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Photoelectrochemical Hydrogen Evolution and CO₂ Reduction over MoS₂/Si and MoSe₂/Si Nanostructures by Combined Photoelectrochemical Deposition and Rapid-Thermal Annealing Process

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Abstract: Diverse methods have been employed to synthesize MoS₂ and MoSe₂ catalyst systems. Herein, a combined photoelectrochemical (PEC) deposition and rapid-thermal annealing process has first been employed to fabricate MoS₂ and MoSe₂ thin films on Si substrates. The newly developed transition-metal dichalcogenides were characterized by scanning electron microscopy, Raman spectroscopy and X-ray photoelectron spectroscopy. PEC hydrogen evolution reaction (HER) was demonstrated in an acidic condition to show a PEC catalytic performance order of MoO_x/Si < MoS₂/Si << MoSe₂/Si under the visible light-on condition. The HER activity (4.5 mA/cm² at -1.0 V vs Ag/AgCl) of MoSe₂/Si was increased by 4.8× compared with that under the dark condition. For CO₂ reduction, the PEC activity was observed to be in the order of MoS₂/Si < MoSe₂/Si was increased by 9.3× compared with that under the dark condition. The reduction activity (0.127 mA/cm²) of MoSe₂/Si was increased by 9.3× compared with that under the dark condition and rapid-thermal annealing method could be a very useful method for fabricating a thin film state catalytic system perusing hydrogen production and CO₂ energy conversion.

Keywords: MoS₂; MoSe₂; photoelectrochemical deposition; rapid-thermal annealing; hydrogen evolution; CO₂ reduction

1. Introduction

Transition-metal dichalcogenides (TMDCs) have widely been studied for applications to energy and environment such as hydrogen evolution and CO₂ reduction [1–10]. Especially, molybdenum disulfide and diselenide (MoS₂ and MoSe₂) materials with two-dimensional character have been synthesized using diverse synthesis methods for their applications [11]. Ye et al. employed a chemical vapor deposition (CVD) method to synthesize monolayer MoS₂ followed by oxygen plasma treatment or hydrogen annealing. They showed that hydrogen evolution reaction (HER) activity (e.g., onset potential and current density) was increased substantially by engineering the defects [12]. To increase HER activity of MoS₂ or MoSe₂, various defect engineering techniques have been employed, which include laser irradiation [13], ion irradiation [14,15] and NaCIO chemical etching [16]. Li et al. examined various defect sites of MoS₂ such as edge sites, S vacancies and grain boundaries and showed that edge sites and S vacancies (with optimal vacancy density of 7–10%) were main HER active sites [17]. Chang et al. employed lithium molten salts to synthesize 2H- and 1T-MoS₂ monolayers at calcination temperatures of 400~600 °C and above 1000 °C, respectively [18]. They observed that metallic 1T-MoS₂ showed a higher HER activity than that of semiconducting 2H-MoS₂. Two step hydrothermal method



was employed to synthesize 1T@2H-MoSe₂ nanosheets, which showed a higher HER activity [19]. Wang et al. prepared MoS₂ nanosheets by mechanical exfoliation, transferred onto a SiO₂ surface and made a HER device [20]. Afterwards, they showed that HER activity was increased by applying an extra positive electric field. Guo et al. prepared oxygen-incorporated MoS₂ sheets on graphene by a hydrothermal method [21] and showed that the active edge sites and conductivity were increased by oxygen-incorporation and the electrical transfer was increased by hybridization. Consequently, the HER activity was found to be substantially increased. Zhu et al. fabricated $h-MoO_3/1T-MoS_2$ heterostructures and tested photoelectrocatalytic HER activity to show better activity compared with those of 1T@2H-MoS₂ and α -MoO₃/MoS₂ [22]. A two-step (MoO₃ + H₂ \rightarrow MoO₂ and MoO₂ + Se vapor \rightarrow MoSe₂) chemical vapor deposition (CVD) process was employed to fabricate vertically aligned core-shell MoO₂/MoSe₂ nanosheet arrays which showed better HER activity than those of MoO₂ and $MoSe_2$ [23]. Electrochemical CO₂ reduction is another potential application area for MoS_2 and MoSe₂ [4,24–29]. Francis et al. tested a single crystal MoS₂ electrode for CO₂ reduction and showed a Faradaic efficiency of ~3.5% at -0.59 V (vs Reversible Hydrogen Electrode) for a reduction product of 1-propanol [4]. Asadi et al. reported that electrochemical CO₂ reduction product for vertically aligned MoS_2 in an ionic liquid was found to be CO with a CO₂ reduction current density of 130 mA cm⁻² at -0.764 V [28,29].

Electrodeposition has popularly been employed for the cheap fabrication of thin films on a substrate, where major factors determining the nature of thin film include electrolyte, pH, deposition time and an applied potential [30]. For electrodeposition (under the dark condition) of Mo oxides on a substrate, some studies have been reported [31–34]. However, no studies have been reported for photoelectrochemical deposition of Mo oxides. Petrova et al. used Al substrates for electrodeposition of Mo oxides in Mo ion electrolyte $(Mo(NH_4)_6Mo_7O_{24}\cdot 4H_2O, 20 \text{ g/L})$ at pH of 8–10 adjusted by a NH_3 -CH₃COONH₄ buffer [31]. Pd–MoO_x catalyst on glassy carbon electrode was reported to be fabricated by electrodeposition at potential ranges between -0.73 and +0.2 V in a mixed solution of 2 mM PdCl₂, 15 mM Na₂MoO₄ and 0.2 M HCl [32]. The dominant oxidation state of Mo was found to be +6. Uniform Mo oxide (+6, +5 and +4 oxidation states) nanostructure arrays (nanotubes at pH = 2.7 and nanowires at pH = 5.5) were prepared by a template electrodeposition in Mo ion electrolyte ((NH₄)₆Mo₇O₂₄·4H₂O, 50 g/L) [33]. Electroless-photochemical deposition (PCD) has also been demonstrated for the preparation of metal sulfide thin films. Soundeswaran et al. prepared CdS films on indium tin oxide (ITO) glass using 1–10 mM Cd(CH₃COO)₂ and 100 mM Na₂S₂O₃ solution at pH = 3.0-4.5 under irradiation of ultraviolet (UV) light (100 mW/cm²) [35]. For this reaction, S and electrons were initially formed by UV-excitation of $S_2O_3^{2-}$ ions and reacted with Cd metal ions to form CdS. Podder et al. prepared Cu_xS thin films on ITO glass using a similar method [36].

Herein, a new methodology of combined photoelectrochemical deposition ($Mo^{6+} + 6OH^- \rightarrow MoO_3 + 3H_2O$ accelerated by an enhanced photocurrent) and rapid-thermal annealing (RTA) sulfurization (or selenization) process ($2MoO_3 + 4S$ or $Se \rightarrow 2MoS_2$ or $MoSe_2 + 3O_2$) was introduced to fabricate thin MoS_2 and $MoSe_2$ films on Si substrates. HER and CO_2 reduction tests were demonstrated to show a potential applicability to energy and environment. A major advantage of the combined method is time-saving and cost effective. Another advantage is morphology and thickness-controlled by tuning applied voltage, deposition time and the electrolyte condition and so forth. Overall, the present developed method could be further improved and widely used for developing better thin film systems for diverse application areas.

2. Results

Surface morphology, crystal phase formation and surface chemical states were examined using scanning electron microscopy (SEM), Raman and X-ray photoelectron spectroscopy (XPS), respectively. Hydrogen evolution reaction (HER) and CO₂ reduction were tested using the three electrode system. The experimental results are described below.

2.1. SEM Morphology

Figure 1 shows the SEM images of MoO_x/Si , MoS_2/Si and $MoSe_2/Si$ samples. For the as-photoelectrodeposited MoO_x/Si sample, larger (200~400 nm diameter) and smaller (< 50 nm) nanoparticles were formed on the Si surface. Two different particle size distributions may be due to mixed Volmer-Weber island growth mode and Ostwald ripening process. The oxidation states were confirmed by XPS, discussed below. Under the dark condition, no electrodeposition was observed. For the SEM image of MoS_2 formed by RTA process of MoO_x/Si sample, two different size distributions were also observed for the sample as expected. For the SEM image of $MoSe_2$ formed by RTA process of MoO_x/Si sample, the surface morphology showed more uniform nanostructure.



Figure 1. Scanning electron microscope (SEM) images of MoO_x/Si (**A** and **A1**), MoS₂/Si (**B** and **B1**) and MoSe₂/Si (**C** and **C1**) samples.

2.2. Raman Spectroscopy

Raman spectra (Figure 2) were obtained to examine the detailed crystal phase formation for the catalyst systems. For all the samples, the strongest peak was commonly observed at 524 cm⁻¹ (not shown in the Figure), attributed to Si used as a support [37]. A weak peak at ~300 cm⁻¹ for MoO_x/Si was due to the phonon mode of Si [37]. No Raman peaks of Mo oxides were observed, indicating that the as-photoelectrodeposited sample was ultrathin and/or amorphous. For MoS₂ sample (Figure 2B), two Raman peaks were observed at 385 and 411 cm⁻¹, attributed to in-plane Mo-S (E_{2g}) and out-of-plane Mo-S (A_{1g}) vibration modes of hexagonal MoS₂ [38,39]. For MoSe₂ sample (Figure 2C), a strong Raman peak was observed at 238 cm⁻¹, attributed to Mo-Se A_{1g} mode. Other two peaks at 169 and 286 cm⁻¹ were assigned to E_{1g} and E_{2g} modes, respectively [40,41]. The A_{1g} mode was found to be stronger than the E_{2g} mode. Overall, based on the Raman data, the RTA process was found to be efficient for the fabrication of MoS₂ and MoSe₂.



Figure 2. Raman spectra of (A) MoO_x/Si, (B) MoS₂/Si and (C) MoSe₂/Si samples.

2.3. X-ray Photoelectron Spectroscopy

X-ray photoelectron spectra (XPS) of the three catalyst systems are displayed in Figure 3. For the as-photoelectrodeposited MoOx/Si, Mo and O elements were dominantly observed. Mo 3d_{3/2} and 3d_{5/2} XPS peaks were observed at 235.5 and 232.5 eV, respectively with a spin-orbit splitting energy of 3.0 eV. This is attributed to Mo^{6+} oxidation state of MoO_3 [42]. Furthermore, the other Mo $3d_{3/2}$ and 3d_{5/2} XPS peaks were observed at 233.8 and 230.8 eV, respectively with a spin-orbit splitting energy of 3.0 eV. This could be due to Mo⁵⁺ oxidation state. Based on the Mo 3d XPS fitting, 42% and 52% of Mo were 6+ and 5+ oxidation states, respectively. The corresponding broad O 1s peak was observed at 530.6 eV, attributed to the lattice oxygen of Mo oxides (MoO_x). For the Mo 3d XPS of the MoS_2/Si sample, $Mo3d_{3/2}$ and $3d_{5/2}$ XPS peaks were observed at 232.2 and 229.0 eV, respectively with a spin-orbit splitting energy of 3.2 eV. This is attributed to Mo^{4+} oxidation state of MoS_2 [43,44]. A small peak at 226.3 eV was due to S 2s [45]. The corresponding S 2p_{1/2} and S 2p_{3/2} XPS peaks were observed at 163.1 eV and 161.9 eV, respectively with a spin-orbit splitting of 1.2 eV. This is in good agreement with the literature reported by Jian et al. for 1T phase MoS_2 [44]. For the Mo 3d XPS of the $MoSe_2/Si$ sample, Mo $3d_{3/2}$ and $3d_{5/2}$ peaks were observed at 231.7 and 228.6 eV, respectively with a spin-orbit splitting energy of 3.1 eV. This is in good agreement with +4 oxidation state of MoSe₂ [5]. The corresponding Se $3d_{5/2}$ and $3d_{3/2}$ peaks were found to be located 55.1 and 54.2 eV, respectively. The O 1s XPS peak was observed at 533.1 eV, attributed adsorbed surface oxygen [42]. For MoO_x/Si sample, the Mo:O ratio was estimated to be 1:4.1. The overestimated oxygen was plausibly due to surface oxygen such as H₂O and OH. Mo:O ratio was estimated to be 1: 2.3 by only considering the lattice O 1s signal. For MoS₂/Si sample, Mo:S ratio was calculated to be 1:1.95, very close to MoS₂. For MoSe₂/Si sample, Mo:Se ratio was calculated to be 1:2.15, close to MoSe₂. For the valence band (VB) XPS spectra, the density of states (DOS) near the Fermi level was more discernible for MoS₂ and MoSe₂ reflecting metallic/semiconducting states.



Figure 3. Mo 3d, O 1s, Se 3d, S 2p and valence band (VB) X-ray photoelectron spectra (XPS) for MoO_x/Si, MoS₂/Si and MoSe₂/Si samples.

2.4. Photoelectrochemcial Hydrogen Evolution

Three different catalyst systems of MoO_x/Si, MoS₂/Si and MoSe₂/Si were tested for hydrogen evolution reaction in 0.1 M H₂SO₄ electrolyte. Linear sweep voltammetry (LSV) curves (Figure 4) were obtained from +0.2 V to -1.0 V at a scan rate of 10 mV/sec after full nitrogen gas purging under the dark and visible light exposure conditions. Under the dark condition, the current density at -1.0 V (vs Ag/AgCl) showed the order of MoO_x/Si (0.08 mA/cm²) < MoS₂/Si (0.11 mA/cm²) << MoSe₂/Si (0.86 mA/cm²) while the order changed to MoS₂/Si (0.51 mA/cm²) < MoO_x/Si (0.64 mA/cm²) << MoSe₂/Si (4.3 mA/cm²) under the visible light exposure condition. They all commonly showed an increase in HER CD under visible light exposure. The inset in Figure 4 displays LSV curves taken under the light ON-and-OFF condition during the scan. It clearly showed that all three samples have photocatalytic activity.



Figure 4. Linear sweep voltammetry curves (voltage range: $+0.2 \sim 1.0$ V) at a scan rate of 10 mV/sec) under visible light exposure for (a) MoO_x/Si, (b) MoS₂/Si and (c) MoSe₂/Si samples. Inset LSV curves were taken under the dark condition. The corresponding light ON-and-OFF LSV curves are displayed in the inset. Inset photo shows the bubble formed on the catalyst surface during LSV.

2.5. Photoelectrochemcial CO₂ Reduction

For CO₂ reduction in 0.1 M NaHCO₃ electrolyte, the LSV measurements (Figure 5) were obtained from +0.2 V to -1.0 V upon full N₂ and CO₂ gas purging at a scan rate of 10 mV/sec under the dark and visible light exposure conditions, respectively. Upon full N₂ gas purging in the electrolyte under dark condition (inset in Figure 5A), the current densities (CDs) at -1.0 V were observed to be 0.0043, 0.0041 and 0.012 mA/cm² for MoO_x/Si, MoS₂/Si and MoSe₂/Si, respectively. Under the visible light exposure condition (Figure 5A), the CDs were found to be drastically increased to 0.037, 0.011 and 0.018 mA/cm² for MoO_x/Si, MoS₂/Si and MoSe₂/Si, respectively. Upon full CO₂ gas purging in the electrolyte under the dark condition (inset in Figure 5B), the CDs at -1.0 V were found to be 0.007, 0.009 and 0.014 mA/cm² for MoO_x/Si, MoS₂/Si and MoSe₂/Si, respectively. Under the visible light exposure condition (Figure 5B), the CDs were found to be increased to 0.043, 0.023 and 0.13 mA/cm² for MoO_x/Si, MoS₂/Si and MoSe₂/Si, respectively. The CDs were increased by 6.0, 2.6 and 9.4×, respectively upon visible light exposure. The inset in Figure 5B displays LSV curves taken under the light ON-and-OFF condition during the scan. It clearly showed that all three samples also have photocatalytic activity.





Figure 5. Linear sweep voltammetry curves (voltage range: $+0.2\sim1.0$ V) in N₂- (**A**) and CO₂-purged (**B**) 0.1 M NaHCO₃ electrolyte at a scan rate of 10 mV/sec under dark (in the corresponding inset Figure) and the visible light exposure condition for (a) MoO_x/Si, (b) MoS₂/Si and (c) MoSe₂/Si samples. The inset (**B**) shows the light ON-and-OFF LSV curves.

3. Discussion

The photo-electrochemical deposition method was first successfully employed to fabricate MoO_x on a Si support. Upadhyay et al. reported MoO_x nanoparticles on a stainless steel support prepared by electrodeposition at -1.0 V in a mixed solution of 0.1 M Na₂MoO₄ and 0.1 M NH₄NO₃ [46]. They reported oxidation states of Mo^{6+} and Mo^{5+} for MoO_x and the corresponding O 1s peak at 530.6 eV. This is in good agreement with our present results. Liu et al. performed electrodeposition of MoO_x films on a Ti (130 nm)/Si substrate in a mixed solution of 0.1 M Na₂MoO₄, 0.1 M Na₂EDTA and 0.1 M CH₃COONH₄ [47]. They concluded that the as-electrodeposited MoO_x film (with oxidation states of Mo⁴⁺ and Mo⁵⁺) was amorphous. This is also in good agreement with the present result, as discussed above (Raman spectra in Figure 2). Based on the SEM image, the photoelectrochemical deposition of MoO_x on a Si support appeared to be occurred through Volmer-Weber island growth process [48]. Small islands were initially formed on the entire surface and then larger islands subsequently were grown. For the SEM images of MoS₂ and MoSe₂ by the RTA process, the morphology of MoS₂ was more similar to that of MoO_x, compared with that of MoSe₂. This indicates that less energy was required for the formation of MoS₂, compared with that for MoSe₂. Overall, the RTA process was found to be efficient for the formation of MoS₂ and MoSe₂ without much impacting the original morphology of electrodeposited MoO_x.

For HER in 0.1 M H₂SO₄, MoSe₂/Si showed a much higher electrochemical activity (or current density) than MoS₂/Si. For HER mechanism in the acidic condition, adsorbed hydrogen is known to be formed via $H_{3}O^{+} + e^{-} \rightarrow H_{ad} + H_{2}O$. Then, hydrogen is generated via $H_{ad} + H_{3}O^{+} + e^{-} \rightarrow H_{2} + H_{2}O$ or $H_{ad} + H_{ad} \rightarrow H_2$ [23]. In the mechanism, hydrogen adsorption Gibbs free energy, ΔG_{HX} (X = S or Se) is known to play a major role in determining the activity [10]. The optimal condition is $\Delta G_{HX} = 0 \text{ eV}$ and ΔG_{HX} of MoSe₂ is closer to the optimal condition than that of MoS₂. The HER activity of MoSe₂ has commonly been reported to be higher than that of MoS₂ [49]. This is in good consistent with the present result. For HER of nanoflowers-like MoS₂ and MoSe₂ materials on GC electrodes in 0.5 M H₂SO₄, Ravikumar et al. reported that the activity (11 mA/cm² at 0.3 V vs RHE) of MoSe₂ showed a higher than that (7 mA/cm² at 0.3 V vs RHE) of MoS₂, attributed to higher electrical properties and defects [50], in good consistent with the present result. Evidently, based on the DOS near the Fermi level as discussed in Figure 3, the enhanced electronic conductivity could play an important

role in HER and CO₂ reduction performances [22]. Because the Gibbs free energy is also known to be dependent on morphology (e.g., defects and edge sites) the catalyst fabrication methods is important for improving a catalyst activity. Upon visible light exposure on the catalyst surface during the LSV, an increased CD was commonly been observed. The enhancement factors (light ON/OFF CD ratio) for HER at -1.0 V upon visible light irradiation were observed to be 8.0, 4.7 and 5.0 for MoO_x/Si, MoS₂/Si and MoSe₂/Si, respectively (Figure 6). The photocatalytic HER activity under visible light was due to photo-generated electron by absorption of light in the visible region [22,42]. As mentioned above, in HER mechanism electron plays a crucial role in generation of hydrogen. Overall, the photocatalytic activity is all dependent on material nature (e.g., electrical conductivity), morphology, surface natures (e.g., defects) and light absorption efficiency. For the splitting of water, the molar stoichiometric ratio of H₂/O₂ is ideally 2.0 [51] assuming that no other side electrochemical reactions are involved for MoS₂ and MoSe₂ [1]. Before further discussion, it should be here mentioned that our conclusion was based only on the CD. The H₂/O₂ production ratios and CO₂ reduction products are needed to be further examined by gas chromatography [51].

For electrochemical CO₂ reduction, the current density was commonly been increased in CO₂-purged 0.1 M NaHCO₃ electrolyte, compared with that in N₂-purged 0.1 M NaHCO₃ electrolyte. This indicates that CO₂ reduction was occurred for all the samples. For CO₂ reduction (Figure 6), under the dark condition, the enhancement factors before (only N₂ bubbling) and after CO₂ bubbling were observed to be 1.6, 2.2, 1.2 for MoO_x/Si, MoS₂/Si and MoSe₂/Si, respectively. Under the visible light-on condition, the enhancement factors before (only N₂ bubbling) and after CO₂ bubbling were observed to be 1.1, 2.1 and 7.2 for MoO_x/Si, MoS₂/Si and MoSe₂/Si, respectively. The CDs upon light exposure were increased by 6.0, 2.6 and 9.4× for MoO_x/Si, MoS₂/Si and MoSe₂/Si, respectively. Overall, MoSe₂ showed the most dramatic photo-electrochemical CO₂ reduction efficiency. For MoSe₂, photogenerated electrons are created by light absorption in the visible region and electron-hole recombination is suppressed by good electron transport [1]. Consequently, the CD by photoelectrochemical CO₂ reduction is enhanced.



Figure 6. Enhancement factors for HER $CD_{light ON}$ / HER $CD_{light OFF}$, $CD_{CO2 bubbling}/CD_{N2 bubbling}$ under light ON condition and $CD_{CO2 bubbling}/CD_{N2 bubbling}$ under the light OFF condition for (**a**) MoO_x/Si , (**b**) MoS_2/Si and (**c**) $MoSe_2/Si$ samples.

4. Materials and Methods

For photoelectrochemical Mo deposition (MoO_x/Si), a three-electrode (Ag/AgCl reference, Pt wire counter and Si working electrode) electrochemical cell was used using a VersaSTAT3 (Princeton Applied Research, Oak Ridge, TN, USA) potentiostat galvanostat. For the preparation of a Si working support electrode before electrodeposition, a single-side polished Si (100) wafer (B-doped p-type, thickness of 525 ± 20 μ m, resistivity of 1–10 Ω ·cm, 2 cm × 0.5 cm) was used as the support, cleaned in 2% HF solution to remove oxide layer and washed with deionized water by sonication. The electrolyte was a mix of 15 mM Na₂MoO₄ (99.0% extra pure, Samchun Chem. Co., Seoul, Republic of Korea), 1.0 M NaCl and 1.0 M NH₃Cl, where pH was adjusted to 9.2 using NH₃OH (28~30%, Samchun Chem. Co., Seoul, Republic of Korea). The photoelectrochemical deposition was performed at an applied potential of -1.5V (versus Ag/AgCl electrode) for 10 sec under visible light exposure onto the working electrode. In the present study, we only showed the samples prepared at fixed parameters among different applied potentials and deposition times. No efficient (or less uniform) Mo deposition occurred under the dark condition although the applied voltages and deposition times were varied. CDs of -0.10and -0.92 mA/cm² were measured at -1.5 V under dark and visible light, respectively. The CD was enhanced by $9-10\times$ in the potential ranges from -1.0 to -2.0 V. For the preparation of MoS₂ and MoSe₂ on Si support, a rapid-thermal annealing (RTA) method was employed using a LABSYS RTP-1200 (Nextron Co., Ltd., Busan, Republic of Korea). For this, a MoO_x/Si substrate was placed on a quartz plate (15 mm × 20 mm) in the RTA chamber. Sulfur (S.P.C. GR reagent, Shinyo Pure Chem. Co., Ltd., Hyogo, Japan) or Selenium (99.5+%, 100mesh, Sigma-Aldrich, St. Louis, MO, USA) powder (~0.02 g) was placed below the substrate. The chamber was maintained in 5% H₂ in He balance. The temperature heating rate was 12 °C/sec and the time was 6 sec at the maximum temperature of 700 °C. The surface morphology of the prepared samples was examined using a Hitachi S-4800 (Tokyo, Japan) scanning electron microscope at an electron acceleration voltage of 10.0 kV. Raman spectra with 514 nm laser line were obtained using a LabRAM HR-800 microRaman spectrometer (HORIBA Jobin Yvon, Kyoto, Japan). X-ray photoelectron spectra were taken using a Thermo Scientific K-Alpha⁺ X-ray photoelectron spectrometer with micro-focused monochromatic Al K α X-ray source and a hemispherical energy analyzer. XPS spectra curve fitting was performed using a XPSPEAK ver. 4.1 software. For XPS element quantification, XPS sensitivity factors of 2.75, 0.66, 0.54, and 0.67 were used for Mo 3d, O 1s, S 2p and Se 3d, respectively [52]. For photoelectrochemical HER and CO₂ reduction, a three-electrode electrochemical cell was also used using a VersaSTAT3 potentiostat/galvanostat. For HER, nitrogen gas was fully purged into the electrolyte (0.1 M H₂SO₄ solution) to minimize an effect of dissolved oxygen. Linear sweep voltammetry (LSV) was carried out at a scan rate of 10 mV s⁻¹ from +0.2 V to -1.0 V under dark and visible light exposure conditions. A white LED USB Flashlight (A-10, Teckmedia) was used for visible light (400~700 nm) [53]. For CO₂ reduction experiment in 0.1 M NaHCO₃ solution, LSV was conducted after N₂ gas purging at a scan rate of 10 mV s⁻¹ from +0.2 V to -1.0 V under dark and visible light irradiation conditions. The same LSV experiment was also conducted after CO2 gas purging into the electrolyte to examine the CO₂ effect.

5. Conclusions

In this work, a combined photoelectrochemical deposition and rapid-thermal annealing method was first been employed to fabricate MoS₂ and MoSe₂ thin films on Si substrates. Photoelectrochemical HER and CO₂ reduction were demonstrated for the newly developed catalytic systems. The main results are as follows:

- 1. Mo oxides were successfully electrodeposited on a Si support under visible light exposure. Under the dark condition, the electrochemical deposition was less efficient.
- 2. A rapid-thermal annealing method was successfully introduced for the electrodeposited MoO_x/Si to fabricate MoS₂/Si and MoSe₂/Si catalyst systems. Other impurity phases were not detected

mainly based on the Raman and XPS results. The maximum temperature was achieved by rapid heating to 700 °C of S or Se powers on the MoO_x/Si and maintained for 6 sec.

- 3. HER tests in 0.1 M H₂SO₄ electrolyte showed a catalytic activity order of MoO_x/Si < MoS₂/Si << MoS₂/Si under dark and visible light-on conditions. The HER activity (4.5 mA/cm² at −1.0 V vs Ag/AgCl) of MoS₂/Si was increased by 4.8× compared with that under the dark condition.
- 4. CO₂ reduction tests in 0.1 M NaHCO₃ electrolyte showed a catalytic activity order of MoO_x/Si, MoS₂/Si << MoSe₂/Si and MoS₂/Si < MoO_x/Si << MoSe₂/Si under dark and visible light-on conditions, respectively. The reduction activity (0.127 mA/cm²) of MoSe₂/Si was increased by 9.3× compared with that under the dark condition.

The newly developed catalyst preparation method could be very useful for developing thin film catalyst systems for diverse application areas.

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