Wafer-scale transferable molybdenum disulfide thin-film catalysts for photoelectrochemical hydrogen production

Supplementary Information

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Detailed experimental procedures

1. MoS$_2$ thin film synthesis. SiO$_2$ (300 nm)/Si wafers were cleaned with a standard piranha solution (3:1 mixture of H$_2$SO$_4$ and H$_2$O$_2$) and conventional cleaning procedures, followed by ultrasonication in acetone, isopropyl alcohol, and deionized (DI) water. To obtain hydrophilic surfaces on the SiO$_2$/Si wafers, O$_2$ plasma and UV-O$_3$ surface treatment were performed for 15 min. The precursor solution was prepared by dissolving (NH$_4$)$_2$MoS$_4$ powder (Sigma-Aldrich, 99.97% purity) in ethylene glycol (Sigma-Aldrich, 99.8% purity, anhydrous) at concentrations of 10, 20, 50, 100, 200, and 500 mM. The precursor solution was spin-coated onto the prepared SiO$_2$/Si substrate at 3500 rpm for 60 s. High-purity H$_2$ and N$_2$ gases were used for the thermolysis process in a thermal CVD system. First, the CVD chamber temperature was increased to 500 °C and maintained at this temperature for 30 min under flowing H$_2$ and N$_2$ at 1 Torr. The flow rate of H$_2$ and N$_2$ was set to 40 and 200 cm$^3$/min, respectively, by mass flow controllers. Under a H$_2$ gas atmosphere at relatively high temperature, the thermolysis process was gradually started. Then, the temperature of the CVD furnace was increased to 950 °C, and maintained for 1 h. Sulfur sublimation was initiated with sulfur powder (Sigma-Aldrich, 99.5% purity) placed in the heating zone, which was set to 300 °C. When the thermolysis process was finished, PMMA was spin-coated onto the CVD-grown MoS$_2$ thin films. The edges of the synthesized MoS$_2$ thin films were scratched by a razor blade to promote rapid separation of MoS$_2$ from the SiO$_2$/Si substrate. The PMMA/MoS$_2$/SiO$_2$/Si substrate was immersed in a buffered oxide etch (BOE, Sigma-Aldrich, NH$_4$F 40%) to separate the MoS$_2$ thin film from the substrate by etching away the SiO$_2$ layers. The obtained MoS$_2$ thin films were washed with DI water seven to nine times to remove residual etchant and transferred to an arbitrary substrate of $p$-Si, $p$-InP, $p$-GaAs, or $p$-GaP. After the PMMA/MoS$_2$ membranes had adhered to the substrates, the PMMA layers were removed using acetone and toluene at 50 °C for 30 min.
2. **PEC measurements.** HER measurements (Ivium Technologies, Model: Nstat) were performed with a three-electrode system using a saturated calomel electrode as the reference electrode and a Pt plate as the counter electrode in a 0.5 M H$_2$SO$_4$ standard electrolyte solution. The three-electrode system was set up inside a quartz vessel, which protected the samples from UV absorption. A Xe arc lamp was used and calibrated to an output of 100 mW/cm$^2$ (AM 1.5 G condition). Because the Pt counter electrode was not stable for long-term (several hours) operation in the strong acid electrolytes such as 0.1M H$_2$SO$_4$ (pH = 1.5) and 0.5M H$_2$SO$_4$ (pH = 1.1), the Pt deposition has been found on the working electrode during chronoamperometry measurements.\(^1\) Thus chronoamperometry measurements were performed for Pt decorated $p$-Si and Pt decorated MoS$_2$/$p$-Si photocathodes. The Pt decoration was conducted by using electrodeposition method in the H$_2$PtCl$_6$ (Sigma-Aldrich, 8 wt% in water) electrolyte. We also measured the chronoamperometry curves of bare $p$-Si and MoS$_2$/$p$-Si photocathodes using a fritted Pt counter electrode (WonATech Co., Ltd) to eliminate Pt deposition on the working electrode. A scan rate of 10 mV/s was used for the linear sweep. The ICPE was measured with a light source and monochromator. The quantum efficiency was measured with a standard Si photodiode. EIS was conducted by applying a constant potential of -0.7 V compared to the open-circuit potential. The sweeping frequency was from 250 kHz to 1 Hz with a 10 mV AC dither. The Faradaic efficiency was conducted by using a gas chromatography measurement system (FID-GC, PerkinElmer, NARL8502 Model 4003).

3. **Characterization.** The Raman spectra of the synthesized MoS$_2$ thin films were obtained with a Lab RAM HR (Horiba JobinYvon, Japan) at an excitation wavelength of 532 nm. Non-contact-mode AFM (XE-100, Park Systems) measurements at a scanning rate of 0.5 Hz
were performed to identify the surface morphologies and thicknesses of the synthesized MoS$_2$ thin films. Synchrotron radiation photoelectron spectroscopy experiments were performed in an ultra-high vacuum chamber (base pressure of ca. $10^{-10}$ Torr) with a 4D beam line, equipped with an electron analyzer and heating element, at the Pohang Acceleration Laboratory. The onset of photoemission, corresponding to the vacuum level at the surface of the MoS$_2$ thin film, was measured using an incident photon energy of 350 eV with a negative bias on the sample. The results were corrected for charging effects using Au 4$f$ as an internal reference. Bright-field and high-resolution TEM (JEOL JEM-2100F) with 200 kV field-emission images were obtained to investigate the microstructures of the synthesized MoS$_2$ thin films. The transmittance and absorption spectra of the synthesized MoS$_2$ thin films were measured by UV-Visible spectroscopy (JASCO-670).
Fig. S1 Schematics for the spin-coating and thermolysis of [(NH₄)₂MoS₄] precursor solution.

Reaction mechanism

(1) (NH₄)₂MoS₄ → 2 NH₃ + H₂S + MoS₃

(2) MoS₂ → MoS₃ + H₂S (under H₂ flow)
Fig. S2 (a) XPS analysis of synthesized MoS$_2$ thin films on Si and SiO$_2$ (300 nm)/Si substrates. (b) Schematic of differences in dangling bonds between Si and SiO$_2$ (300 nm)/Si substrates.

Solution precursor-based CVD synthesis of MoS$_2$ thin films on different substrates. The XPS results show whether MoS$_2$ thin films were successfully grown. MoS$_2$ thin films were grown in the type II condition, which used oxide substrates.
**Fig. S3** Optical microscopy images of transferred MoS$_2$ thin films on SiO$_2$ (300 nm)/Si wafers using different etchant solutions. Pinhole-free MoS$_2$ thin films are obtained using BOE-only etchant.

Optical microscopic images of MoS$_2$ thin films after transferring process. The images are shown in order of decreasing ratios of hydrofluoric acid (HF): buffered oxide etchant (BOE). As the amount of BOE increases, the number of pinholes is decreased.
Fig. S4 AFM images of synthesized MoS$_2$ thin films with precursor solutions of different concentrations. Thicker MoS$_2$ thin films are obtained with higher-concentration precursor solutions. The thicknesses of the MoS$_2$ thin films are increased with increasing precursor concentrations.

AFM images of synthesized MoS$_2$ thin film edges synthesized from precursor solutions of different concentrations. The thickness of the MoS$_2$ film is increased with increased precursor concentration. The 5, 7, 10, 13, 19, and 29 nm MoS$_2$ thin films are from solution precursors of 10, 20, 50, 100, 200, and 500 mM concentrations, respectively.
Fig. S5 SRPES analysis of synthesized MoS$_2$ thin films. Peak shapes and atomic compositions of synthesized MoS$_2$ thin films are similar to each other, regardless of precursor concentrations.
Fig. S6 Normalized absorbance spectra of synthesized MoS$_2$ thin films. The optical band gaps are calculated by extrapolating the initial peaks in the absorption spectra. The optical band edges of MoS$_2$ thin films are shifted to higher wavelength with respect to thickness of MoS$_2$ film.
The films show absorbance above 800 nm, which is consistent with the previous reports.\textsuperscript{1-3} Eda \textit{et al.}\textsuperscript{1} observed non-zero light absorbance above 800 nm even in a MoS\textsubscript{2} monolayer. We believe that the absorbance above the band gap energies may be related with electronic band structures of the 2D material that is distinct from those of conventional bulk semiconductors. To evaluate the optical band gaps of the MoS\textsubscript{2} films more specifically, we used $(\alpha h\nu)^2$ vs. $h\nu$ plot where $\alpha$ is the absorption coefficient of each film. Since the light scattering at the air/solid is negligible, the absorption coefficient can be determined using the following equation,\textsuperscript{4}

$$T = \exp[\alpha(\lambda)d]$$

where $T$ is optical transmittance, $\alpha$ is absorption coefficient, and $d$ is the thickness of the film. Fig. 1(b) shows $\alpha$ of the MoS\textsubscript{2} films as a function of wavelength. After the plotting $(\alpha h\nu)^2$ vs. $h\nu$, as shown in Fig. 1(c), the optical band gap could be easily evaluated using the following equation,

$$\alpha h\nu = B(h\nu - E_g)^{1/2}$$

where $h$ is the Planck’s constant, $\nu$ is the frequency of the incident photon, and $B$ is constant that depends on the electron-hole mobility. The optical band gap energies of the films could be determined by the extrapolation of the linear region from the $\alpha^2$ vs. $h\nu$ plot near the onset of the absorption edge to the photon energy axis.

The change of optical band gap energy with respect to the thickness of MoS\textsubscript{2} film ($\Delta E_g = 0.35$ eV between 5-nm-thick and 29-nm-thick MoS\textsubscript{2} films) is in agreement with the previous report,\textsuperscript{5} where the optical band gap energies of MoS\textsubscript{2} films on SiO\textsubscript{2}/Si substrates were evaluated using reflectance measurements ($\Delta E_g = 0.32$ eV between 2-nm-thick and 20-nm-thick MoS\textsubscript{2} films). Also, Mak \textit{et al.}\textsuperscript{6} and Lee \textit{et al.}\textsuperscript{7} characterized the optical band gap
energies of mechanically exfoliated single and few layer MoS$_2$ using photoluminescence spectra and electrical measurements, respectively. Our experimental data are quite comparable with those of the exfoliated materials.

Fig. S7 (a) Plotting against the Transmittance at 550 nm to MoS$_2$ thickness. (b) The absorption coefficient of the MoS$_2$ thin films with different thicknesses. (c) Plots of $(\alpha h\nu)^2$ versus photon energy of the MoS$_2$ thin film with different thicknesses.
In order to evaluate the Faradaic efficiency of MoS$_2$/p-Si heterojunction photocathodes, gas chromatography measurements were carried out under continuous illumination and vigorous stirring to ensure a rapid exchange of hydrogen between the aqueous and gas phase. The generation of hydrogen was measured four times at intervals of 20 minutes and we evaluated a Faradaic efficiency of 97 ± 5% (within experimental error).

Fig. S8 Faradaic efficiency measurements for the 13-nm-thick MoS$_2$/p-Si heterojunction photocathode under continuous illumination at -1.2 V vs. RHE in 0.5 M H$_2$SO$_4$ electrolyte, which displays almost 100% Faradaic efficiency for hydrogen production.
Fig. S9 Three key results from 5 different samples for each 7-nm-thick, 13-nm-thick, and 29-nm-thick MoS$_2$/p-Si heterojunction photocathodes. (a) Potential @ 10 mA/cm$^2$. (b) Current density @ 0 V. (c) Tafel slope values.
In order to investigate the thickness dependent stability of the device, we measured cyclic tests for 7-nm-thick, 13-nm-thick, and 29-nm-thick MoS$_2$ thin films. The 7 times measured curves are displayed in Fig. S10. The 7-nm-thick and 13-nm-thick MoS$_2$/p-Si photocathodes are quite stable. For the 29-nm-thick MoS$_2$/p-Si photocathode, the onset potential of 1 mA/cm$^2$ significantly shifts to the negative potential as a function of cycle. From the cyclic test results, it is inferred that the stability of the electrodes could be varied due to the difference of adhesion of the top MoS$_2$ film. The top MoS$_2$ thin films have relatively weak van der Waals force compared to bottom MoS$_2$ films which are located at the heterointerface with the p-Si.

**Fig. S10** The cyclic test for the MoS$_2$ thin films with various thicknesses. The 7 times cyclic test shows the thickness dependent stability. The cyclic tests with (a) 7-nm-thick MoS$_2$/p-Si, (b) 13-nm-thick MoS$_2$/p-Si, (c) 29-nm-thick MoS$_2$/p-Si heterojunction photocathode are displayed.
The Pt counter electrode was not stable for long-term (several hours) operation in the strong acid electrolytes such as 0.1 M H$_2$SO$_4$ (pH = 1.5) and 0.5 M H$_2$SO$_4$ (pH = 1.1). We have identified Pt deposition on the working electrode (MoS$_2$/p-Si photocathode) by performing the XPS analysis. From the XPS analysis, the Pt deposition was clearly identified after stability test over 20 hours. The initial increase of current density in Fig. S11 for the MoS$_2$/p-Si photocathode originates from the Pt deposition on the MoS$_2$ thin films. To exclude the influence of the Pt deposition, we have measured the chronoamperometry measurements for two kinds of photocathodes, which are 1) Pt decorated p-Si and 2) Pt decorated MoS$_2$/p-Si photocathodes, over 50 hours with potential at 0 V vs. RHE. For the Pt decorated p-Si photocathode, it is observed that the current density of the Pt decorated p-Si photocathode rapidly decreases during the measurement and retains only 0.1 % of the original current density after 9.6 hours. As we mentioned in the introduction, the metal nanoparticles cannot prevent the photocorrosion of the p-Si photocathode. Meanwhile, the Pt decorated MoS$_2$/p-Si photocathode maintain the initial current density, even after 50 hours, demonstrating the behavior of the transferred MoS$_2$ thin film as a passivation layer that prevents the p-Si photocathode from experiencing severe photocorrosion. The more efficient method for evaluating the stability of the photocathodes is using a fritted Pt counter electrode. The chronoamperometry measurements of bare p-Si and MoS$_2$/p-Si heterojunction photocathodes using a fritted Pt counter electrode are displayed in Fig. S11. The MoS$_2$/p-Si heterojunction photocathode maintains the initial current density even after 50 hours indicating that the transferred MoS$_2$ thin film can act as an excellent passivation layer as well as a good catalyst for hydrogen production.
Fig. S11 (a) Chronoamperometry measurements of bare $p$-Si and 13-nm-thick MoS$_2$/p-Si photocathodes. (b) The identification of Pt deposition using XPS analysis for before and after 20 hours. The Pt deposition was clearly identified after 20 hours stability measurement. (c) Chronoamperometry measurements of Pt decorated $p$-Si and Pt decorated MoS$_2$/p-Si photocathodes.
Fig. S12 (a) Photographic images of Pt plate, fritted Pt counter electrode (left), and the measurement cell which contains three electrodes i) reference, ii) working, and iii) fritted Pt counter electrode (right). (b) Chronoamperometry measurements of bare $p$-Si and MoS$_2/p$-Si photocathodes by using the fritted Pt counter electrode.
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<th>Ref No.</th>
<th>Materials</th>
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<th>Overpotential @10mA/cm²</th>
<th>Current density @ 0V vs. RHE</th>
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Table S1 Comparison of the PEC performances between our 13-nm-thick MoS₂/p-Si heterojunction photocathode and other similar and state-of-the-art materials on p-Si photocathodes.
Fig. S13 The electrocatalytic HER performance. (a) LSV curves and (b) Tafel slope for MoS$_2$ thin films on Au plate with various thicknesses.
**Fig. S14** Flat band and band bending diagram of $n$-MoS$_2$ thin film and $p$-Si heterojunction.
Fig. S15 Surface morphology analyses of synthesized MoS$_2$ thin films using AFM measurements. The serrated surfaces of the MoS$_2$ thin films have higher surface areas than atomically flat surfaces.
Fig. S16 (a), (b) High-resolution (HR) TEM images of Moiré fringes from in-plane rotation between two basal planes. (c) Selected-area electron diffraction (SAED) pattern images of in-plane rotation. (d) Schematic of structure producing Moiré fringes, corresponding to Fig. S12(c).
Fig. S17 High-resolution (HR) TEM images of synthesized MoS$_2$ thin films (5-nm-, 13-nm- and 29-nm-thick) with different magnifications. More c-domains and larger crystalline phases are observed in the 13-nm-thick MoS$_2$ thin films.
References


