

Directly Assembled 3D Molybdenum Disulfide on Silicon Wafer for Efficient Photoelectrochemical Water Reduction

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MoS₂ composed of earth-abundant elements is considered as a promising hydrogen evolution reaction (HER) catalyst for p-type Si photocathode owing to its appropriate hydrogen adsorption free energy for the edge sites and high photochemical stability in acidic electrolytes. However, the direct synthesis of uniform and atomically thin MoS₂ on Si by usual chemical vapor deposition techniques remains challenging because of the weak van der Waals interaction between Si and MoS₂. Herein, by controlling the gas phase kinetics during metal–organic chemical vapor deposition, wafer-scale direct synthesis of 3D MoS₂ films on TiO₂-coated p-type Si substrates is demonstrated. The 3D MoS₂ layer with a number of edge sites exposed to ambient substantially reduces the HER overpotential of Si photocathode and simultaneously increases the saturation current density due to the antireflection effect. Directly grown 3D MoS₂ thin films are stable under extended water reduction duration. The strategy paves the way for efficient assembly of transition metal disulfide HER catalysts on the p-type photocathode.

1. Introduction

After Fujishima and Honda reported the splitting mechanism of water into its constituent molecule H₂ and ½O₂ using TiO₂ photoelectrodes, conversion of solar energy to storable

chemical fuels became an alternative path for the search of clean energy sources.^[1] Therefore, a diverse class of semiconductor photoelectrodes and nonprecious catalytic materials has been investigated for solar water splitting.^[2–5] Only a few semiconductor photocathodes and noble metal-free catalysts showed encouraging solar water splitting performances for hydrogen productions.^[6–9] Silicon (Si) is an ideal photocathode material with a narrow bandgap ($E_g = 1.12$ eV) with a wide spectral absorption upon solar radiation^[10] and appropriate band-edge positions. However, the poor stability in the liquid electrolytes and the high overpotential for charge transfers at the solid/liquid interfaces are yet to be overcome. Furthermore, the charge generation efficiency of Si photocathodes is limited by the high optical reflectance, i.e., 37% (arithmetic


mean) of the incident light is reflected in the entire visible range.^[11] Therefore, choosing appropriate catalytic materials to mitigate the overpotentials of Si photocathodes is critical to stabilize the liquid electrolyte for the extended operation time and reduce the substantial reflectance of Si for the higher photoelectrochemical (PEC) performance.

Currently, among the noble metal-free catalysts to decrease the overpotential of the p-type Si (p-Si) photocathode for the PEC hydrogen production, molybdenum disulfide (MoS₂) has gained considerable attention as a promising hydrogen evolution reaction (HER) catalyst owing to its low hydrogen adsorption free energy and the high photochemical stability at the affordable expenses, compared to conventional catalysts based on precious metals.^[12–15] The transition from the indirect bandgap structures in bulk MoS₂ to the direct bandgap one in MoS₂ monolayers may also improve the charge transport efficiencies.^[16,17] There are three main techniques to enhance the catalytic activity of MoS₂ layer.^[18–21] First, the phase transition of 2H-MoS₂ to 1T-MoS₂ is effective way to improve the catalytic activity because the 1T-MoS₂ has metallic nature. The 1T-MoS₂ has many catalytic active sites compared to 2H-MoS₂.^[18,19] Second, the introduction of sulfur vacancy and strain in MoS₂ is one of promising way to elevate its catalytic activity. By demonstrating the theoretical and experimental results related to

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the sulfur vacancies and strain in MoS₂, the hydrogen adsorption Gibbs free energy of sulfur vacancy sites is much lower than that of basal plane MoS₂.^[20] Furthermore, the strain in MoS₂ layer can help adsorb hydrogen ions on their structure effectively.^[21] Finally, the increase of catalytic edges of MoS₂ during its growth steps. The MoS₂ synthesized by chemical vapor deposition (CVD) or metal–organic CVD (MOCVD) should be 2H-MoS₂ because the thermodynamically metastable 1T-MoS₂ would be transformed to 2H-MoS₂ by high growth temperature. Thus, multiplying the exposed edge site density is directly related to developing efficient p-Si photocathodes with MoS₂ HER catalysts.

p-Si is not the best substrate for the direct deposition of atomically thin MoS₂ using the usual vapor deposition techniques because of the weak van der Waals interaction between Si and sulfur (the surface terminating atom in MoS₂).^[22,23] To date, most of the MoS₂ films have been deposited on silicon dioxides^[24] or sapphires and manually transferred to the p-Si substrates^[25–27] to form HER catalysts. However, this manual transfer is not immune from unwanted organic contaminants, and the poor adhesion of transferred MoS₂ layers to the p-Si substrates deteriorates the interfacial charge transport. In addition, the MoS₂ catalyst layers can be easily peeled off from the p-Si photocathode after several tens of hours of hydrogen production. Thus, direct synthesis of MoS₂ catalysts on p-Si substrates is crucial to achieving the efficient solar HER.^[28,29] The direct growth of MoS₂ catalysts on p-Si substrate is difficult because of the oxidation of Si substrate and poor adhesion between directly grown MoS₂ and p-Si. The highly crystalline MoS₂ nanosheets or particles could be synthesized onto oxide substrates such as SiO₂ and Al₂O₃.

In this study, we demonstrate the high-PEC performance of Si-based photocathodes by incorporating directly grown 3D MoS₂ HER catalysts with the high density of the exposed edge sites and nanoscale grain boundaries. We utilized the TiO₂ layer as an oxide layer to enhance the nucleation of MoS₂ directly on p-Si substrate and as a passivation layer to inhibit the oxidation of p-Si substrate. The directly grown 3D MoS₂ on TiO₂/p-Si photocathodes achieved a high saturation current density of 37 mA cm⁻² and a short-circuit current density of 28 mA cm⁻² at 0.0 V [the voltage is relative to the reversible hydrogen electrode (RHE), unless noted otherwise] and an onset potential of 0.35 V, if the onset potential is defined as the potential at 1.0 mA cm⁻². The chronoamperometry of the photocathode was measured for ≈181 h without noticeable degradation, specifically ≈108 at 0.0 V and 73 h at a maximum power point potential, V_{mpp} = 0.16 V.

2. Results and Discussion

2.1. 3D MoS₂ Film Growth on TiO₂/p-Si Photocathode Substrates

Figure 1a shows a schematic illustration of 3D MoS₂ films, directly deposited on the 4 in. TiO₂/p-Si photocathode substrates, by MOCVD using molybdenum hexacarbonyl (MHC), (Mo(CO)₆), and diethyl sulfide (DES), ((C₂H₅)₂S) precursors (see more details in the Experimental Section). In stark contrast with the conventional layer-by-layer growth of 2D MoS₂,

this growth is characterized by 3D film morphology, where a large fraction of vertically aligned MoS₂ on the top of underlying MoS₂ polycrystalline films of a relatively small grain size of <10 nm (Figure 1a,b). This unique film texture was obtained at a higher flux rate growth, i.e., an MHC flow rate of 0.4 sccm and the DES rate of 8.5 sccm for 15 min. Figure 1c shows a plane view of a transmission electron microscopy (TEM) image, where the edge-exposed vertical MoS₂ few-layers coexist with the underlying MoS₂ films. The high-resolution TEM images, obtained from each region marked in Figure 1c, verify the corresponding vertical and in-plane crystal structures of few-layer MoS₂. The measured interplanar distances were 0.660 nm (Figure 1d) and 0.312 nm (Figure 1e), consistent with the (0001) and (10–10) plane of hexagonal MoS₂, respectively. The areal density of the vertical MoS₂ was estimated to be ≈50%, according to the representative scanning electron microscope image in Figure 1f and Figure S1 (Supporting Information). In Figure 1g, the in-plane dark-field TEM image with false colors, each of which corresponds to the in-plane crystal orientations, defined by diffraction patterns of Figure 1h, shows a polycrystalline grain distribution. Quantitatively, its grain size ranged from 2–20 nm (Figure 1i, green curve) with an average size of 8 nm by counting its size from more than five TEM images taken from the entire wafer—see also Figure S2 (Supporting Information) for the wafer-scale uniformity. In contrast, the lower flux rate growth at an MHC flow rate of 0.0001 sccm and the DES rate of 0.15 sccm establishes the conventional layer-by-layer growth mode without any vertical MoS₂ films, requiring 16 h to cover up the entire wafer (Figure S3, Supporting Information). In this growth mode, the typical grain size was found to be ≈60 nm (Figure 1i–k).

Evidently, the 3D film texture was achieved by growth kinetics controls in our MOCVD growth. For example, the higher precursor flow rate substantially increases the numbers of nucleation sites for MoS₂ embryos and the growth rate, resulting in smaller grains and various vertical textures in the growth products, respectively (Figure 1i and Figure 2a). Based on the cross-sectional TEM images as shown in, such 3D features were categorized into three types (Figure 2b–d; Figures S4 and Figure S5, Supporting Information): (i) the direct vertical growth on the top of either TiO₂ or the bottom MoS₂ layers, (ii) the second one occurs when the two propagating MoS₂ layers collide head-on, pushing them in the upright direction, and (iii) when the MoS₂ layers are bent and rolled over, presumably at the defect sites. The energy dispersive spectroscopy (EDS) mapping shows the clear distinction between the coated layer TiO₂ film and the 3D MoS₂ catalysts on p-Si as shown in Figure 2e. The uniform coverage of our 3D MoS₂ films was investigated by Raman scattering spectra (Figure 2f,g), obtained at various areas over the entire wafer. The representative Raman spectra obtained from the marked spots as [1] to [5] in Figure 2f consistently show two characteristic peaks of few-layer MoS₂, i.e., the in-plane vibrational E_{2g} mode in the range ≈380–381 cm⁻¹ and the out-of-plane vibrational A_{1g} mode in the range ≈404–405 cm⁻¹. The frequency difference of the two peaks, Δω, which is strongly dependent on the layer number, was consistently observed to be in the range ≈23–25 cm⁻¹ (Δω ≈ 19.5 cm⁻¹ for MoS₂ monolayer), indicating the nominal layer number is greater than 3 in our 3D films.^[30,31] We also observed that the

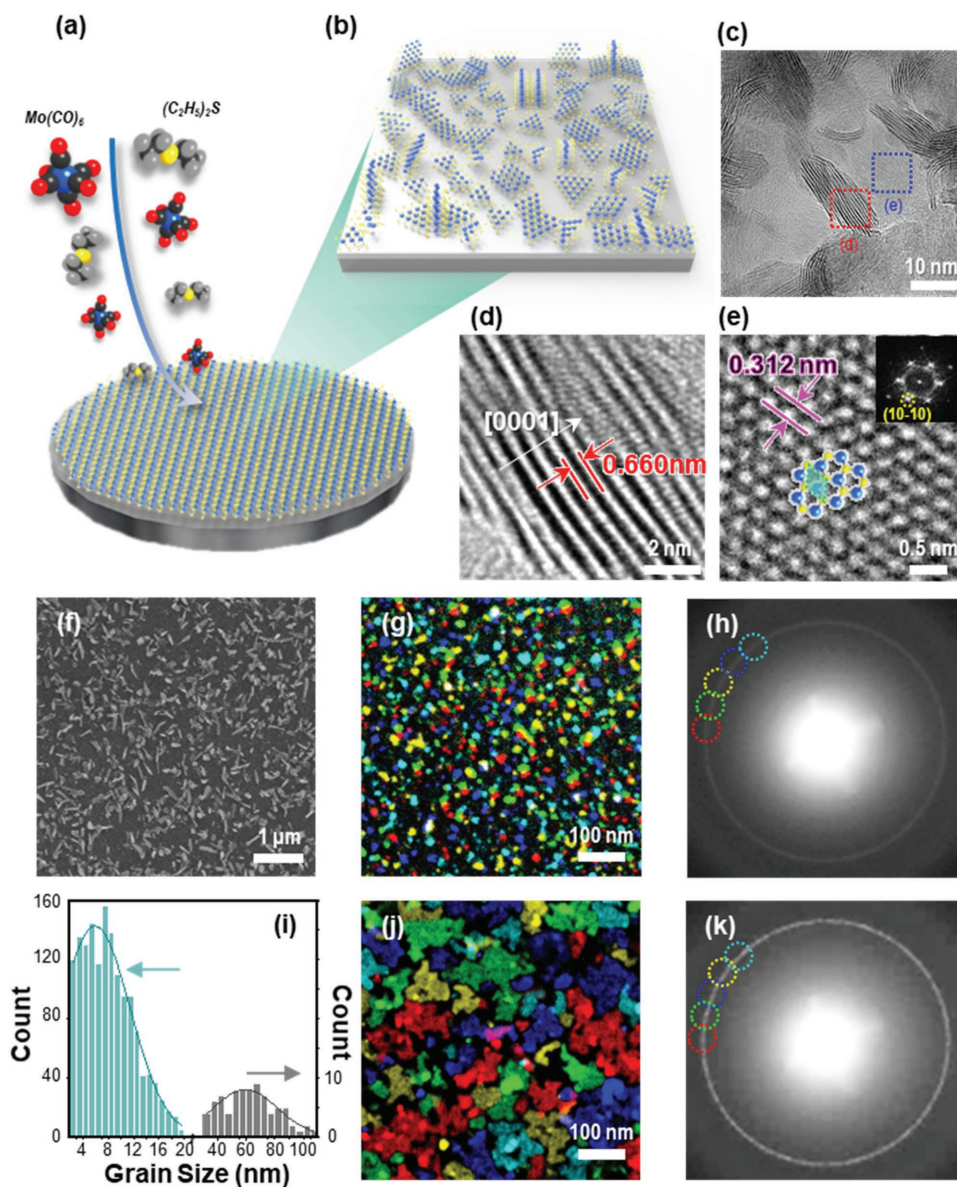


Figure 1. Wafer-scale 3D MoS₂ film growth by metal–organic chemical vapor deposition (MOCVD). a,b) Schematic illustration for direct growth of 3D MoS₂ film on 4 in. TiO₂/p-Si wafer by MOCVD. c) Low-magnification transmission electron microscope (TEM) image of 3D MoS₂ film. d,e) High-magnification TEM images of d) vertically aligned and e) in-planar region taken from marked areas in (c). f) Scanning electron microscope image, g) false-color dark-field-TEM (DF-TEM) image, and h) selected area electron diffraction (SAED) pattern taken from 3D MoS₂. i) Grain size distribution of 3D MoS₂ film (green) and layer-by-layer grown MoS₂ film (gray). j) False-color DF-TEM image and k) SAED pattern taken from layer-by-layer grown MoS₂.

E_{2g} peaks are weaker, compared to the A_{1g} peaks, with generic peak broadening, suggesting that the film is 3D-textured, instead of 2D monolayer or bilayer;^[32] the full-width half-maximum (FWHM) was estimated to be 13.8 and 11.2 cm⁻¹ for the E_{2g} and A_{1g} modes, respectively, while the FWHM in our monolayer films is 12.1 cm⁻¹ (E_{2g}) and 8.4 cm⁻¹ (A_{1g}).

Figure 3 shows the optical reflectance (R) of 3D MoS₂/TiO₂/p-Si and TiO₂/p-Si samples. The observed color contrast in the photographic images of both 3D MoS₂/TiO₂/p-Si and TiO₂/p-Si specimens were an indication of the reduction of optical reflectance (Figure 3a,b). The absorption spectra and optical reflectance data of different MoS₂ growth time were summarized

in Figure S6 (Supporting Information). The intensity of light absorption significantly increased with respect to increase of MoS₂ growth time. Furthermore, the dramatic reduction of reflectance with the 15 min grown 3D MoS₂/TiO₂/p-Si substrate is observed. For further analysis, the optical reflectance was measured in the wavelength (λ) range of 400–1000 nm at incident angle (θ) range of 10°–70° and confirmed that the 3D MoS₂ films decreased reflectance of the bare sample (Figure 3c,d). Moreover, the arithmetic mean of the R versus λ at $\theta = 40^\circ$ and the R versus θ measured at $\lambda = 550$ nm are found to be 35.2% and 34.0% for the TiO₂/p-Si and 21.9% and 21.9% for the 3D MoS₂/TiO₂/p-Si photocathode, respectively (Figure 3e,f). The

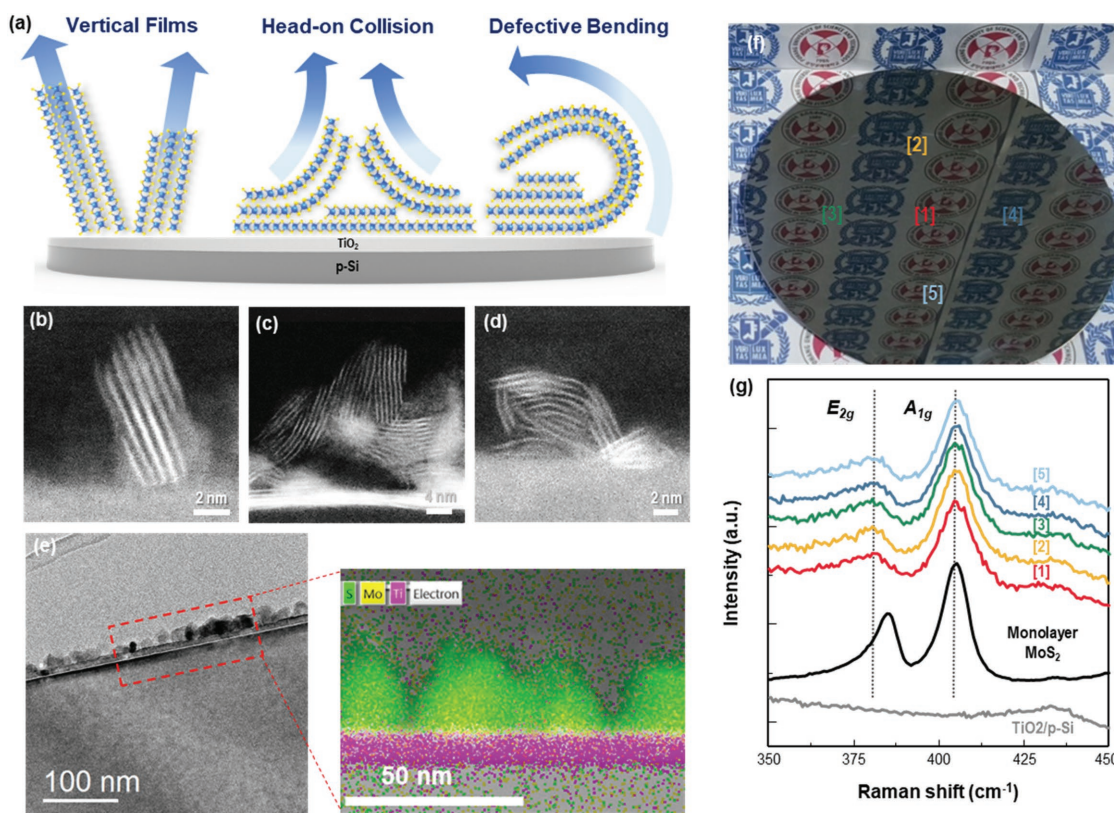


Figure 2. Vertically aligned 3D MoS₂ film with exposed edge by kinetic control. a) Schematic illustration of vertically aligned textures observed in 3D MoS₂ films at high precursor flux rate. b–d) Representative cross-sectional high-angle annular dark field-scanning TEM (HAADF-STEM) images showing different growth features. e) TEM image of 3D MoS₂ films and EDS mapping of the specimens (inset). f) Photograph of 3D MoS₂ film grown on 4 in. TiO₂/p-Si substrate. g) Raman scattering spectra acquired from different regions in (f) with those of monolayer MoS₂ film (black) and TiO₂/p-Si (gray) for comparison.

θ - and λ -dependent R of both the samples are smaller than that of the pristine TiO₂/p-type Si because of a gradient refractive index, 2.545/2.64/5.6.^[33,34] The refractive index of the 3D MoS₂ structures covering 50% of the TiO₂/p-Si area was estimated to 2.545, considering the refractive index of the MoS₂ in parallel direction and areal density.^[35,36] More importantly, in the 3D MoS₂/TiO₂/p-Si photocathode, the variation of R in both R versus θ and R versus λ is negligible, indicating that the 3D MoS₂ film has omnidirectional and broadband antireflective properties for p-Si, presumably because of the size effect below the diffraction limit.^[37]

2.2. Photoelectrochemical Performance

Figure 4a shows the linear sweep voltammograms (LSV) of our 3D MoS₂/TiO₂/p-Si (red color), 2D layered MoS₂/TiO₂/p-Si (blue color), and TiO₂/p-Si (black color) photocathodes. The saturation current density of the 3D MoS₂/TiO₂/p-Si is ≈ 37 mA cm⁻², whereas it was 33 and 32 mA cm⁻² for the layered MoS₂/TiO₂/p-Si and TiO₂/p-Si, respectively. The enhanced saturation photocurrent density of MoS₂/TiO₂/p-Si photocathodes is due to the decrease of the R that increases the charge generation efficiency of the photocathode. The electrochemical performance of 3D MoS₂/TiO₂/glassy carbon electrode

was demonstrated in Figure S7 (Supporting Information). The overpotential at 10 mA cm⁻² is -0.255 V and the Tafel slope of fabricated cell is 87.01 mV dec⁻¹. The chronopotentiometry of both 2D and 3D MoS₂/TiO₂/p-Si photocathodes at 1.00 mA cm⁻² was measured using chopped light as shown in Figure 4b. The onset potential of TiO₂/p-Si photocathode was found to be -0.41 V, whereas it was 0.2 and 0.35 V for the 2D MoS₂/TiO₂/p-Si and 3D MoS₂/TiO₂/p-Si, respectively, assuming that the onset potential of the photocathode is the potential at which the photocathode can generate a current density of 1.00 mA cm⁻². The onset potential of 3D MoS₂/TiO₂/p-Si photocathode shifted anodically by 0.76 and 0.15 V relative to those of TiO₂/p-Si and 2D MoS₂/TiO₂/p-Si photocathode, respectively, whereas it anodically shifted by 0.61 V for 2D MoS₂/TiO₂/p-Si photocathode, compared to that of the pristine TiO₂/p-Si photocathode. The high anodic onset potential shift in the 3D MoS₂/TiO₂/p-Si photocathode can be attributed to the existence of MoS₂ edge sites in high density and much smaller size of grain boundaries, lacking in the 2D layered MoS₂/TiO₂/p-Si photocathode. A comparison of the PEC performance between the 3D MoS₂/TiO₂/p-Si photocathode and the state-of-the-art photocathodes reported using similar catalytic and optical absorption materials is shown in Figure S8 (Supporting Information). Because of the highly populated edge-sites, the potential of our photocathodes at

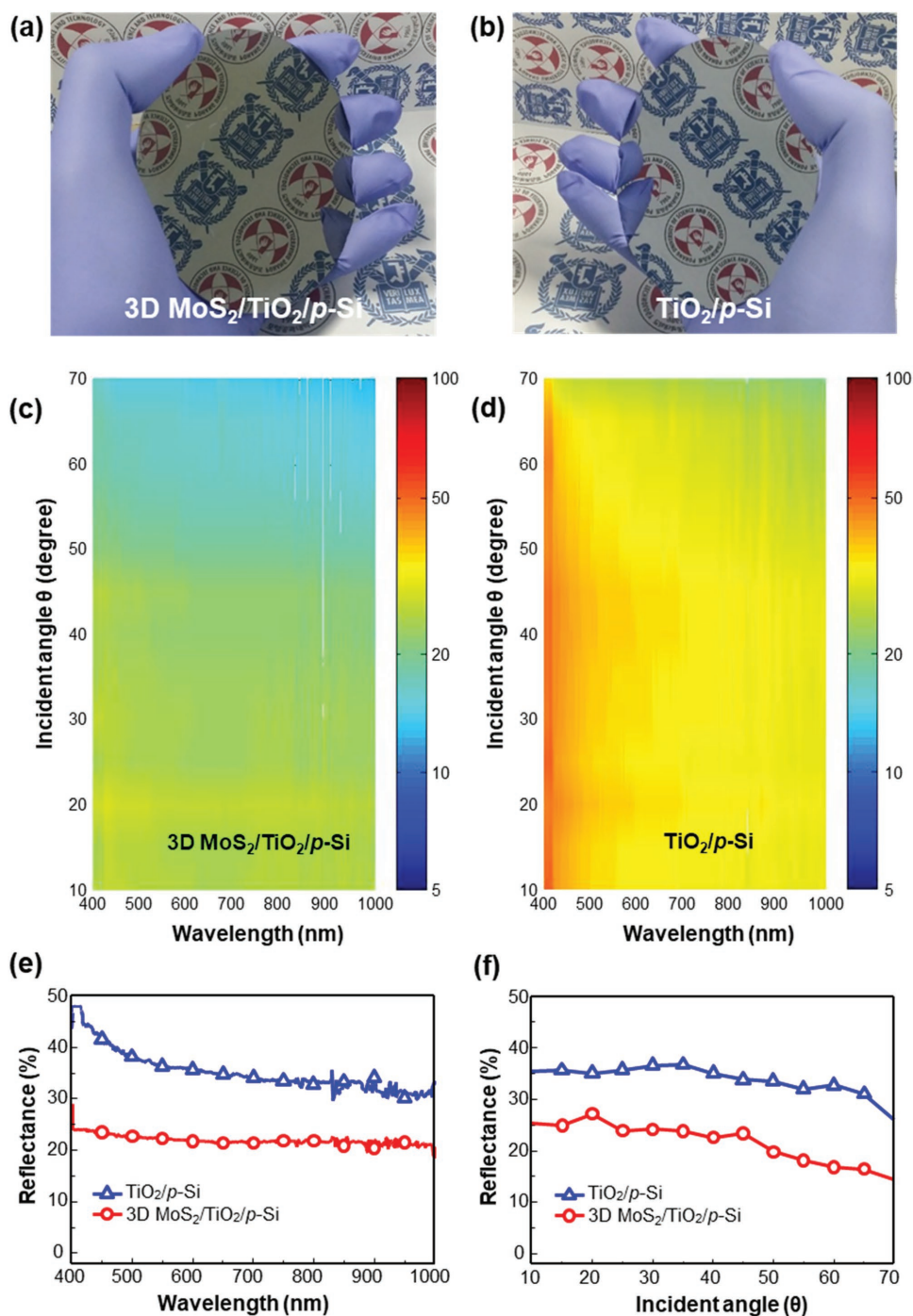


Figure 3. Optical reflectance of the specimens. a, b) Photograph of 3D MoS₂ film on TiO₂/p-Si and TiO₂ films on p-Si substrate. c, d) Reflectance of 3D MoS₂/TiO₂/p-Si and TiO₂/p-Si specimens. e) Reflectance spectra of 3D MoS₂/TiO₂/p-Si (red) and TiO₂/p-Si (blue) at the incident angle 40°. f) Reflectance versus incident angle at the wavelength of 550 nm irradiation.

1 mA cm⁻² is comparable with those of the previously reported photocathodes which are MoS_x/MoS₂/Mo/n⁺p-Si,^[38] MoS₂/Ti/n⁺p-Si,^[39] [Mo₃S₁₃]²⁻/MoS₂/Mo/n⁺p-Si^[40] or MoS₂/Al₂O₃/n⁺p-Si.^[41] For the saturation current density and the current density at zero bias voltage, our photocathode shows the highest photocurrent density, mostly because of the improvement of charge generation efficiency and lower interfacial charge resistance.

Electrochemical impedance spectroscopy (EIS) measurements were performed to deduce the charge transfer resistance of the 3D MoS₂/TiO₂/p-Si and TiO₂/p-Si photocathodes. The Nyquist impedance plots are shown in Figure 4c, where the TiO₂/p-Si photocathode has a greater diameter than 3D MoS₂/TiO₂/p-Si. The fitted equivalent circuit of the Nyquist plot consists of a constant phase element and resistances such as series

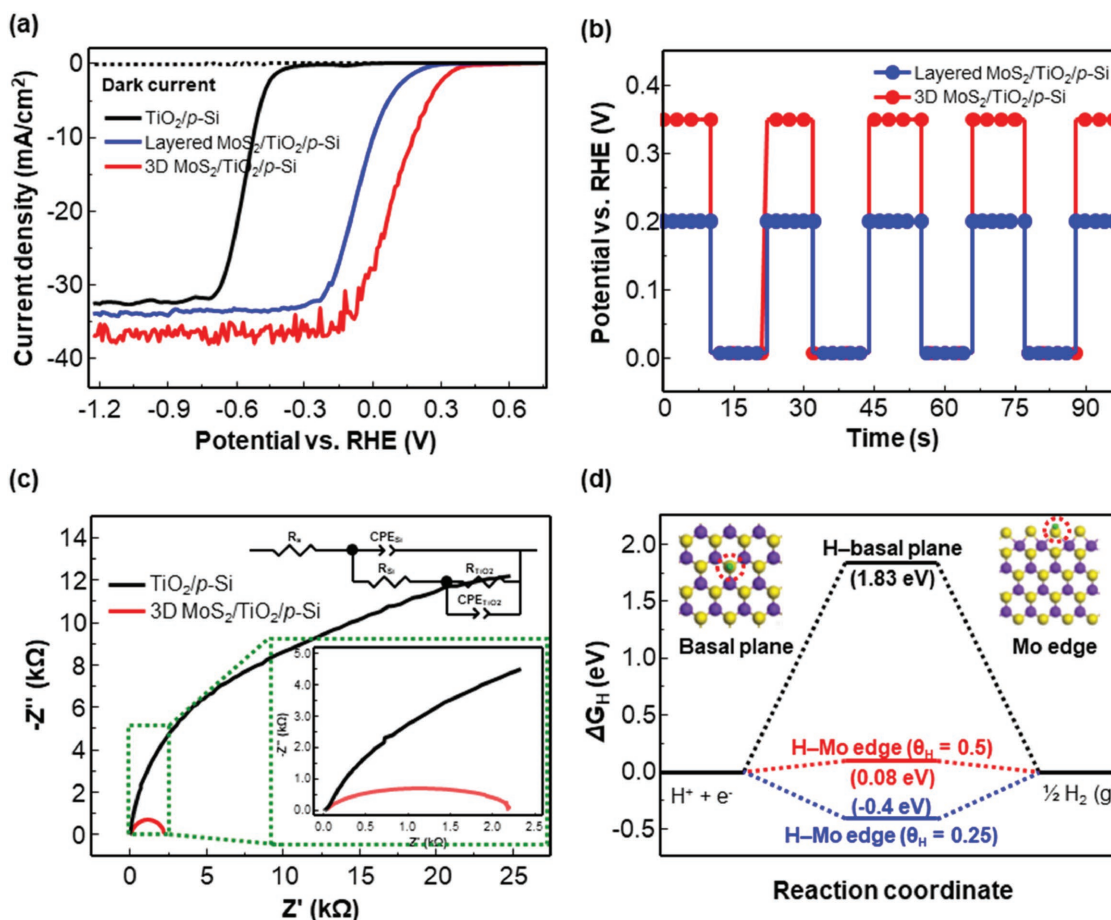


Figure 4. The PEC performance of the working electrodes, MoS₂/TiO₂/p-Si, TiO₂/p-Si, and bare Si photocathode. a) The LSV of MoS₂/TiO₂/p-Si and TiO₂/p-Si. b) The onset potential of layered and 3D MoS₂/TiO₂/p-Si at -1 mA cm⁻². c) Nyquist plots of the working electrodes 3D MoS₂/TiO₂/p-Si and TiO₂/p-Si d) hydrogen adsorption free energy of MoS₂ basal plane, Mo edge calculated using DFT.

resistance (R_s), charge transfer resistance from silicon to TiO₂ (R_{Si}), and charge transfer resistance from TiO₂ to electrolyte through MoS₂ (R_{TiO_2}), as shown in the inset of Figure 4c. The fitted charge transfer resistances of the photocathodes are listed in Table 1, where the charge transfer resistance from silicon to TiO₂ was almost equal for both the photocathodes, 3D MoS₂/TiO₂/p-Si and TiO₂/p-Si, which are 45 and 40 Ω cm², respectively. However, the charge transferred resistance from TiO₂ to electrolyte through a MoS₂ was found to be quite small compared to the charge transferred resistance from TiO₂ to electrolytes, which were 128 and 634 Ω cm² for 3D MoS₂/TiO₂/p-Si and TiO₂/p-Si photocathode, respectively. To clarify the electron transport in fabricated samples, the ultraviolet photoemission spectroscopy and X-ray photoemission spectroscopy valence spectra were conducted as shown in Figure S9 (Supporting Information). Based on these results, the energy band diagram clearly shows that the photogenerated electrons from p-Si can be effectively transported to the TiO₂ and 3D MoS₂ layers. Furthermore, the holes from the photogenerated carriers were blocked by TiO₂ thin films due to its valence band position, indicating that the recombination of photogenerated carriers is inhibited as shown in Figure S9 (Supporting Information).

The Gibbs free energy of hydrogen adsorption (ΔG_H) on the basal plane and edge sites of MoS₂ was calculated using density functional theory (DFT) to support the experimental results, because Gibbs free energy is considered as a descriptor for HER efficiency (see the Experimental Section for detail of the DFT calculation).^[42–45] The Gibbs free energy of hydrogen adsorption closer to zero indicates the highest catalytic activities of the material for HER.^[21] The ΔG_H on the H–Mo edge was considered, because more than half of the 3D MoS₂ surfaces are covered by exposed edges of MoS₂ (Figures 1c,d and 3b–d). For a hydrogen coverage θ_H , 0.5 and 0.25 were considered. Figure 4d shows the calculated results of ΔG_H on MoS₂ on the basal plane and Mo edges. On the basal plane of MoS₂, the ΔG_H was found to be thermodynamically unstable (1.83 eV), indicating that the basal plane is inert for HER. The ΔG_H on the Mo edge sites with 0.5 and 0.25 hydrogen coverage was

Table 1. The fitted charge transfer resistance.

Photocathode	R_{Si} [Ω cm ²]	R_{TiO_2} [Ω cm ²]	Appl. volt versus OCP
TiO ₂ /p-Si	40.7	4634.4	340 mV
MoS ₂ /TiO ₂ /p-Si	45.3	128	340 mV

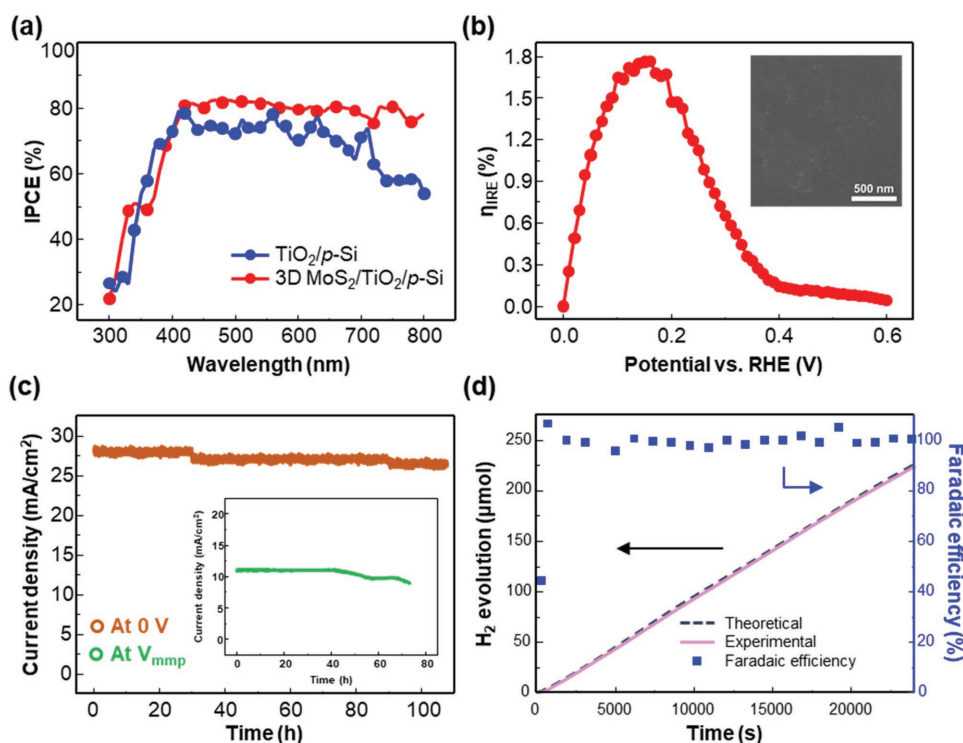


Figure 5. Efficiency and stability of the photocathode. a) IPCE curves of 3D MoS₂/TiO₂/p-Si and TiO₂/p-Si. b) Ideal regenerative cell efficiency of 3D MoS₂/TiO₂/p-Si. c) Stability of photocathode, 3D MoS₂/TiO₂/p-Si at zero versus RHE bias potential and at the maximum power point potential V_{mpp} . The inset shows an SEM image of 3D MoS₂/TiO₂/p-Si after measurement of photoelectrochemical properties. d) Calculated amounts of H₂ evolution of theoretical and experimental (left axis), and Faradaic efficiency measurements under illumination at -0.05 V versus RHE (right axis).

0.08 and -0.4 eV, respectively. The obtained ΔG_H values validated the experimental result of EIS and LSV analysis of 3D MoS₂/TiO₂/p-Si photocathode.

The incident photon-to-current conversion efficiency (IPCE) of 3D MoS₂/TiO₂/p-Si and TiO₂/p-Si samples was measured at a bias voltage of 0.0 and -0.65 V, respectively, as shown in Figure 5a. The IPCE of the photocathodes are ≈ 85 and 75% for 3D MoS₂/TiO₂/p-Si and TiO₂/p-Si, respectively, in the entire visible light spectrum. The ideal regenerative cell efficiency^[46] of the 3D MoS₂/TiO₂/p-Si photocathode was measured, as shown in Figure 5b. The photocathode exhibited $V_{mpp} = 0.16$ V photovoltage and $J_{mpp} = 11.06$ mA cm⁻² current density at the maximum power point. The ideal regenerative cell efficiency of the photocathode was found to be 1.8%.

Figure 5c shows the measured chronoamperometry of 3D MoS₂/TiO₂/p-Si photocathode for an extended time at a bias potential of 0.0 V and the maximum power point potential ($V_{mpp} = 0.16$ V) to elucidate the stability for more than 108 h (brown color curve) at 0.0 V versus RHE and ≈ 73 h (green color curve) at the maximum power point bias voltage. To elucidate the passivation effect of 3D MoS₂ on the TiO₂/p-Si photocathodes, we measured the chronoamperometry curve for the fabricated samples which are bare p-Si, TiO₂/p-Si and 3D MoS₂/TiO₂/p-Si photocathodes as shown in Figure S10 (Supporting Information). The TiO₂/p-Si photocathode exhibited the gradual degradation (63% of initial photocurrent density after 10 000 s) compared to the bare p-Si (13% of initial

photocurrent density after 10 000 s) which showed rapid degradation. The TiO₂ thin film used in this study was only 10 nm, it is not sufficient to passivate the p-Si photocathode during the PEC measurements in the acidic condition. However, for the 3D MoS₂ deposited TiO₂/p-Si photocathode, the photocurrent density was stable after 10 000 s without notable degradation, indicating that the 3D MoS₂ acts as not only a catalyst for hydrogen production but also an excellent passivation layer. For the electrochemical stability, we have investigated the stability of the 3D MoS₂/TiO₂/glassy carbon(GC) by continuous cyclic voltammetry for 3000 cycles at a constant scanning rate of 100 mV s⁻¹. Comparing the first cycle of the samples with the final one, there is no obvious change in the polarization curve, indicating that 3D MoS₂ is a superior stable HER electrocatalyst. The prolonged time stability of 3D MoS₂/TiO₂/p-Si photocathode is attributed to the MoS₂ nanostructure that serves as a passivation of the TiO₂/p-Si electrode. The spillover of hydrogen from the surface of 3D MoS₂/TiO₂/p-Si and TiO₂/p-Si photocathode at 0.0 V is recorded and shown in the Videos S1 and S2 (Supporting Information). The H₂ evolution of 3D MoS₂/TiO₂/p-Si photocathode is measured by gas chromatography at -0.05 V versus RHE. The blue-colored dots in Figure 5d display $\approx 100\%$ Faradaic efficiency over 8 h. The calculated amounts of H₂ evolution are very close to that of theoretical value according to the passed charge, indicating that the most of the photogenerated charges are consumed for H₂ evolution reaction not for other side reaction.

3. Conclusion

We successfully demonstrated an efficient TiO₂ coated 4 in. p-Si photocathode with a directly grown 3D MoS₂ HER catalyst. The photoelectrochemical performance of the photocathode for a 3D MoS₂/TiO₂/p-Si exhibited the onset potential of 0.35 V with the short-circuit current density $J_{sc} = 28 \text{ mA cm}^{-2}$ and the saturated current density of 37 mA cm^{-2} ; for the layered MoS₂/TiO₂/p-Si photocathode, the onset potential was 0.2 V at a $J_{sc} = 10 \text{ mA cm}^{-2}$ and a saturated current density of 33 mA cm^{-2} . The onset potential of the 3D MoS₂/TiO₂/p-Si photocathode shifted anodically by 0.76 V relative to the onset potential of the pristine TiO₂/p-Si photocathode. Passivation of the TiO₂/p-Si photocathodes with MoS₂ layers secured the stable operation for $\approx 181 \text{ h}$ without noticeable degradation. The obtained high anodic shift in the 3D MoS₂/TiO₂/p-Si photocathode is attributed to the high density of exposed edge sites and grain boundaries. The enhanced saturation current of the photocathode resulted from the decrease in optical reflectance. Our work can pave a way in the development of efficient catalysts for the PEC hydrogen evolution reactions.

4. Experimental Section

TiO₂ Coating on a p-Type Silicon Substrate: A p-type Si (100) substrate was cleaned using acetone and isopropanol alcohol assisting with sonication, and washed repeatedly in deionized water (DI) water. Subsequently, it was soaked in 2% HF for 1 min to remove residues and native oxides and was washed in DI water. Then, a 10 nm thick TiO₂ film was deposited at a rate of 0.1 \AA sec^{-1} using an electron-beam evaporator (KVE-E2004L) at $3.5 \times 10^{-6} \text{ Torr}$.

Growth Methods of 3D MoS₂ Layers in Wafer Scale: The 4 in. wafer-scale growth of MoS₂ films was carried out using high purity gas precursor MHC (99.9%) and DES (98%). A 4 in. TiO₂ (10 nm) coated p-Si wafer is located in the center of a hot-walled quartz-tube furnace. Prior to heating, the furnace was purged for 30 min to eliminate residual gases, and subsequently was ramped up to 560 °C for 20 min. Then, the precursors and a carrier gas were flowed. The growth was proceeded for 15 min and was rapidly cooled down to room temperature. The flow rates of precursors were 0.4 sccm for MHC, 8.5 sccm for DES, 20 sccm for H₂ (99.9999%), and 150 sccm for Ar (99.9999%).

TEM Characterizations: For TEM specimen preparations, 3D MoS₂ was transferred using a wet transfer method. The grown sample was spin-coated by poly(methyl methacrylate) (PMMA) and baked at 180 °C for 1 m and 30 s. Then, substrate (SiO₂) was etched in HF (10%). Floating PMMA/samples were transferred to a TEM grid (holey carbon coated with 400 meshed Cu), and then, PMMA films were removed in acetone for 6 h and annealed in a tube furnace at 300 °C. High-resolution TEM analysis was taken using a JEOL JEM-2100F operated at 200 kV (equipped with a Cs-corrector).

Photoelectrochemical Measurement: The photoelectrochemical properties of the photocathode were measured using a computer controlled potentiostat (IVIUM Technologies, nSTAT). All the PEC measurements were performed with a 0.5 M H₂SO₄ electrolyte, single compartment cuvette, and three electrodes configuration, such as, the prepared photocathode, saturated calomel electrode, and graphite rod as working, reference, and counter electrode, respectively. A Xe arc lamp was used as a light source and calibrated to 100 mW cm^{-2} using a standard silicon photodiode at the sample location. In all of the linear sweep voltammogram measurements, the photoanodes were cathodically polarized at the scan rate of 20 mV sec^{-1} during both illumination and in the dark measurement. The measured potential V versus calomel were converted to reference hydrogen electrode (RHE) using the following Equation (1)

$$V_{\text{RHE}} = E + E_{\text{calomel}} + 0.059 \times \text{pH} \quad (1)$$

where E is applied potential versus calomel and calomel is 0.24 V versus RHE and V_{RHE} is the applied bias potential versus RHE. The external quantum efficiency of the samples was measured at applied bias potential versus calomel using computer controlled monochromator (MonoRa150) and an amplifier for photocurrent detection. The EIS was measured at 0.0 V versus calomel with respect to open-circuit potential (OCP) and sweeping in the frequency range of 350 kHz–0.1 Hz with an AC amplitude of 10 mV. The EIS Nyquist curves were fitted to equivalent circuit using Z-plot 2x software. The Faradaic efficiency was measured by two-compartment photoelectrochemical cells which are separated by the Nafion 117 membrane. Before reaction, the two compartments of the reactor were degassed by bubbling with Ar gas for 30 min. During the reaction, the Ar gas was continuously flowed into electrolyte in the cathodic compartment with a rate of 10 sccm and vented directly into a gas-sampling loop of a gas chromatography measurement system (Agilent GC 7890B), which is equipped with a thermal conductivity detector and a micropacked column (ShinCarbon ST 100/120). The Ar gas was used as the carrier gas and the evolved H₂ was detected by thermal conductivity detector. A gas sample was analyzed automatically every 20 min.

DFT Calculations: DFT calculations were performed by a projector augmented wave method,^[47] with Vienna Ab initio Simulation Package (VASP).^[48,49] The generalized gradient approximation suggested by Perdew, Burke, and Ernzerh^[50,51] was used for exchange correlation function. Van der Waals force was considered by the Grimme D2 scheme.^[52] The basal plane was modeled as $4 \times 4 \times 1$ single layer supercell, and the unit cell for the Mo-edge site was modeled by stripe with 5 Mo atoms in both the x - and y -direction as shown in Figure 4d inset. Two types of Mo-edges exist in MoS₂; one terminated with S-monomer and the other terminated with S-dimer. It is known in previous researches that hydrogens are absorbed on Mo-edge terminated with S-monomer,^[53] so only one with S-monomer was calculated. The vacuum region was implemented as 15 Å thickness and used to avoid spurious electrostatic interactions. The plane-wave cutoff energy of 260 eV was used. The Brillouine zone was sampled by $5 \times 5 \times 1$ Monkhorst-Pack mesh for unit cell, $2 \times 2 \times 1$ for the basal plane, and $4 \times 4 \times 1$ for the Mo-edge site. Gibbs free energy of the adsorption was obtained as follows

$$\Delta G_{\text{H}} = \Delta E_{\text{H}} + \text{ZPE} - T\Delta S_{\text{H}} \quad (2)$$

where ΔE_{H} is hydrogen adsorption energy, ZPE is zero-point energy, T is the temperature, and ΔS_{H} is entropy change on H adsorption. The entropy is only considered for hydrogen gas. Coverage of hydrogen θ was defined as the proportion of S-monomers at which hydrogen atoms are attached. Adsorption energy ΔE_{H} was calculated using following equation

$$\Delta E_{\text{H}} = E(^*n\text{H}) - E(^*(n-1)\text{H}) - \frac{1}{2}E(\text{H}_2) \quad (3)$$

where $E(^*n\text{H})$ is the total energy of MoS₂ system that n edge sites are covered with hydrogen, and $E(\text{H}_2)$ is the total energy of a hydrogen molecule.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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