



MoS₂ on topological insulator Bi₂Te₃ thin films: Activation of the basal plane for hydrogen reduction

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ABSTRACT

2H-MoS₂ is a well-studied and promising non-noble metal electrocatalyst for heterogeneous reactions, such as the hydrogen evolution reaction (HER). The performance is largely limited by the chemically inert basal plane, which is unfavorable for surface adsorption and reactions. Herein, we report a facile method to boost the HER activities of 2H-MoS₂ by coupling with epitaxial Bi₂Te₃ topological insulator films. The as-obtained MoS₂/Bi₂Te₃/SrTiO₃ catalyst exhibits prominent HER catalytic activities compared to that of pure MoS₂ structures, with a 189 mV decrease in the overpotential required to reach a current density of 10 mA cm⁻² and a low Tafel slope of 58 mV dec⁻¹. Theoretical investigations suggest that the enhanced catalytic activity originates from the charge redistribution at the interface between the Bi₂Te₃ topological insulator films and the MoS₂ layer. The delocalized *sp*-derived topological surface states could denote electrons to the MoS₂ layer and activate the basal plane for hydrogen adsorption. This study demonstrates the potential of manipulating topological surface states to design high-performance electrocatalysts.

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1. Introduction

Emerging topological materials provide an ideal platform to explore the relationship between exotic topological properties and surface chemical reactions. Benefiting from symmetry-protected topological orders, topological materials exhibit distinctively different behaviors compared to those of topologically trivial materials, from robust topological surface states (TSSs) to high-mobility carriers [1]. Acceptor- or donor-like TSSs are active for the adsorption of reaction intermediates and can act as electron baths for reduction or oxidation reactions [2,3]. As the existence of a TSS is protected by the bulk band structure, they cannot be eliminated by surface defects, dangling bonds, or molecular adsorption [4,5]. These properties have evoked a wave of research interest to understand and design topological phase catalysts for heterogeneous reactions such as hydrogen evolution reactions (HERs).

Topological insulators (TIs) in the Bi₂Se₃ family, such as Bi₂Se₃ and Bi₂Te₃, are commonly believed to be model topological insulator systems with a well-defined bulk bandgap and a single-Dirac-cone surface state, which are ideal for studying the role of TSSs in catalytic reactions [6–8]. Early theoretical investigations indicate that the adsorption energies of small molecules such as CO and O₂ can be enhanced due to the delocalized surface states when Bi₂Se₃ thin films are used as substrates [9]. This strategy has proved effective in tailoring the adsorption behavior of other transition metals, including Au, Ag, Cu, Pt, and Pd [10]. However, topological Bi₂Se₃-family compounds themselves are not suitable as HER catalysts. The *sp*-like TSSs result in weak bonding between the HER intermediates and catalyst surfaces, leading to a slow Volmer process because of the low coverage of the reaction intermediates [11]. Even when using Bi₂Se₃ and Bi₂Te₃ nanostructures, an extremely high overpotential of above 600 mV is needed to deliver a current density of 10 mA cm⁻² [12]. Thus, it remains a challenge to combine the advantages of robust TSSs and favorable Gibbs free energy in the design of high-performance HER catalysts.

Coupling topological materials with transition-metal-based compounds has been considered an effective strategy to address the problems mentioned above. The vertical position of the TSSs

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can be adjusted by depositing a conventional insulator overlayer onto a TI substrate due to topological proximity effects [13]. In other words, the TSSs can float onto the top of the conventional insulator layer, suggesting the possibility of tailoring the surface catalysis behavior. This theory was verified by constructing monolayer ZnSe on Bi₂Te₃ films, resulting in favorable Gibbs free energy for the HER [14]. The enhanced HER performance is ascribed to the decrease in the band gap, as well as the low surface resistivity resulting from the metallic TSSs [15]. However, most of the reported experimental works have focused on the design of nanocomposites with uncertain exposed crystal surfaces and unexpected defects, causing difficulties in precisely understanding the contribution of TSSs [16–18].

To overcome the problem of an uncertain crystal structure, we constructed a new heterostructure with well-defined, chemically stoichiometric compositions and atomically shaped interfaces. First, high-quality stoichiometric single-crystalline Bi₂Te₃ films with determined crystal surfaces were used as the substrates. Next, 2H-MoS₂ thin layers, with their HER mechanism having been unambiguously determined, were deposited on the Bi₂Te₃ films [19–22]. Our experimental results indicate that the MoS₂/Bi₂Te₃ heterostructure exhibits a lower overpotential and Tafel slope than those of pure MoS₂ nanostructures. In situ scanning electrochemical microscopy (SECM) revealed high HER kinetics in the presence of Bi₂Te₃ films. In combination with density functional theory calculations, it was found that the originally inert basal plane of MoS₂ can be activated due to charge redistribution in the MoS₂ layer as a result of electron transfer from the *p* orbitals of TSSs. This study provides an alternative strategy to utilize the large area of the basal plane for MoS₂, although they are still not as active as the edges [23,24].

2. Experimental

2.1. Synthesis of Bi₂Te₃ topological insulator thin films

The Bi₂Te₃ films were grown on niobium-doped SrTiO₃(111) (STO) substrates in an ultra-high vacuum molecular beam epitaxy (MBE) system with a base pressure of $\sim 8 \times 10^{-11}$ mbar. High-purity Bi (99.9999%) and Te (99.9999%) were evaporated from separated standard Knudsen cells. The critical growth parameters were the flux ratio of Te₂/Bi (θ) and substrate temperature (T_{sub}). The conditions for layer-by-layer growth of Bi₂Te₃ films were established with θ maintained at approximately 15–20 and T_{sub} set at approximately 115 °C.

2.2. Synthesis and exfoliation of MoS₂ nanostructures

(NH₄)₂MoS₄ (50 mg) was placed in a 30 mL autoclave filled with 20 mL of N, N-dimethylformamide. N₂H₄·H₂O (0.1 mL) was added dropwise. The mixed solution was transferred into an oven and heated at 180 °C for 24 h. The resulting product was washed with water, then with ethanol, and dried at 60 °C. For the exfoliation process, the as-prepared bulk MoS₂ precursor was added to a 50 mL glass vial containing 30 mL of N, N-dimethylformamide. The mixtures were sonicated in a water-cooled bath at 25 °C for 12 h and then centrifuged at 6000 rpm for 10 min to remove the residual bulk MoS₂. The suspensions were dried and re-dispersed in ethanol for the following drop-casting process.

2.3. Synthesis of MoS₂/Bi₂Te₃ nanostructured catalysts

Bi₂Te₃ nanoplates were synthesized first with a solvothermal method. 0.4 g of polyvinylpyrrolidone, 0.32 g of NaOH, 0.45 g of Bi(NO₃)₃·xH₂O, and 0.4 g of NaTeO₃ were placed in a beaker and

filled with 30 mL of ethylene glycol. The precursor solution was stirred for 5 h and then sealed in the autoclave and heated at 180 °C for 24 h. The residue was washed thoroughly and then dried under vacuum at 60 °C for 24 h. For the deposition of MoS₂ nanoparticles, 50 mg of the Bi₂Te₃ nanoplates and 10 mg of (NH₄)₂-MoS₄ were mixed. This experimental procedure is the same as the description in section 2.2.

2.4. Materials characterization

The film deposition was monitored by *in situ* reflection high-energy electron diffraction (RHEED), and *ex-situ* X-ray diffraction (XRD, Bruker D8), and atomic force microscopy (AFM). The surface morphology of the film of MoS₂ nanoparticles was recorded using a TESCAN scanning electron microscope. Raman spectra were recorded using a customary confocal micro-Raman spectrometer with a HeNe-laser (wavelength 632 nm) as the excitation source and a single-grating spectrograph with 1 cm⁻¹ resolution.

2.5. Electrochemical measurements

The electrochemical performance was assessed in a 0.5 M H₂SO₄ electrolyte on an Autolab PGSTAT302N with a conventional three-electrode cell configuration. The MoS₂ ink was drop-cast on the required substrate (STO or Bi₂Te₃/STO) and simultaneously baked to evaporate the solvent. Substrates with different catalysts were attached to a Ti wire and used directly as a working electrode. An Ag/AgCl (3 M KCl) electrode was used as the reference electrode, and a graphite rod was used as the counter electrode. Linear sweep voltammetry was performed at a scan rate of 1 mV/s. All of the polarization curves were IR-corrected using electrochemical impedance spectroscopy (EIS). All of the potentials reported in this work were converted to the reversible hydrogen electrode potential according to E (versus RHE) = E (versus Ag/AgCl) + (0.207 + 0.059 pH) V.

SECM was carried out using an SECM setup (Sensolytics, Bochum, Germany) in combination with an Autolab PGSTAT302N potentiostat. The electrochemical cell was composed of four electrodes. A Pt wire with a diameter of 10 μm sealed in a soda-lime glass served as working electrode 1. A Pt mesh was used as the counter electrode, and Ag/AgCl (3 M KCl) in the aqueous phase was used as the reference electrode. The studied catalyst on the substrate acted as working electrode 2.

3. Results and discussion

3.1. Structure characterization of topological thin films and 2H-MoS₂

The final device (MoS₂/Bi₂Te₃/STO) used for the electrocatalytic HER assessment is illustrated in Fig. 1a. First, high-quality Bi₂Te₃ single-crystalline films were grown on conductive Nb-doped STO substrates by MBE, with the method optimized based on a previous study [25]. The surface morphology and roughness were characterized by AFM. It is interesting to observe that the films exhibited flat surfaces at a large scale with atomically flat terraces, indicating high-quality thin films (Fig. 1b and Fig. S1). The atomically flat morphology was further confirmed by the sharp streaky pattern resulting from RHEED under electron incidence in the 11 $\bar{2}$ direction (Fig. 1c). A lattice spacing of 4.38 Å is indicated by the corresponding principal diffraction lines, which is consistent with rhombohedral Bi₂Te₃. The phase and crystallinity of the films were identified by XRD (Fig. 1d). Only diffraction peaks belonging to the (003) family are observed in the θ -2 θ scan, indicating preferential *c*-axis-oriented epitaxial growth of the Bi₂Te₃ films along the [111] plane of the SrTiO₃ substrate. Bulk MoS₂ thin films were deposited

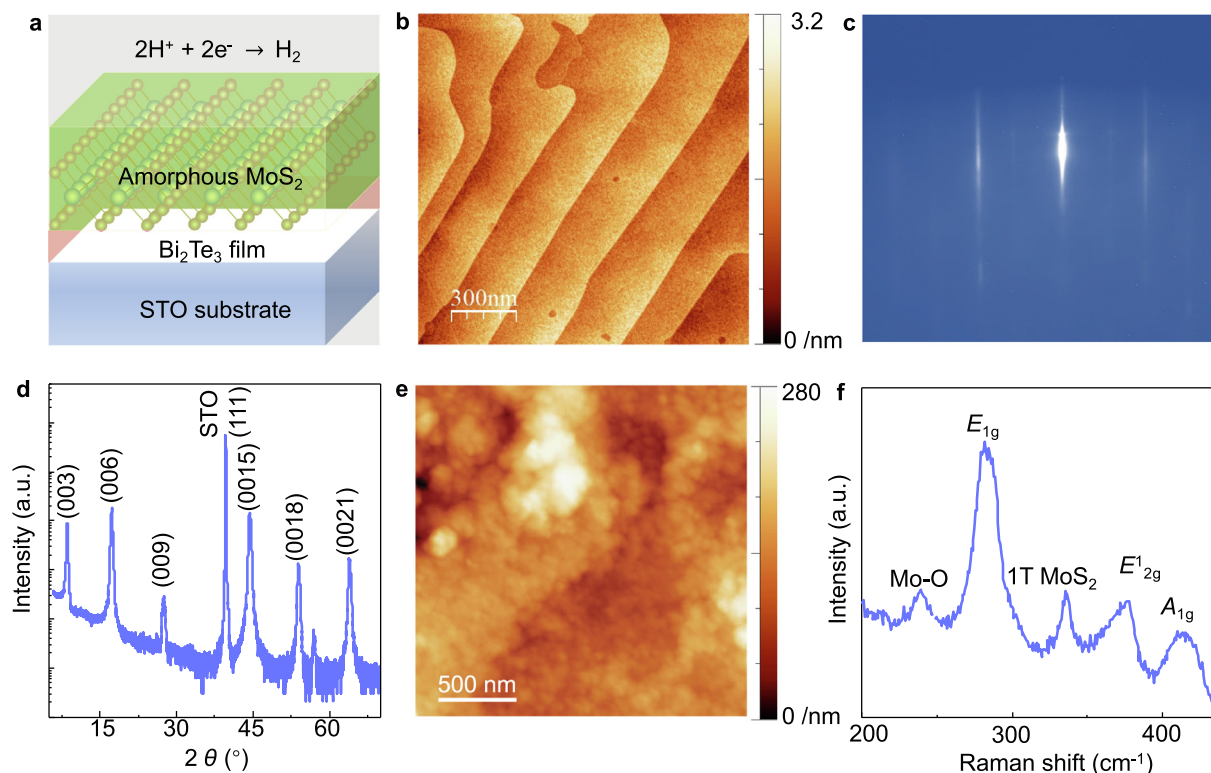


Fig. 1. (a) Illustration of the MoS₂/Bi₂Te₃/STO heterostructure catalysts. (b). AFM surface morphology of Bi₂Te₃ films grown on STO substrate, and (c) the corresponding RHEED pattern. (d) XRD scan of the as-prepared single-crystalline Bi₂Te₃ films. (e) AFM image of the drop-casted MoS₂ thin layer on Bi₂Te₃ films. (f) Raman spectroscopy of the exfoliated MoS₂ thin layer.

on the as-prepared Bi₂Te₃/STO substrate using a drop-casting method [26]. As revealed by the AFM image (Fig. 1e), the liquid-exfoliated MoS₂ nanoparticles were uniformly distributed with an average film thickness of ~100 nm on the top of the Bi₂Te₃ layer. The crystal structure of the exfoliated MoS₂ nanoparticles was characterized by Raman spectroscopy (Fig. 1f). The Raman shifts (283, 377, and 414 cm⁻¹) are associated with the phonon modes of E_{1g}, E_{2g}¹, and A_{1g} in 2H-MoS₂, respectively [27,28]. The peak at 336 cm⁻¹ suggests the existence of a small amount of 1T-MoS₂ [29]. Minor surface oxidation was observed from Mo–O stretching frequencies at 240 cm⁻¹. The successful deposition was further confirmed by energy-dispersive X-ray spectroscopy, in which Mo, S, Bi, and Te were detected (Fig. S2).

3.2. Electrochemical HER performance of MoS₂ based catalysts

The experiments were conducted in an Ar-saturated 0.5 M H₂SO₄ electrolyte solution using a standard three-electrode electrochemical setup with a graphite rod as the counter electrode. The device was attached to a Ti wire and served as the working electrode. For a clear understanding of the role of topological thin films, several other devices, including a pure substrate (STO), MoS₂-deposited STO without TI films (MoS₂/STO), and TI films without MoS₂ layers (Bi₂Te₃/STO) were also investigated. As shown by the iR corrected polarization curves in Fig. 2a, the STO substrate and Bi₂Te₃ thin films have negligible activities in the HER. This is consistent with previous research stating that, even with exfoliated Bi₂Te₃ few-layered nanosheets, an overpotential of nearly 700 mV is needed to deliver a current density of 10 mA cm⁻² [12].

The slow reaction kinetics are a result of the extremely weak hydrogen adsorption at the Bi₂Te₃ (001) surface (0.8 eV), leading to a low reaction intermediate coverage [11]. The direct deposition of exfoliated MoS₂ nanoparticles onto the STO substrate (MoS₂/

STO) led to an enhanced HER efficiency with an overpotential of 437 mV to reach the same current density, which is consistent with previous research on various MoS₂ films [30]. Thus, it was concluded that Bi₂Te₃ thin films and exfoliated pristine MoS₂ nanosheets are not active in the HER. In sharp contrast, an overpotential of only 248 mV was required to reach a current density of 10 mA cm⁻² when a layer of Bi₂Te₃ thin film was introduced between the MoS₂ nanosheets and STO substrate (MoS₂/Bi₂Te₃/STO). It should be pointed out that the use of high-quality epitaxial thin films is not necessary, as the interaction of 2H MoS₂ (001) surface and Bi₂Te₃ (001) surface is pretty strong with an adsorption energy of -1.7 eV. We expect a similar enhancement catalytic activity with Bi₂Te₃ nanostructures. Thus, MoS₂/Bi₂Te₃ nanostructured catalysts were synthesized successfully as evidenced by the SEM images, XRD diffraction, and element analysis (Fig. S3). The drop-casted MoS₂/Bi₂Te₃ nanostructured on STO exhibited displayed a similar HER activity with the thin film's system (Fig. S4). The overpotential decreased to only 160 mV at a current density of 10 mA cm⁻² and shows high stability when deposited on the more conductive Ni foam (Fig. 2a, Fig. S5). This overpotential places the modified thin films in the top tier of MoX₂ (X = S, Se)-based hydrogen evolution catalysts [21,31] and better than the recently reported topological Bi₂X₃ (X = Se, Te) catalysts (Table S1) [11,32,33].

The enhanced catalytic performances were confirmed kinetically from the Tafel slopes derived from the polarization curves of the three samples (Fig. 2b). An extremely high Tafel slope of 168 mV dec⁻¹ was observed for the Bi₂Te₃ thin film catalyst, which is consistent with the poor HER activity. The Tafel slope of the MoS₂ nanosheet catalyst has a two-step characteristic, starting from 80 mV dec⁻¹ at the low overpotential range and shifting to as high as 361 mV dec⁻¹ at potentials above 380 mV. Similar results were observed for a state-of-the-art Pt/C catalyst, with

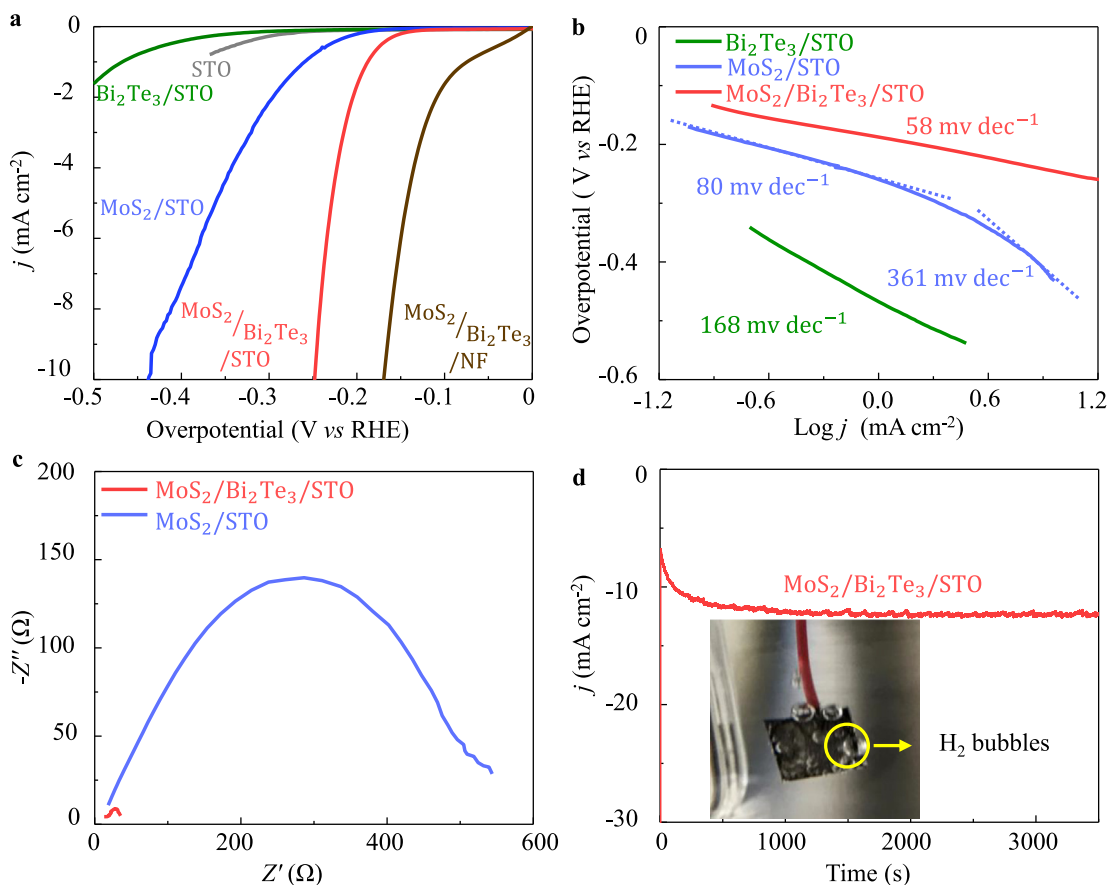


Fig. 2. (a) HER polarization curves of the pure STO substrate, MoS₂/STO, Bi₂Te₃/STO, and MoS₂/Bi₂Te₃/STO catalysts. (b) Corresponding Tafel plots were obtained from the polarization curves. (c) Nyquist plots of MoS₂/STO and MoS₂/Bi₂Te₃/STO catalysts. (d) Stability test of the MoS₂/Bi₂Te₃/STO heterostructure catalysts; inset: the electrolytic evolution of hydrogen bubbles at the catalyst surface.

the Tafel slope shifting from 30 to 120 mV dec⁻¹ as the overpotential increased, indicating that the reaction kinetics and mechanisms are strong potential and coverage dependent [34,35]. However, the Tafel slope of the MoS₂/Bi₂Te₃/STO catalysts was significantly lower at 58 mV dec⁻¹, which compares favorably with other recently reported high-performance earth-abundant HER electrocatalysts [36]. Impressively, there is no transition in the Tafel slopes over a wide overpotential range, suggesting high stability of the rate constant even at a high intermediate species coverage [37]. To better understand the role of Bi₂Te₃ thin films on the boosted HER activity of MoS₂, EIS analyses of the two electrodes with and without the Bi₂Te₃ interlayer were performed under the same conditions (Fig. 2c). The Nyquist plots show that MoS₂/Bi₂Te₃/STO catalysts have a much smaller charge transfer resistance than bare MoS₂, indicating a faster Faradaic process and better HER kinetics with the introduction of a Bi₂Te₃ thin film layer. As another important criterion for HER catalysts, the long-term electrocatalytic stability of the MoS₂/Bi₂Te₃/STO catalyst was determined by the constant current–time curve, with a clear hydrogen bubble forming at the surface (Fig. 2d).

3.3. In-situ SECM investigation of HER performance

To spatially probe the difference in catalytic activities with and without the Bi₂Te₃ interlayer, SECM was used to map the local electron transfer kinetics. MoS₂ nanosheets were deposited on an STO substrate half-covered with Bi₂Te₃ thin films. This served as working electrode 2, as illustrated in Fig. 3a. A Pt wire with a diameter of 10 μm was sealed in soda-lime glass and served as a work-

ing electrode for current collection. Ag/AgCl (3 M KCl) in the aqueous phase was used as the reference electrode. The approach curve was constructed with the feedback model in a solution of 5 mM [Fe(CN)₆]³⁻ in 100 mM KCl (Fig. S6). The tip current (*i*)-distance curve exhibited a typical SECM negative feedback model, indicating a low conductivity of the semi-conductive 2H phase MoS₂. The HER activities of the catalysts with and without the Bi₂Te interlayer thin films were detected using the substrate generation/tip collection (SG/TC) mode. An HClO₄ electrolyte with a concentration of 100 mM was used for stable tip current collection. Fig. 3b depicts CVs performed at different positions and clearly shows that the MoS₂/Bi₂Te₃/STO catalysts have higher activities than those without the Bi₂Te₃ interlayer. The HER catalytic activity maps of the catalysts at a constant applied potential are displayed in Fig. 3c. Low activity was observed in areas without the Bi₂Te interlayer, and activity increased rapidly when the tip was moved to the top of the MoS₂/Bi₂Te₃/STO catalyst. The corresponding line profile extracted from the SG/TC mode provides an intuitive view of the differences in HER activity. The HER activity increased three-fold in the presence of the Bi₂Te₃ interlayer (Fig. 3d).

3.4. Theoretical understanding of the role of TI substrate

TIs such as those in the Bi₂Se₃ family have unfilled TSSs around the Fermi level, which is derived from the delocalized *sp*-band. They could donate or accept electrons from the surface adsorbates and tailor the adsorption energy [9]. To probe the role of the Bi₂Te₃ interlayer in the HER catalytic process, a three-dimensional charge density difference simulation for the heterostructure catalysts was

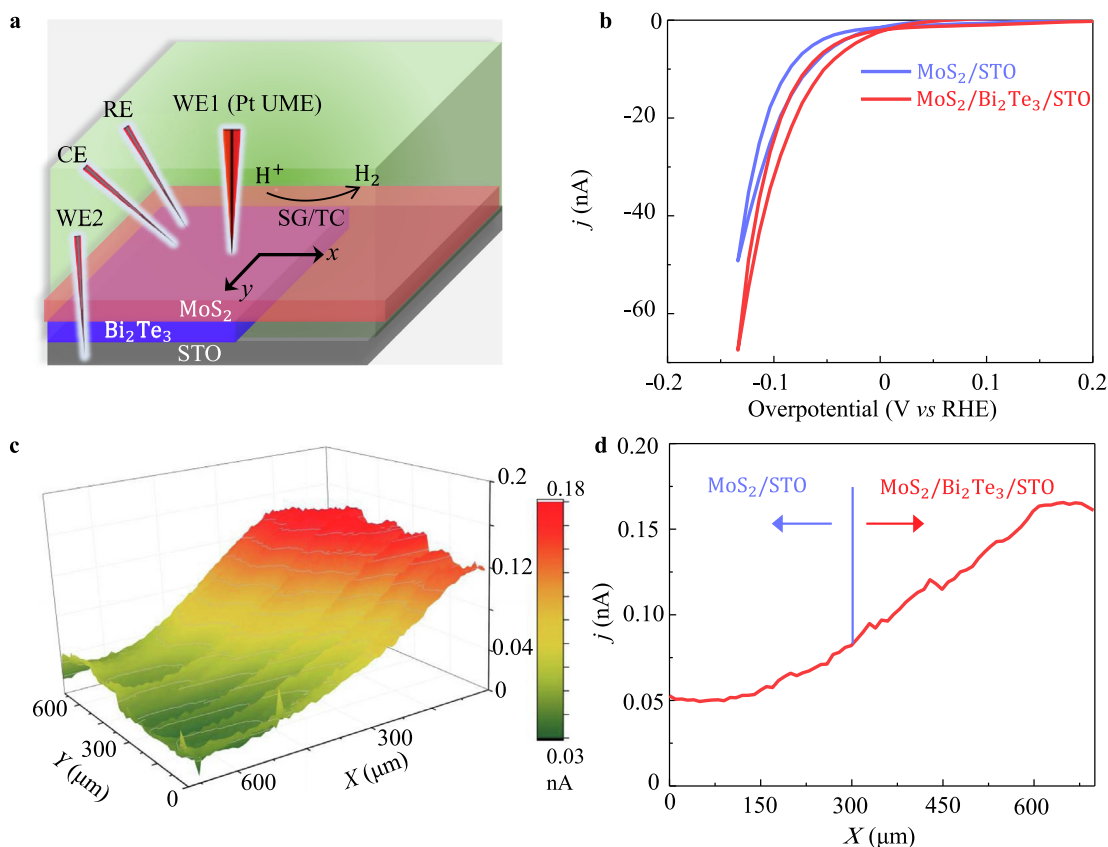


Fig. 3. (a) Schematic representation of the setup for SECM measurements. (b) CV curves were obtained with the tip on the position of MoS₂/STO and MoS₂/Bi₂Te₃/STO areas. (c) SG/TC mode (HER activity) image of the catalysts containing MoS₂/STO and MoS₂/Bi₂Te₃/STO. (d) HER SG/TC line profile with the tip scanned from MoS₂/STO to MoS₂/Bi₂Te₃/STO area.

carried out. It can be seen clearly that charge redistribution mainly occurs near the interfacial region between MoS₂ and the Bi₂Te₃ substrate (Fig. 4a). More specifically, charge accumulation

occurs in the central region of the interface, while the charge depletion is mostly distributed on the topological Bi₂Te₃ substrate, suggesting charge transfer to the MoS₂

layer. This is important for tailoring the adsorption energy of the MoS₂ basal plane, which is well agreed to be catalytically inert toward adsorption and catalysis. To further elucidate the influence of charge redistribution on the HER, we considered the adsorption of hydrogen on the MoS₂ basal plane. The electron depletion region occurs mainly around the S atoms, suggesting their tendency to donate electrons to the adsorbed H atom. At the same time, clear charge accumulation was observed between the S atoms and the adsorbed H atom. Bader charge analysis revealed an electron loss of 0.04 from the MoS₂ monolayer, indicating better adsorption of hydrogen at the basal plane (Fig. 4b). The electron re-distribution in the interface is further evidenced by the Raman spectroscopy recorded on pure Bi₂Se₃ and MoS₂/Bi₂Se₃ hybrid (Fig. 4c). Four Raman active modes were observed for pure Bi₂Se₃, which is consistent with the literature [38]. However, with MoS₂ loaded, the intensity of A_{1g}¹ peak decreased significantly. This suggests an increase in electron density and lowered energy at atoms on the surface, which making the vibration weak out of the plane and thus Raman inactive [38,39]. The Gibbs free energy of hydrogen adsorption decreased from 2.43 eV for the basal plane to 1.4 eV for the MoS₂/Bi₂Te₃/STO heterostructures, although it is still inferior to the edges of the MoS₂ catalyst (Fig. 4d). These theoretical investigations suggest the importance of the Bi₂Te₃ layer. The *sp*-band-derived topological non-trivial surface states of Bi₂Te₃ could deli-

ver electrons to the surface adsorbates even when they are covered with a thin layer of topological trivial thin films [14]. Such an electron transfer process is accompanied by a position shift of the Dirac points associated with the topological non-trivial surface states, but they will not be destroyed due to the bulk band protection (Fig. 4e). The electron redistribution leads to electron depletion at the S atoms, especially at the surface layer of the MoS₂ basal plane (Fig. 4c). Correspondingly, there is an upward shift of the *p*-band center with respect to the Fermi energy, which enhances the binding energy of the H atom at the S sites (Fig. 4f) [40].

4. Conclusions

In summary, we explored the role of topological non-trivial surface states in the surface reactivity of HER catalysts. The introduction of the topological Bi₂Te₃ layer enhanced the activity exhibited by the inert basal plane of MoS₂ toward hydrogen evolution. The formation of MoS₂/Bi₂Te₃/STO heterostructures resulted in significant charge redistribution in the interface. The *sp*-derived surface states could donate electrons to the MoS₂ layer and reshape the *p*-band orbitals of the surface S atoms. This leads to an upshift of the *p*-band center and an increased H binding energy, which activates the originally chemically inert basal plane of MoS₂. These results are significant for the design of high-performance catalysts by manipulating topological non-trivial surface states.

Author contributions

Li G, Chang K, and Felsler C supervised the project and designed the research. Li G, and Huang J contribute equally to this work.

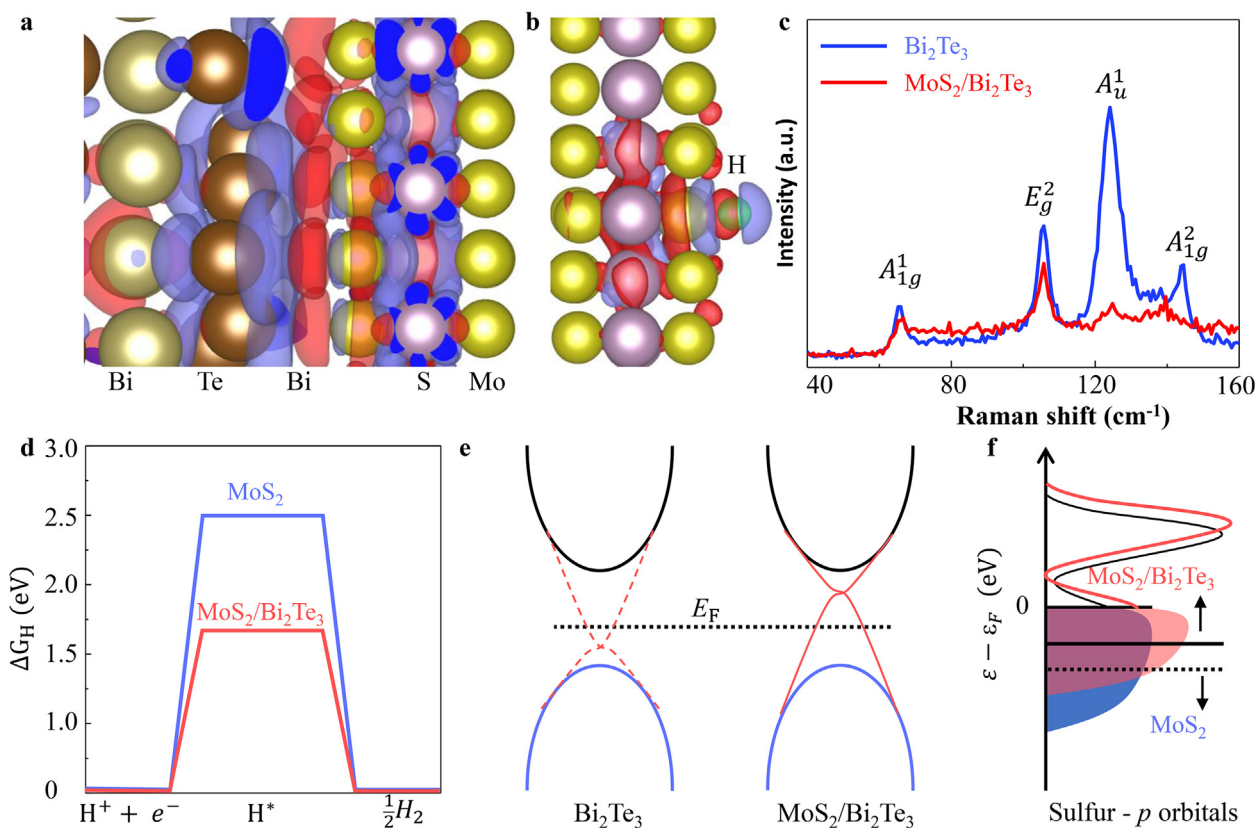


Fig. 4. Three-dimensional charge density difference for the $\text{MoS}_2/\text{Bi}_2\text{Te}_3$ heterostructure (a) without and (b) with H adsorption. Red and blue iso-surfaces represent charge accumulation and depletion in the space. (c) Gibbs free energy of hydrogen adsorption for the basal plane of MoS_2 and $\text{MoS}_2/\text{Bi}_2\text{Te}_3$ heterostructure. (d) An illustration of the changing of Dirac point regarding the TSSs of Bi_2Te_3 . (e) A comparison of p band center with and without Bi_2Te_3 layer for MoS_2 catalyst.

Huang J synthesized the topological thin films and characterized them under the supervision of Chang K and Parkin S. Yang Q and Sun Y performed the theoretical calculation and analysis, Li G performed electrochemical measurements and analysis. Huang J and Zhang L carried out the AFM measurement. Mu Q measured the Raman spectroscopy. Li G wrote the paper with support from Huang J., and Chang K. All authors contributed to the general discussion.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jechem.2021.04.010>.

References

- [1] C. Fu, Y. Sun, C. Felser, *APL Mater.* 8 (2020) 040913.
- [2] G. Li, Q. Xu, W. Shi, C. Fu, L. Jiao, M.E. Kamminga, M. Yu, H. Tuysuz, N. Kumar, V. Suss, R. Saha, A.K. Srivastava, S. Wirth, G. Auffermann, J. Gooth, S. Parkin, Y. Sun, E. Liu, C. Felser, *Sci. Adv.* 5 (2019) eaaw9867.
- [3] G. Li, C. Fu, W. Shi, L. Jiao, J. Wu, Q. Yang, R. Saha, M.E. Kamminga, A.K. Srivastava, E. Liu, A.N. Yazdani, N. Kumar, J. Zhang, G.R. Blake, X. Liu, M. Fahlman, S. Wirth, G. Auffermann, J. Gooth, S. Parkin, V. Madhavan, X. Feng, Y. Sun, C. Felser, *Angew. Chem.* 131 (2019) 13241–13246.
- [4] L. Muchler, H. Zhang, S. Chadov, B. Yan, F. Casper, J. Kubler, S.C. Zhang, C. Felser, *Angew. Chem.* 51 (2012) 7221–7225.
- [5] L.M. Schoop, F. Pielnhofer, B.V. Lotsch, *Chem. Mater.* 30 (2018) 3155–3176.
- [6] X. Wang, G. Bian, T. Miller, T.C. Chiang, *Phys Rev Lett* 108 (2012) 096404.
- [7] L. Zhang, D. Zhao, Y. Zang, Y. Yuan, G. Jiang, M. Liao, D. Zhang, K. He, X. Ma, Q. Xue, *APL Mater.* 5 (2017) 076106.
- [8] Y.Y. Li, G. Wang, X.G. Zhu, M.H. Liu, C. Ye, X. Chen, Y.Y. Wang, K. He, L.L. Wang, X.C. Ma, H.J. Zhang, X. Dai, Z. Fang, X.C. Xie, Y. Liu, X.L. Qi, J.F. Jia, S.C. Zhang, Q.K. Xue, *Adv. Mater.* 22 (2010) 4002–4007.
- [9] H. Chen, W. Zhu, D. Xiao, Z. Zhang, *Phys. Rev. Lett.* 107 (2011) 056804.
- [10] J. Xiao, L. Kou, C.-Y. Yam, T. Frauenheim, B. Yan, *ACS Catal.* 5 (2015) 7063–7067.
- [11] Q. Qu, B. Liu, J. Liang, H. Li, J. Wang, D. Pan, I.K. Sou, *ACS Catal.* 10 (2020) 2656–2666.
- [12] A. Ambrosi, Z. Sofer, J. Luxa, M. Pumera, *ACS Nano* 10 (2016) 11442–11448.
- [13] G. Wu, H. Chen, Y. Sun, X. Li, P. Cui, C. Franchini, J. Wang, X.Q. Chen, Z. Zhang, *Sci. Rep.* 3 (2013) 1233.
- [14] L. Li, J. Zeng, W. Qin, P. Cui, Z. Zhang, *Nano Energy* 58 (2019) 40–46.
- [15] K. Yin, Z.D. Cui, X.R. Zheng, X.J. Yang, S.L. Zhu, Z.Y. Li, Y.Q. Liang, *J. Mater. Chem. A* (2015) 22770–22780.
- [16] C. Nethravathi, A. Manganahalli, M. Rajamathi, *A.C.S. Appl. Nano Mater.* 2 (2019) 2005–2012.
- [17] R. Ma, G. Lin, Y. Zhou, Q. Liu, T. Zhang, G. Shan, M. Yang, J. Wang, *npj Comput Mater.* 5 (2019) 1.
- [18] G. Li, B. Zhang, J. Rao, D. Herranz Gonzalez, G.R. Blake, R.A. de Groot, T.T.M. Palstra, *Chem. Mater.* 27 (2015) 8220–8229.
- [19] G. Li, D. Zhang, Q. Qiao, Y. Yu, D. Peterson, A. Zafar, R. Kumar, S. Curtarolo, F. Hunte, S. Shannon, Y. Zhu, W. Yang, L. Cao, *J. Am. Chem. Soc.* 138 (2016) 16632.
- [20] D. Zhao, Z. Zhuang, X. Cao, C. Zhang, Q. Peng, C. Chen, Y. Li, *Chem. Soc. Rev.* 49 (2020) 2215–2264.

- [21] Q. Ding, B. Song, P. Xu, S. Jin, *Chem.* 1 (2016) 699–726.
- [22] Q. Zhou, J. Feng, X. Peng, L. Zhong, R. Sun, *J. Energy Chem.* 45 (2020) 45–51.
- [23] G. Li, C. Fu, J. Wu, J. Rao, S.-C. Liou, X. Xu, B. Shao, K. Liu, E. Liu, N. Kumar, X. Liu, M. Fahlman, J. Gooth, G. Auffermann, Y. Sun, C. Felser, B. Zhang, *Appl. Catal. B* 254 (2019) 1–6.
- [24] D. Yang, Q. Zhu, B. Han, *The Innovation* 1 (2020) 100016.
- [25] C.Z. Chang, K. He, L. Wang, X. Ma, M. Liu, Z. Zhang, X. Chen, Y. Wang, Q. Xue, *Spin* 01 (2012) 21–25.
- [26] Y.K. Srivastava, A. Chaturvedi, M. Manjappa, A. Kumar, G. Dayal, C. Kloc, R. Singh, *Adv. Opt. Mater.* 5 (2017) 1700762.
- [27] H. Fan, R. Wu, H. Liu, X. Yang, Y. Sun, C. Chen, *J. Mater. Sci.* 53 (2018) 10302–10312.
- [28] S. Cong, X. Liu, Y. Jiang, W. Zhang, Z. Zhao, *The Innovation* 1 (2020) 100051.
- [29] S. Shi, D. Gao, B. Xia, P. Liu, D. Xue, *J. Mater. Chem. A* 3 (2015) 24414–24421.
- [30] G. Li, D. Zhang, Y. Yu, S. Huang, W. Yang, L. Cao, *J. Am. Chem. Soc.* 139 (2017) 16194–16200.
- [31] C. Tang, M.-M. Titirici, Q. Zhang, *J. Energy Chem.* 26 (2017) 1077–1093.
- [32] D. Li, J. Lao, C. Jiang, Y. Shen, C. Luo, R. Qi, H. Lin, R. Huang, G.I.N. Waterhouse, H. Peng, *J. Catal.* 381 (2020) 590–598.
- [33] J. Yang, C. Wang, H. Ju, Y. Sun, S. Xing, J. Zhu, Q. Yang, *Adv. Funct. Mater.* 27 (2017) 1703864.
- [34] B.E. Conway, L. Bai, *J. Electroanal. Chem.* 198 (1986) 149–175.
- [35] J. Gan, Z. Huang, W. Luo, W. Chen, Y. Cao, G. Qian, X. Zhou, X. Duan, *J. Energy Chem.* 52 (2021) 33–40.
- [36] S. Jayabal, G. Saranya, J. Wu, Y. Liu, D. Geng, X. Meng, *J. Mater. Chem. A* 5 (2017) 24540–24563.
- [37] T. Shinagawa, A.T. Garcia-Esparza, K. Takanabe, *Sci. Rep.* 5 (2015) 13801.
- [38] L. Ren, X. Qi, Y. Liu, G. Hao, Z. Huang, X. Zou, L. Yang, J. Li, J. Zhong, *J. Mater. Chem.* 22 (2012) 4921–4926.
- [39] G.B. Osterhoudt, R. Carelli, K.S. Burch, F. Katmis, N. Gedik, J.S. Moodera, *Phys. Rev. B* 98 (2018) 014308.
- [40] C. Tsai, F. Abild-Pedersen, J.K. Nørskov, *Nano Lett.* 14 (2014) 1381–1387.