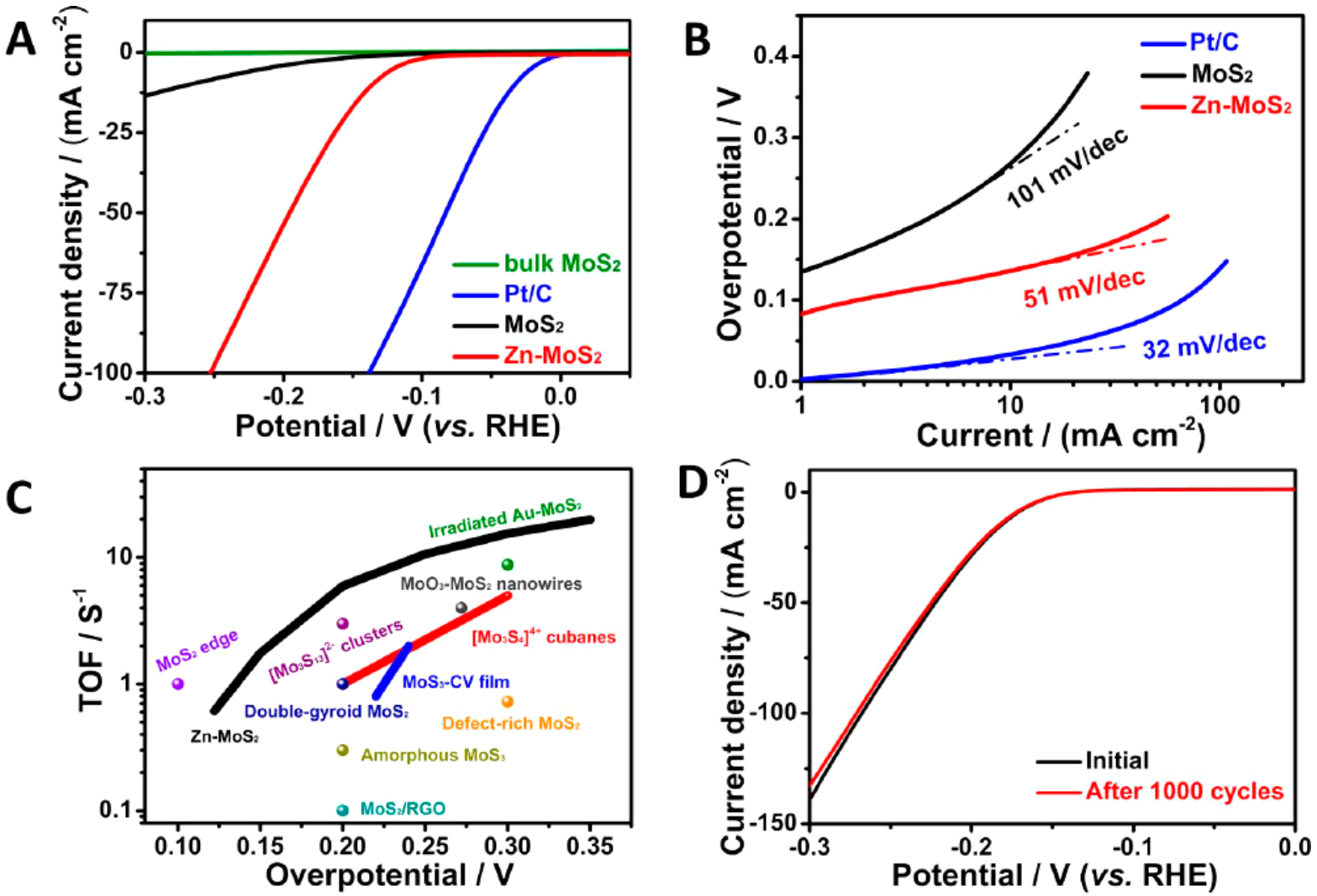
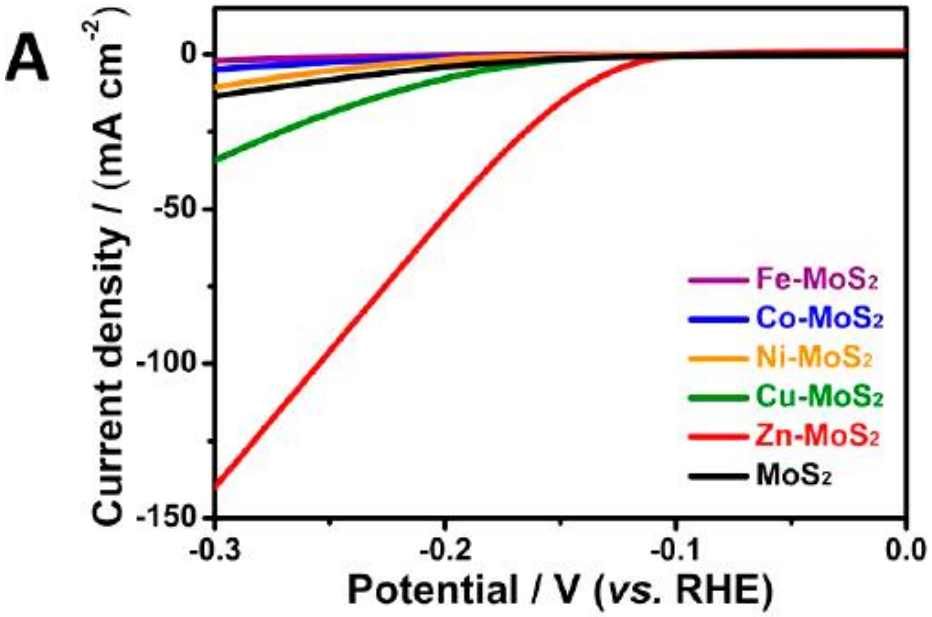


Figure 3. Electrochemical activities of various catalysts toward HER. (A) Polarization curves of HER for various catalysts. (B) Tafel plots of the corresponding electrocatalysts derived from the early stages of HER polarization curves. (C) TOF values of the Zn-MoS_2 catalyst (black line) and other MoS_2-based catalysts reported recently. (D) Stability tests by measuring the polarization profiles for Zn-MoS_2 catalyst before and after 1000 cyclic potential scans in 0.5 M H_2SO_4 at a scan rate of 20 mV s^{-1}.



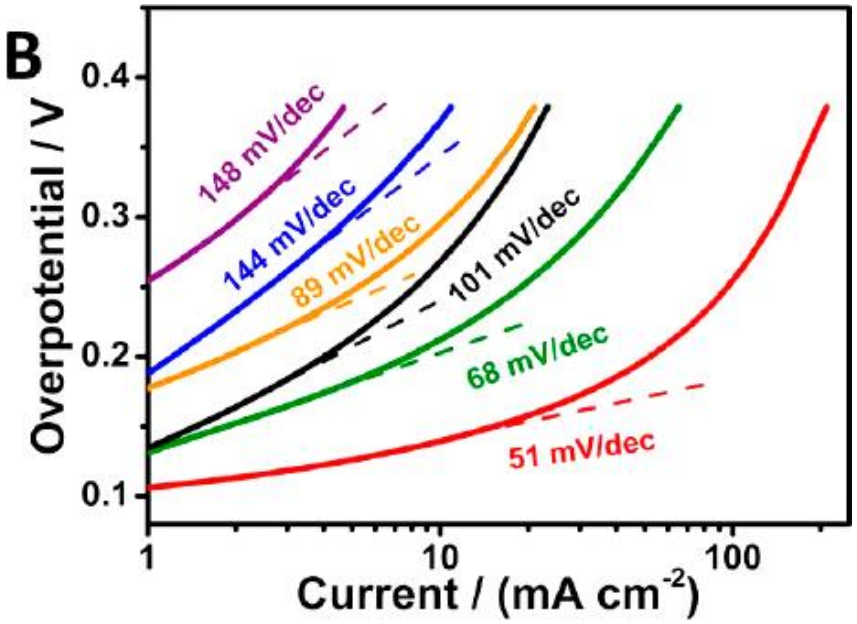


Figure 4. Electrochemical activities of various catalysts toward HER. (A) HER polarization curves of various catalysts as indicated. (B) Tafel plots of the corresponding electrocatalysts derived from the early stages of HER polarization curves.

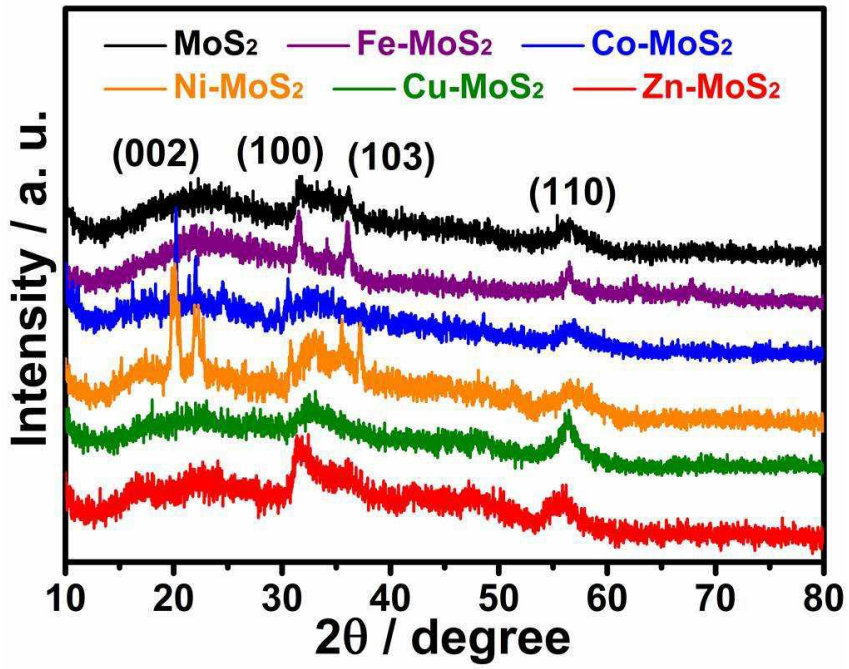


Figure 5. XRD patterns of various TM-doped MoS_2 in comparison to pure MoS_2.

Table S3. Specific atomic ratios of the transition metals in M-MoS_2.

	Fe	Co	Ni	Cu	Zn
0.5-fold	6.2%	6.05%	6.08%	5.24%	1.86%
1-fold	10.77%	10.94%	10.45%	8.71%	4.33%
2-fold	23.48%	26.82%	17.99%	14.44%	9.40%
3-fold	29.88%	33.14%	25.69%	23.61%	14.25%

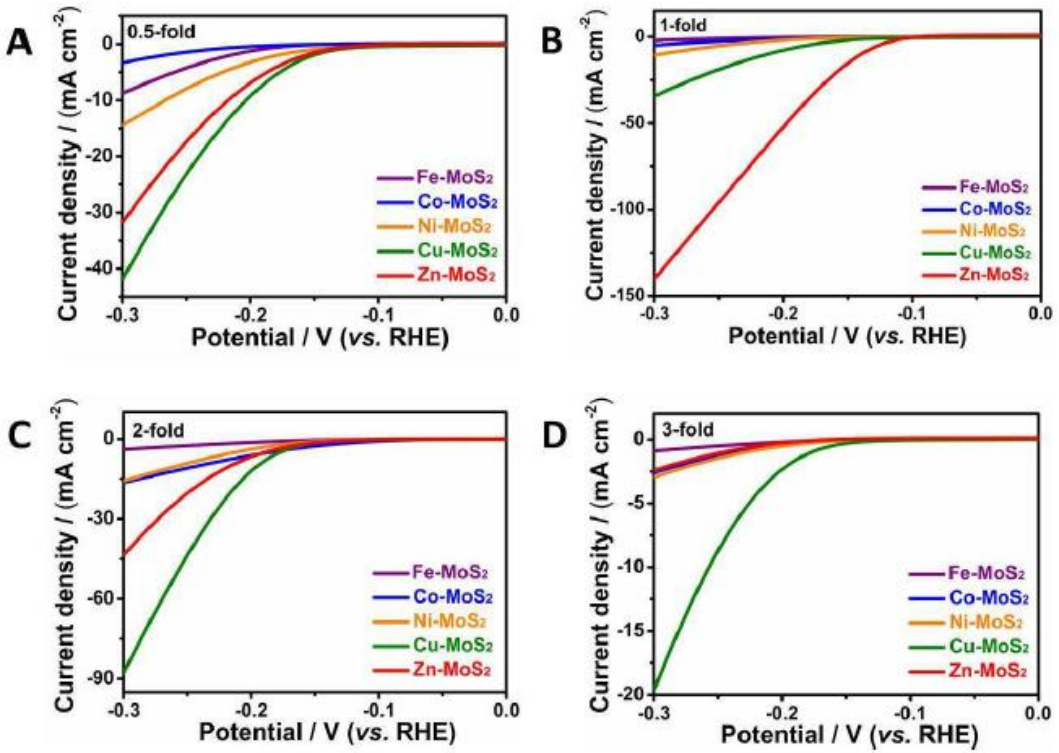


Figure 6. HER polarization curves obtained on Cu-MoS_2 and Zn-MoS_2 of different doping amounts as indicated and corresponding HER current density at 0.3 V *vs.* RHE.

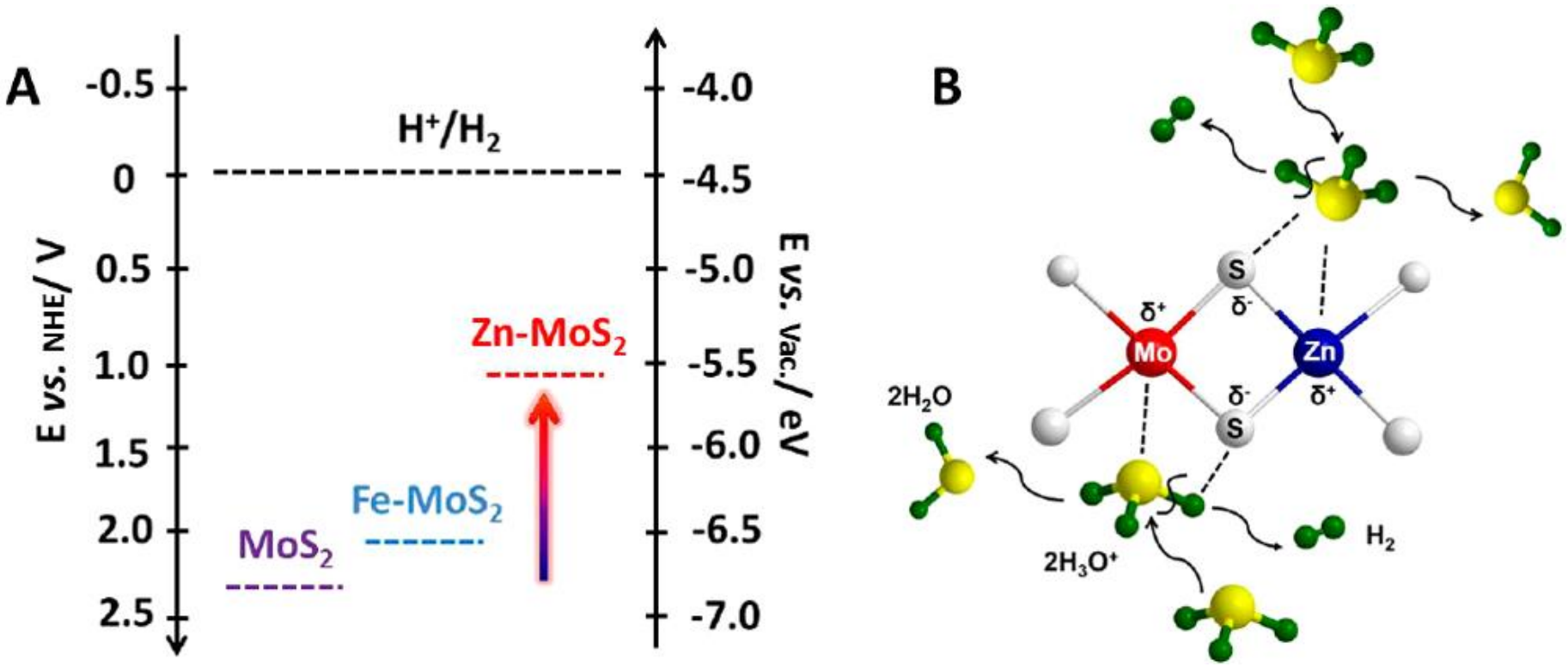


Figure 7. Energy level related HER mechanism. (A) Band structure diagram for Zn-MoS_2, Fe-MoS_2, and pure MoS_2. (B) Schematic illustration of formation of undercoordinated Mo (δ+) and Zn (δ+) centers during the HER and the plausible reaction mechanism.

Conclusion

- Their results demonstrate that engineering the electronic density of MoS_2 via different transition-metal doping can significantly influence the HER performance.
- Zinc-doped MoS_2 (Zn-MoS_2) has been designed as a model system to understand the fundamental relationship between the MoS_2 nanostructure and the thermodynamics and kinetics of HER.
- Zn-MoS_2 exhibits the superior electrochemical activity toward HER with the onset potential of −0.13 V vs RHE and the Tafel slope of 51 mV dec^{-1}.
- The large enhancement can be attributed to the synergistic effect of electronic effect (energy level matching) and morphological effect (rich active sites) via thermodynamic and kinetic acceleration, respectively.