1	Wafer-scale transferable molybdenum disulfide thin-film catalysts for				
2	photoelectrochemical hydrogen production				
3	3				
4	Supplementary Information				
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## 1 Detailed experimental procedures

1. MoS<sub>2</sub> thin film synthesis. SiO<sub>2</sub> (300 nm)/Si wafers were cleaned with a standard piranha 2 solution (3:1 mixture of H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>) and conventional cleaning procedures, followed by 3 ultrasonication in acetone, isopropyl alcohol, and deionized (DI) water. To obtain hydrophilic 4 surfaces on the SiO<sub>2</sub>/Si wafers, O<sub>2</sub> plasma and UV-O<sub>3</sub> surface treatment were performed for 5 15 min. The precursor solution was prepared by dissolving (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> powder (Sigma-6 Aldrich, 99.97% purity) in ethylene glycol (Sigma-Aldrich, 99.8% purity, anhydrous) at 7 concentrations of 10, 20, 50, 100, 200, and 500 mM. The precursor solution was spin-coated 8 onto the prepared SiO<sub>2</sub>/Si substrate at 3500 rpm for 60 s. High-purity H<sub>2</sub> and N<sub>2</sub> gases were 9 used for the thermolysis process in a thermal CVD system. First, the CVD chamber 10 temperature was increased to 500 °C and maintained at this temperature for 30 min under 11 flowing H<sub>2</sub> and N<sub>2</sub> at 1 Torr. The flow rate of H<sub>2</sub> and N<sub>2</sub> was set to 40 and 200 cm<sup>3</sup>/min, 12 respectively, by mass flow controllers. Under a H<sub>2</sub> gas atmosphere at relatively high 13 temperature, the thermolysis process was gradually started. Then, the temperature of the 14 CVD furnace was increased to 950 °C, and maintained for 1 h. Sulfur sublimation was 15 initiated with sulfur powder (Sigma-Aldrich, 99.5% purity) placed in the heating zone, which 16 was set to 300 °C. When the thermolysis process was finished, PMMA was spin-coated onto 17 18 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<sub>2</sub> from the SiO<sub>2</sub>/Si substrate. 19 The PMMA/MoS<sub>2</sub>/SiO<sub>2</sub>/Si substrate was immersed in a buffered oxide etch (BOE, Sigma-20 Aldrich, NH<sub>4</sub>F 40%) to separate the MoS<sub>2</sub> thin film from the substrate by etching away the 21  $SiO_2$  layers. The obtained  $MoS_2$  thin films were washed with DI water seven to nine times to 22 remove residual etchant and transferred to an arbitrary substrate of p-Si, p-InP, p-GaAs, or p-23 GaP. After the PMMA/MoS<sub>2</sub> membranes had adhered to the substrates, the PMMA layers 24 were removed using acetone and toluene at 50 °C for 30 min. 25

2. PEC measurements. HER measurements (Ivium Technologies, Model: Nstat) were 2 performed with a three-electrode system using a saturated calomel electrode as the reference 3 electrode and a Pt plate as the counter electrode in a 0.5 M H<sub>2</sub>SO<sub>4</sub> standard electrolyte 4 solution. The three-electrode system was set up inside a quartz vessel, which protected the 5 samples from UV absorption. A Xe arc lamp was used and calibrated to an output of 100 6 mW/cm<sup>2</sup> (AM 1.5 G condition). Because the Pt counter electrode was not stable for long-7 term (several hours) operation in the strong acid electrolytes such as  $0.1M H_2SO_4$  (pH = 1.5) 8 and  $0.5M H_2SO_4$  (pH = 1.1), the Pt deposition has been found on the working electrode 9 during chronoamperometry measurements.<sup>1</sup> Thus chronoamperometry measurements were 10 performed for Pt decorated p-Si and Pt decorated MoS<sub>2</sub>/p-Si photocathodes. The Pt 11 decoration was conducted by using electrodeposition method in the H<sub>2</sub>PtCl<sub>6</sub> (Sigma-Aldrich, 12 8 wt% in water) electrolyte. We also measured the chronoamperometry curves of bare p-Si 13 and  $MoS_2/p$ -Si photocathodes using a fritted Pt counter electrode (WonATech Co., Ltd) to 14 eliminate Pt deposition on the working electrode. A scan rate of 10 mV/s was used for the 15 linear sweep. The ICPE was measured with a light source and monochromator. The quantum 16 efficiency was measured with a standard Si photodiode. EIS was conducted by applying a 17 constant potential of -0.7 V compared to the open-circuit potential. The sweeping frequency 18 was from 250 kHz to 1 Hz with a 10 mV AC dither. The Faradaic efficiency was conducted 19 by using a gas chromatography measurement system (FID-GC, PerkinElmer, NARL8502 20 Model 4003). 21

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3. Characterization. The Raman spectra of the synthesized MoS<sub>2</sub> 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<sub>2</sub> 1 thin films. Synchrotron radiation photoelectron spectroscopy experiments were performed in 2 an ultra-high vacuum chamber (base pressure of ca. 10<sup>-10</sup> Torr) with a 4D beam line, 3 equipped with an electron analyzer and heating element, at the Pohang Acceleration 4 Laboratory. The onset of photoemission, corresponding to the vacuum level at the surface of 5 the MoS<sub>2</sub> thin film, was measured using an incident photon energy of 350 eV with a negative 6 bias on the sample. The results were corrected for charging effects using Au 4f as an internal 7 reference. Bright-field and high-resolution TEM (JEOL JEM-2100F) with 200 kV field-8 emission images were obtained to investigate the microstructures of the synthesized MoS<sub>2</sub> 9 thin films. The transmittance and absorption spectra of the synthesized MoS<sub>2</sub> thin films were 10 measured by UV-Visible spectroscopy (JASCO-670). 11



2 Fig. S1 Schematics for the spin-coating and thermolysis of  $[(NH_4)_2MoS_4]$  precursor solution.



2 **Fig. S2** (a) XPS analysis of synthesized  $MoS_2$  thin films on Si and SiO<sub>2</sub> (300 nm)/Si 3 substrates. (b) Schematic of differences in dangling bonds between Si and SiO<sub>2</sub> (300 nm)/Si 4 substrates.

6 Solution precursor-based CVD synthesis of  $MoS_2$  thin films on different substrates. The 7 XPS results show whether  $MoS_2$  thin films were successfully grown.  $MoS_2$  thin films were 8 grown in the type II condition, which used oxide substrates.



2 Fig. S3 Optical microscopy images of transferred  $MoS_2$  thin films on  $SiO_2$  (300 nm)/Si 3 wafers using different etchant solutions. Pinhole-free  $MoS_2$  thin films are obtained using 4 BOE-only etchant.

6 Optical microscopic images of  $MoS_2$  thin films after transferring process. The images are

7 shown in order of decreasing ratios of hydrofluoric acid (HF): buffered oxide etchant (BOE).

8 As the amount of BOE increases, the number of pinholes is decreased.



2 **Fig. S4** AFM images of synthesized  $MoS_2$  thin films with precursor solutions of different 3 concentrations. Thicker  $MoS_2$  thin films are obtained with higher-concentration precursor 4 solutions. The thicknesses of the  $MoS_2$  thin films are increased with increasing precursor 5 concentrations.

AFM images of synthesized  $MoS_2$  thin film edges synthesized from precursor solutions of

8 different concentrations. The thickness of the MoS<sub>2</sub> film is increased with increased precursor

9 concentration. The 5, 7, 10, 13, 19, and 29 nm  $MoS_2$  thin films are from solution precursors

10 of 10, 20, 50, 100, 200, and 500 mM concentrations, respectively.



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2 Fig. S5 SRPES analysis of synthesized  $MoS_2$  thin films. Peak shapes and atomic 3 compositions of synthesized  $MoS_2$  thin films are similar to each other, regardless of precursor 4 concentrations.



2 **Fig. S6** Normalized absorbance spectra of synthesized  $MoS_2$  thin films. The optical band 3 gaps are calculated by extrapolating the initial peaks in the absorption spectra. The optical 4 band edges of  $MoS_2$  thin films are shifted to higher wavelength with respect to thickness of 5  $MoS_2$  film.

1 The films show absorbance above 800 nm, which is consistent with the previous reports.<sup>1-3</sup> 2 Eda *et al*.<sup>1</sup> observed non-zero light absorbance above 800 nm even in a  $MoS_2$  monolayer. We 3 believe that the absorbance above the band gap energies may be related with electronic band 4 structures of the 2D material that is distinct from those of conventional bulk semiconductors.

To evaluate the optical band gaps of the MoS<sub>2</sub> films more specifically, we used  $(\alpha hv)^2$  vs. *hv* 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,<sup>4</sup>

$$T = exp^{[n]}[\alpha(\lambda)d] \tag{1}$$

9

14

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<sub>2</sub> films as a function of wavelength. After the plotting  $(\alpha hv)^2$  vs. *hv*, as shown in Fig. 1(c), the optical band gap could be easily evaluated using the following equation,

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

where *h* is the Planck's constant, *v* 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. *hv* 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<sub>2</sub> film ( $\Delta E_g =$ 0.35 eV between 5-nm-thick and 29-nm-thick MoS<sub>2</sub> films) is in agreement with the previous report,<sup>5</sup> where the optical band gap energies of MoS<sub>2</sub> films on SiO<sub>2</sub>/Si substrates were evaluated using reflectance measurements ( $\Delta E_g = 0.32$  eV between 2-nm-thick and 20-nmthick MoS<sub>2</sub> films). Also, Mak *et al.*<sup>6</sup> and Lee *et al.*<sup>7</sup> characterized the optical band gap 1 energies of mechanically exfoliated single and few layer  $MoS_2$  using photoluminesecene 2 spectra and electrical measurements, respectively. Our experimental data are quite 3 comparable with those of the exfoliated materials.





6 **Fig. S7** (a) Plotting against the Transmittance at 550 nm to  $MoS_2$  thickness. (b) The 7 absorption coefficient of the  $MoS_2$  thin films with different thicknesses. (c) Plots of  $(\alpha hv)^2$ 8 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, 2 gas chromatography measurements were carried out under continuous illumination and 3 vigorous stirring to ensure a rapid exchange of hydrogen between the aqueous and gas phase. 4 The generation of hydrogen was measured four times at intervals of 20 minutes and we 5 evaluated a Faradaic efficiency of  $97 \pm 5$  % (within experimental error).



8 **Fig. S8** Faradaic efficiency measurements for the 13-nm-thick  $MoS_2/p$ -Si heterojunction 9 photocathode under continuous illumination at -1.2 V vs. RHE in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte, 10 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 29nm-thick MoS<sub>2</sub>/p-Si heterojunction photocathodes. (a) Potential @ 10 mA/cm<sup>2</sup>. (b) Current
density @ 0 V. (c) Tafel slope values.

In order to investigate the thickness dependent stability of the device, we measured cyclic 1 tests for 7-nm-thick, 13-nm-thick, and 29-nm-thick MoS<sub>2</sub> thin films. The 7 times measured 2 curves are displayed in Fig. S10. The 7-nm-thick and 13-nm-thick MoS<sub>2</sub>/p-Si photocathodes 3 are quite stable. For the 29-nm-thick MoS<sub>2</sub>/p-Si photocathode, the onset potential of 1 4 5 mA/cm<sup>2</sup> 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 6 difference of adhesion of the top MoS<sub>2</sub> film. The top MoS<sub>2</sub> thin films have relatively weak 7 van der Waals force compared to bottom MoS<sub>2</sub> films which are located at the heterointerface 8 with the *p*-Si. 9



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 1 strong acid electrolytes such as 0.1 M  $H_2SO_4$  (pH = 1.5) and 0.5 M  $H_2SO_4$  (pH = 1.1).<sup>1</sup> We 2 have identified Pt deposition on the working electrode (MoS<sub>2</sub>/p-Si photocathode) by 3 performing the XPS analysis. From the XPS analysis, the Pt deposition was clearly identified 4 after stability test over 20 hours. The initial increase of current density in Fig. S11 for the 5 MoS<sub>2</sub>/p-Si photocathode originates from the Pt deposition on the MoS<sub>2</sub> thin films. To exclude 6 the influence of the Pt deposition, we have measured the chronoamperometry measurements 7 for two kinds of photocathodes, which are 1) Pt decorated p-Si and 2) Pt decorated MoS<sub>2</sub>/p-Si 8 photocathodes, over 50 hours with potential at 0 V vs. RHE. For the Pt decorated p-Si 9 photocathode, it is observed that the current density of the Pt decorated *p*-Si photocathode 10 rapidly decreases during the measurement and retains only 0.1 % of the original current 11 density after 9.6 hours. As we mentioned in the introduction, the metal nanoparticles cannot 12 prevent the photocorrosion of the p-Si photocathode. Meanwhile, the Pt decorated MoS<sub>2</sub>/p-Si 13 photocathode maintain the initial current density, even after 50 hours, demonstrating the 14 behavior of the transferred MoS<sub>2</sub> thin film as a passivation layer that prevents the p-Si 15 photocathode from experiencing severe photocorrosion. The more efficient method for 16 evaluating the stability of the photocathodes is using a fritted Pt counter electrode. The 17 18 chronoamperometry measurements of bare p-Si and MoS<sub>2</sub>/p-Si heterojunction photocathodes using a fritted Pt counter electrode are displayed in Fig. S11. The MoS<sub>2</sub>/p-Si heterojunction 19 photocathode maintains the initial current density even after 50 hours indicating that the 20 transferred MoS<sub>2</sub> thin film can act as an excellent passivation layer as well as a good catalyst 21 for hydrogen production. 22



2 **Fig. S11** (a) Chronoamperometry measurements of bare *p*-Si and 13-nm-thick  $MoS_2/p$ -Si 3 photocathodes. (b) The identification of Pt deposition using XPS analysis for before and after 4 20 hours. The Pt deposition was clearly identified after 20 hours stability measurement. (c) 5 Chronoamperometry measurements of Pt decorated *p*-Si and Pt decorated  $MoS_2/p$ -Si 6 photocathodes.



2 **Fig. S12** (a) Photographic images of Pt plate, fritted Pt counter electrode (left), and the 3 measurement cell which contains three electrodes i) reference, ii) working, and iii) fritted Pt 4 counter electrode (right). (b)Chronoamperometry measurements of bare *p*-Si and  $MoS_2/p$ -Si 5 photocathodes by using the fritted Pt counter electrode.

Ref No.	Materials	Preparation method	Photocathode	Overpotential @10mA/cm <sup>2</sup>	Current density @ 0V vs. RHE
1	rGO	Hummer's method	<i>p</i> -Si narowires	+ 0.145 V	2.3 mA/cm <sup>2</sup>
2	N:graphene	CVD growth (N2 plasma for N doping)	planar <i>p</i> -Si	+ 0.041 V	7.1 mA/cm <sup>2</sup>
	1T-MoS <sub>2</sub>	Li intercalation	planar <i>p-</i> Si	+ 0.055 V	9.6 mA/cm <sup>2</sup>
3	$1T-MoS_2$	CVD growth		-0.045 V	17.6 mA/cm <sup>2</sup>
	2H-MoS <sub>2</sub>	$(MoCl_5, S)$		+ 0.221 V	$4.5 \text{ mA/cm}^2$
	a-MoS <sub>x</sub>	Photoassisted deposition	planar <i>p-</i> Si	+ 0.065 V	6.0 mA/cm <sup>2</sup>
4	a-CoMoS <sub>x</sub>			- 0.085 V	17.5 mA/cm <sup>2</sup>
5	MoSe <sub>x</sub> Cl <sub>y</sub>	CVD growth (MoCl <sub>5</sub> , S, Se)	planar <i>p</i> -Si	+ 0.1 V	8.0 mA/cm <sup>2</sup>
	$MoS_{x}Cl_{y}$			– 0.127 V	20.6 mA/cm <sup>2</sup>
6	Ni-Mo <sup>2</sup>	Galvanostatic /potentiostatic deposition	<i>n+p-</i> Si MW	- 0.09 V	10.35 mA/cm <sup>2</sup>
7	$W_2C^3$	Reactive ballistic deposition	planar <i>p</i> -Si	+ 0.085 V	4.5 mA/cm <sup>2</sup>
8	CoSe <sub>2</sub> Nanorod <sup>4</sup>	Hydrothermal deposition	planar <i>p</i> -Si	+ 0.042 V	8.7 mA/cm <sup>2</sup>
Our Wor k	13-nm 2H-MoS <sub>2</sub>	Thermolysis ([(NH <sub>4</sub> ) <sub>2</sub> MoS <sub>4</sub> ], S)	planar <i>p</i> -Si	- 0.082 V	24.6 mA/cm <sup>2</sup>

**Table S1** Comparison of the PEC performances between our 13-nm-thick  $MoS_2/p$ -Si 3 heterojunction photocathode and other similar and state-of-the-art materials on *p*-Si 4 photocathodes.



Fig. S13 The electrocatalytic HER performance. (a) LSV curves and (b) Tafel slope for MoS<sub>2</sub>
thin films on Au plate with various thicknesses.



Fig. S14 Flat band and band bending diagram of n-MoS<sub>2</sub> thin film and p-Si heterojunction.



2 Fig. S15 Surface morphology analyses of synthesized  $MoS_2$  thin films using AFM 3 measurements. The serrated surfaces of the  $MoS_2$  thin films have higher surface areas than 4 atomically flat surfaces.



2 Fig. S16 (a), (b) High-resolution (HR) TEM images of Moiré fringes from in-plane rotation

3 between two basal planes. (c) Selected-area electron diffraction (SAED) pattern images of in-

4 plane rotation. (d) Schematic of structure producing Moiré fringes, corresponding to Fig.
5 S12(c).



2 Fig. S17 High-resolution (HR) TEM images of synthesized MoS<sub>2</sub> thin films (5-nm-, 13-nm-

- 3 and 29-nm-thick) with different magnifications. More c-domains and larger crystalline phases
- 4 are observed in the 13-nm-thick  $MoS_2$  thin films.

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