Abstract: The thickness of transition metal dichalcogenides (TMDs) plays a key role in enhancing their photocatalytic CO$_2$ reduction activity. However, the optimum thickness of the layered TMDs that is required to achieve sufficient light absorption and excellent crystallinity has still not been definitively determined. In this work, ultra-thin molybdenum disulfide films (MoS$_2$ TF) with 25 nm thickness presented remarkable photocatalytic activity, and the product yield increased by about 2.3 times. The photocatalytic mechanism corresponding to the TMDs’ thickness was also proposed. This work demonstrates that the thickness optimization of TMDs provides a cogent direction for the design of high-performance photocatalysts.

Keywords: thickness optimization; transition metal dichalcogenides; ultra-thin molybdenum disulfide film; photocatalytic activity

1. Introduction

Photocatalytic CO$_2$ reduction reaction (PC-CO$_2$RR) is an elegant pathway in heterogeneous catalysis that transforms the CO$_2$ molecule, which is a widely known pollutant and one of the major causes of global warming, into a variety of useful chemicals by solar light-driven conversion [1,2], and it is also expected to help achieve the goal of net-zero industrial emissions [3]. However, the materials that have so far been investigated under the PC-CO$_2$RR principle still show poor conversion efficiencies and are still far from satisfying practical applications [4]. One of the main issues is the lack of high efficiency in photocatalysts that can be engaged in CO$_2$ reduction. Although a large number of metal oxide-based catalysts that can respond to ultraviolet light (such as titanium dioxide (TiO$_2$)) have been reported to be suitable for PC-CO$_2$RR applications, most of these materials still possess relatively low conversion efficiencies [5,6]. Consequently, researchers have devoted a great deal of time and effort to developing visible-light-active photocatalysts with appreciable conversion efficiencies [7,8]. In addition to the issue of the absorption of a broad range of wavelengths present in sunlight, another major factor that enhances the performance of a photocatalyst is the ability of excellent carrier separation and transportation. Presently, the conundrum faced by researchers in this field is that the low
charge separation efficiency of the photocatalyst leads to the rapid recombination of pho-
togenerated electrons (e\(^{-}\)) and holes (h\(^{+}\)) in the entire photocatalytic process, making the
conversion efficiency very poor [9]. Therefore, a myriad of strategies have been explored to
manipulate the catalyst’s charge transfer and/or spatial separation capabilities to obtain
higher catalytic activity [7–10], including doping [11], co-catalysts, reduced particle size,
and heterojunctions.

Two-dimensional transition metal dichalcogenide (TMD)-based catalysts have been
predicted to be promising candidates for improving photocatalytic hydrogen evolution
and CO\(_2\) conversion efficiency in recent times [7,12,13], with several glowing mentions
of layered molybdenum disulfide (MoS\(_2\)). Many reports indicate that MoS\(_2\) shows great
promise as a catalyst due to its tunable optical characteristics, suitable band-gap potential,
and high stability under continuous light illumination, allowing it to perform visible-light
photocatalysis [7,12–14]. For instance, MoS\(_2\) exhibits a good ability to convert CO\(_2\) into
valuable fuels (CH\(_4\), CO, CH\(_3\)OH, HCOOH) through PC-CO\(_2\)RR [15]. As a visible light-
driven photocatalyst for PC-CO\(_2\)RR processes, it is necessary to conduct a thorough and
systematic study of the changes in light absorption and charge recombination caused by
tuning the number of layers of MoS\(_2\) and the subsequent photocatalytic activity. It has
been widely reported that a controlled number layers of MoS\(_2\) nanosheets can be made by
mechanical and chemical exfoliation methods [16,17]. When the size of MoS\(_2\) nanosheets
is reduced, it will not only change the ratio of the length of the edge to the base surface
of the MoS\(_2\) nanosheets but will also change the surface chemistry [16,17] of the material.
In the past, many publications have reported that the edge sites in MoS\(_2\) are more active
than the basal plane (which is relatively inert) [17,18], with respect to catalytic activity.
Therefore, it is understandably challenging to choose a method of MoS\(_2\) production that
can avoid excessive edge exposure while only tuning the number of layers in the catalyst
to solve the above-mentioned problems. The surface properties and edge size of the thin
film-type photocatalyst can remain unchanged when the film thickness changes. In this
way, the influence of thickness on the overall catalytic performance can be isolated from
other convoluting factors.

In this study, we have successfully synthesized ultra-thin MoS\(_2\) films (MoS\(_2\)TFs) with
different thicknesses as model catalysts and investigated their PC-CO\(_2\)RR activities under
visible light. We demonstrated that the layer numbers and crystallinity of MoS\(_2\)TFs can
be fine-tuned by a three-step post-sulfurization and chemical vapor deposition process.
The results indicate that the photocatalytic activity was significantly enhanced with the
increasing thickness of the MoS\(_2\)TFs. Impressively, 25 nm MoS\(_2\)TFs exhibit the highest
photocatalytic activity because they have excellent optical absorption and an appropriate
grain size. This strategy not only provides a new perspective for enhancing photocatalytic
activity by controlling the thickness of the film but also gives us a deeper understand-
ing of the mechanism of optical absorption and charge separation in promising layered
photocatalysts such as MoS\(_2\).

2. Results and Discussion

2.1. Synthesis of Photocatalytic Ultra-Thin Film

In this paper, we report the growth and characterization of MoS\(_2\)TFs on sapphire
substrates, wherein we used thermal evaporation in combination with chemical vapor
to synthesize the thin films to be studied. This method is similar to the one that was
reported in our previous publication [19]. Herein, we provide a detailed report on the
actual preparation of the MoS\(_2\)TFs. We also elaborate upon the methods that can be
utilized to control and identify the disorder that could be observed in the thin film that we
synthesized. Figure 1a depicts the schematic diagram of the three-step method proposed
in this study. The first step is the deposition of the precursor MoO\(_3\) film on the c-sapphire
substrate by thermal evaporation. MoO\(_3\) films prepared by thermal evaporation have
the distinct advantages of adjustable thickness, large area, continuous film growth, good
uniformity, and high quality. The second step involves annealing the MoO\(_3\) film using a
gaseous mixture of Ar and H$_2$ at 500 °C for a total duration of 1 h. In this step, the MoO$_3$ film underwent partial reduction and was converted to an MoO$_2$ film, which is a form that is easier to convert to our target MoS$\textsubscript{2}$TFs. The final step is the sulfurization of the MoO$_2$ films using a gaseous mixture of Ar and H$_2$S at 900 °C for 0.5 h to produce the target product (MoS$\textsubscript{2}$TFs). Figure 1b shows the temperature profile of the MoS$\textsubscript{2}$TFs growth process for hydrogenation and sulfurization steps. Figure 1c shows the optical photographs of the c-sapphire substrate before and after the growth of MoS$\textsubscript{2}$ thin films. From this picture, it can be clearly seen that the MoS$\textsubscript{2}$TFs fully cover the entire sapphire substrate and have excellent uniformity. In addition, the color of the sample surface changes from transparent to dark yellow, as there is an increase in film thickness.

2.2. Characterization of Photocatalytic Ultra-Thin Film

Figure 2a–d illustrate the thicknesses and surface roughness of the MoS$\textsubscript{2}$TFs measured by atomic force microscopy. All specimens for the thickness measurements were prepared by scratching the TFs. The area that was scanned in the AFM measurements is 10 × 10 µm for these MoS$\textsubscript{2}$ TF samples (see the first column in Figure 2). The height profiles of the AFM images (second column in Figure 2) show that the thickness of the four MoS$\textsubscript{2}$TFs samples was 7, 17, 25, and 50 nm, respectively. In addition, the surface roughness (Rq value) of the four MoS$\textsubscript{2}$TFs samples was between 0.5 and 2.7 nm (third column in Figure 2). From these AFM results, it can be conclusively stated that the MoS$\textsubscript{2}$TFs prepared by this three-step method are layer-controlled, have excellent homogeneity, and have very smooth surfaces.

Confocal Raman spectroscopy was used to further characterize the quality and uniformity of synthesized MoS$\textsubscript{2}$TFs with various thicknesses. Figure 3 shows the Raman spectra of the 25 nm MoS$\textsubscript{2}$TFs on sapphire substrates synthesized under different reaction temperatures of 500 °C, 700 °C, and 900 °C, respectively. Figure 3a shows the two main characteristic Raman peaks of MoS$\textsubscript{2}$ for all of the MoS$\textsubscript{2}$TFs samples, namely the in-plane E$_{2g}$ peak at ≈384 cm$^{-1}$ and the out-of-plane A$_{1g}$ peak at ≈409 cm$^{-1}$. In addition, a small LA(M) sub-peak at ≈227 cm$^{-1}$ related to the defects in MoS$\textsubscript{2}$ can also be observed, which is attributed to the longitudinal phonons at the M point in the Brillouin zone [20–22]. The peak at 418 cm$^{-1}$ comes from the sapphire substrate (A$_{1g}$ mode) [23]. Furthermore, the intensity ratio of the LA(M) sub-peak to the A$_{1g}$ peak can be considered to be a marker for evaluating the quality of MoS$\textsubscript{2}$TFs. In general, the good quality MoS$\textsubscript{2}$ samples with lower disorder can be determined by lower LA(M)/A$_{1g}$ values [24,25]. In order to elucidate our point, we plotted the LA(M) to A$_{1g}$ peak intensity ratio of the MoS$\textsubscript{2}$TFs samples as a function of the reaction temperature, as shown in Figure 3b. The result shows that when the reaction temperature increases (from T = 500 to 700 °C), the LA(M)/A$_{1g}$ intensity ratio...
shows a downward trend (from 0.15 down to 0.1). No clear LA(M) peak was identified as the reaction temperature approaches 900 °C (Figure 3a). To the best of our knowledge, in comparison to previous studies [24,25], the LA(M) to A1g peak intensity ratios reported in this study are the lowest values to date. These data clearly indicate that the MoS2TFs samples grown by the high-temperature process described herein have better film quality.

**Figure 2.** The AFM images (first column), height profiles (second column), and surface roughness (third column) of MoS2TFs on a sapphire substrate with different thickness: (a) 7 nm, (b) 17 nm, (c) 25 nm, and (d) 50 nm, respectively. The thickness of MoS2TFs was measured along the marked red lines.

**Figure 3.** (a) Raman spectra of the 25 nm MoS2TFs on sapphire substrates as a function of the reaction temperature using 532 nm laser for sample excitation. The inset figure shows the Raman peak position of the LA(M) mode at 227 cm\(^{-1}\). (b) The LA(M) to A1g peak intensity ratio of MoS2TFs with different reaction temperatures. No clear LA(M) mode can be found in the Raman spectrum of the T = 900 °C MoS2TF sample (green color).
Figure 4a presents the typical Raman spectra of the prepared MoS$_2$TFs with thicknesses increasing from 7 to 50 nm. The Raman spectra of commercial monolayer MoS$_2$ on sapphire substrate and bulk MoS$_2$ crystal is also shown in Figure 4a, for ease of comparison. Raman spectra of the monolayer MoS$_2$ clearly showed the two characteristic peaks at 406.5 cm$^{-1}$ ($A_{1g}$ mode) and 386.1 cm$^{-1}$ ($E_{1g}$ mode). The separation between these two peaks ($A_{1g}$ and $E_{1g}$ modes) is 20.4 cm$^{-1}$. According to previous reports [20, 21], the frequency difference between the two main modes ($A_E$) could be used to identify the number of MoS$_2$ layers. When the number of MoS$_2$ layers increases, the $E_{1g}$ mode will display a red-shift, whereas the $A_{1g}$ mode undergoes a blue-shift [20, 21]. It is worth noting that the incremental shift becomes smaller and smaller as the number of layers increases. When the number of MoS$_2$ layers increases, the $E_{1g}$ mode will display a red-shift, whereas the $A_{1g}$ mode undergoes a blue-shift [20, 21]. It is worth noting that the incremental shift becomes smaller and smaller as the number of layers increases. When the number of MoS$_2$ layers is four or more, the frequencies of these two modes will approach the values for bulk MoS$_2$ [26]. In Figure 4a, we can clearly observe that when the MoS$_2$TF thickness increases from 7 nm up to 50 nm, there is no main peak shift phenomenon that is apparent in the Raman spectra of these MoS$_2$ samples, i.e., the two main Raman peaks ($A_{1g}$ and $E_{1g}$ modes) of these MoS$_2$TF samples were observed at ~410 cm$^{-1}$ and ~384 cm$^{-1}$, respectively. In addition, we also found that the two main Raman peak positions for all MoS$_2$TF samples are close to the Raman peaks of commercial bulk MoS$_2$ crystals, and there is a slight shift (MoS$_2$TFs have a blue shift (~1 cm$^{-1}$) compared to the bulk MoS$_2$), as shown in Figure 4b. It is worth noting that the few-Layer MoS$_2$ films (4 to 6 layers) synthesized by mechanical exfoliation didn’t present this slight shift phenomenon [26]. We assume it may be related to the fact that MoS$_2$TF is grown on sapphire substrates, instead of being directly peeled off from the bulk MoS$_2$. In addition, it has been reported that due to factors inherent to the substrate (such as, deformations and mismatch in the coefficient of thermal expansion), the single-layer and double-layer TMD materials will generate strain, which causes these two Raman modes to shift slightly [27, 28].

The detailed mechanism of the onset of shifts in the Raman peaks in multilayer MoS$_2$ or the ultra-thin films synthesized by us on sapphire substrates is still unclear, and further investigation is needed.

![Figure 4a](image1.png)

![Figure 4b](image2.png)

![Figure 4c](image3.png)

**Figure 4.** (a) Raman spectra of MoS$_2$TFs with thickness increasing from 7 to 50 nm. (b) Raman shift of $A_{1g}$ and $E_{1g}$ peak as a function of MoS$_2$TFs thickness. (c) The frequency difference between the $A_{1g}$ and $E_{1g}$ of the 16 different points on MoS$_2$TFs as a function of the thickness. The Raman spectra of sapphire substrate, commercial monolayer, and bulk MoS$_2$ have been used as reference.
In order to evaluate the uniformity of the MoS$_2$TFs prepared by our process, we measured the $\Delta k$ value at 16 different points on the MoS$_2$TFs with increasing thickness, as shown in Figure 4c. The results show that the measured $\Delta k$ values of all MoS$_2$TF samples are between 25.4 to 25.9, which are close to the values of bulk MoS$_2$ crystals. This result demonstrates the excellent uniformity of our custom-grown MoS$_2$TFs with various thicknesses. All Raman results also indicate that uniform thickness-controlled MoS$_2$TFs can have the advantage of large scalability of growth on sapphire substrate.

Evolution of the optical properties of the as-prepared MoS$_2$TFs was further investigated by measuring the optical absorbance spectra of MoS$_2$TFs as a function of thickness. Figure 5a shows the UV-Vis-NIR absorption spectra of 7, 17, 25, and 50 nm MoS$_2$TFs, respectively. All deposited films exhibit four prominent peaks characteristically indicating 2H-MoS$_2$ excitonic features in the visible wavelength region. More specifically, the A and B excitons that form at the K-point of the Brillouin zone appeared in the 600 to 700 nm wavelength region, while the C and D excitonic peaks were located in the wavelength range from 400 to 450 nm. The absorption spectrum of the sapphire substrate has been shown in Figure 5a. Looking at Figure 5b we found that with increasing thickness of MoS$_2$TFs from 7 to 25 nm, the absorbance at peak of A exciton increased rapidly from 0.25 to 0.6. However, when the film thickness increased to 50 nm, the MoS$_2$TFs showed a saturation trend of absorbance, similar to the absorbance spectrum of 25 nm film. The absorbance at peak of B exciton presents a trend similar to the A exciton. We also observed that the A exciton energy ($E_A$) of MoS$_2$TFs on sapphire samples will decrease as film thickness increase (from 1.851 eV to 1.834 eV), and it will converge when the thickness reaches 25 nm (about 40 layers), as shown in Figure 5c. It is worth noting that these results are not the same as previously reported in literature [29]. In a previous study, the A exciton position of the micromechanically-exfoliated nanosheets was seen to decrease from 1.89 to 1.83 eV as the thickness increases from 1 to 6 layers. When the number of layers reaches 5 or 6, the downward trend of A exciton position begins to converge. In addition, in the case of liquid-phase exfoliated nanosheet samples, when the number of layers reaches 10 layers, the exciton peak position will begin to converge. We think this may be related to the difference between the dielectric constant of the CVD-grown MoS$_2$TFs samples and the exfoliated samples. Since the interlayer electronic hybridization and dielectric shielding effect was changed as a function of the number of MoS$_2$ layers, the resulting properties of A excitons also changed comparably. However, the detailed mechanism of the position shift pertaining to the energy of the A exciton of MoS$_2$TFs on sapphire substrates is still unclear. Therefore, we suggest that the dielectric constant of MoS$_2$TFs grown on a sapphire substrate should be measured directly using spectroscopic ellipsometry combined with quantum electrostatic heterostructure (QEH) model calculation [29]. This approach can help to elucidate the layer-related exciton effect of MoS$_2$TFs more quantitatively.

![Figure 5](image_url)

**Figure 5.** (a) UV-Vis-NIR absorption spectra of the MoS$_2$TFs on sapphire as a function of absorbance with thickness. (b) Absorbance at the peak position of A and B excitons of the MoS2 TFs as a function of thickness. (c) Plot of A exciton energy ($E_A$) from absorbance as a function of MoS$_2$TFs thickness.

The optical band gap of a photocatalyst can be calculated by the following formula: 

\[(\alpha h\nu)^{1/n} = A(h\nu - E_g)\]  

[30,31] In this equation, ‘$\alpha$’ is the absorption coefficient, ‘$h$’ is Planck’s
constant, ‘υ’ is the photon frequency, ‘A’ is a constant, and ‘Eg’ is the band-gap energy. The ‘n’ is the exponent term, which denotes the nature of the electronic transition. When n = 1/2, it signifies a direct allowed transition, and when n = 2, it represents an indirect allowed transition. According to previous reports [32], monolayer MoS₂ is a direct energy band-gap semiconductor, and an increase in the number of layers (including multi-layer, film, and bulk crystal) causes a shift of behavior to an indirect band-gap semiconductor. Not only that, the Eg value of MoS₂ will change from 1.9 eV for a monolayer to 1.2 eV for bulk crystal. Tauc plots as a function of photon energy for MoS₂ TFs can be used to determine the Eg value by extrapolating the straight-line portion of the indirect electronic transitions, as shown in Figure 6. Here, we used the indirect transition value (n = 2) to calculate the Eg value of all MoS₂ TF samples (Figure 6a–d). The results show that when the film thickness is increased from 7 to 50 nm, the Eg value of MoS₂ TFs will decrease from 1.71 to 1.60 eV (Figure 6e). The Eg values of monolayer and bulk crystal also shown in Figure 6e for reference purposes.

![Figure 6. Tauc plots for the estimation of the band gap of MoS₂ TFs on sapphire with thickness increasing from (a) 7 nm, (b) 17 nm, (c) 25 nm, to (d) 50 nm, respectively. (e) The band gap of MoS₂ TFs as a function of thickness.](image-url)

Photoluminescence (PL) is another optical spectroscopic technique used to measure the band gap of semiconductors. Monolayer MoS₂ is a direct bandgap semiconductor that exhibits significant PL intensity and prominent excitonic features (A and B exciton peaks) in PL spectra [33]. Multi-layer MoS₂ is an indirect band gap semiconductor, and its PL intensity will decrease rapidly as the number of layers increases. In bulk crystal MoS₂, the PL intensity is relatively weak; so much so, that in some cases no PL excitation at all is observable. Figure 7 shows the PL spectra of MoS₂ TFs on sapphire with various thicknesses. Not only that, the Eg value of MoS₂ TFs do not exhibit strong PL intensity. When the thickness of MoS₂ TFs is increased from 7 to 50 nm, the PL intensity will decrease dramatically (Figure 7a). No clear A exciton peak was identified in the PL spectra of 25 nm and 50 nm MoS₂ TFs. The prominent MoS₂ Raman modes were observed at around 550 nm wavelength region for all MoS₂ TFs samples. Not only that, the broad PL spectra profile and non-obvious excitonic features (A and B exciton peak) of the MoS₂ TFs are similar to bulk crystal MoS₂ (Figure 7b). The PL signal of the sapphire substrate is still visible and overlap with A exciton peak of MoS₂ occurs at a wavelength of around 690 nm (Figure 7a,c). Therefore, it is difficult to determine the position of the A exciton peak and bandgap for all MoS₂ TFs samples. The PL spectra of our as-prepared MoS₂ TFs
exhibited similar excitation phenomena as chemically exfoliated MoS\textsubscript{2} layers. In the case of chemically exfoliated MoS\textsubscript{2} layers [33], when the thickness of the MoS\textsubscript{2} layer is greater than 7 nm, no clear A exciton peak can be observed in the PL spectrum.

![Figure 7. Photoluminescence spectra of (a) MoS\textsubscript{2} thin films grown on a sapphire substrate with different thicknesses, (b) sapphire, and (c) bulk MoS\textsubscript{2} crystal.](image)

X-ray diffraction (XRD) was used to study the structural properties and crystalline parameters of the as-prepared MoS\textsubscript{2} TFs. From the XRD patterns shown in Figure 8, it can be observed that all MoS\textsubscript{2} TF samples are unequivocally identified as 2H MoS\textsubscript{2} with a strong characteristic peak appearing at 2\(\theta\) = 14.3\(^{\circ}\), which was assigned to the MoS\textsubscript{2} (002) lattice plane [34]. However, the peak denoting the (004) lattice plane of MoS\textsubscript{2} at 2\(\theta\) = 29\(^{\circ}\) cannot be observed in our MoS\textsubscript{2} TF samples. Furthermore, we used the Scherrer Equation to analyse the grain size of the MoS\textsubscript{2} TFs, as listed in Table 1. According to the Scherrer formula, D = \(\frac{K\lambda}{\beta \cos \theta}\) [35], where ‘D’ is the average grain size in vertical direction of crystal structure, ‘K’ is the shape factor having a typical value of about 0.9, ‘\(\lambda\)’ is the wavelength of the X-ray source, ‘\(\beta\)’ is the full width at half maximum intensity of the peak (in Rad), and ‘\(\theta\)’ is the Bragg angle. As seen in Figure 8b, we found that as the thickness of MoS\textsubscript{2} TFs increased from 7 to 25 nm, the grain size of the MoS\textsubscript{2} TFs increased from 5.6 to 21 nm. However, when the film thickness increased to 50 nm, the grain size of MoS\textsubscript{2} TFs was constrained to around 25 nm. This data indicates that all the MoS\textsubscript{2} TF samples have good crystallinity, and the grain size is almost identical to the measured film thickness, except in the case of the 50 nm sample.

Table 1. The calculated grain size of MoS\textsubscript{2} TFs on sapphire from the (002) peak using Scherrer’s formula.

| Thickness (nm) | \(\beta\)/Degree | 2\(\theta\)/Degree | D/nm |
|---------------|------------------|-------------------|------|
| 7             | 1.43             | 14.29             | 5.60 |
| 17            | 0.64             | 14.47             | 12.51|
| 25            | 0.38             | 14.50             | 21.07|
| 50            | 0.32             | 14.47             | 25.02|
Figure 8. (a) XRD pattern of the MoS$_2$TFs on sapphire with different thicknesses. (b) The grain size of MoS$_2$TFs as a function of thickness.

2.3. Photocatalytic Performance

The evaluation of the PC-CO$_2$RR performance of the MoS$_2$TFs with various thicknesses was performed in a visible light-driven gas-phase photoreaction vessel for 24 h, as shown in Figure 9. Briefly, the MoS$_2$TFs with an area of 2 cm$^2$ were placed at the center of the photoreactor. Then, N$_2$ gas and moist CO$_2$ gas were sequentially passed through the photoreactor for 30 min and 1 h, respectively. A 100 W Xe solar simulator with an AM1.5 filter was used as the light source to study the photoconversion of CO$_2$ and water vapor over a time period of 24 h. The schematic representation of our gas-phase and batch-type PC-CO$_2$RR system is shown in Figure 9a. In order to avoid the overestimation of the catalytic activity of our samples due to carbon contamination on the surface of the reactor, we carried out two blank tests as the background for all MoS$_2$TF samples (Supporting Figure S1 in Supplementary Material). This background value will be subtracted from the spectral data of the final gas products produced by the MoS$_2$TF catalysts after 24 h of photocatalysis. Figure 9b,c show the product yields of the MoS$_2$TFs with different reaction temperatures and different thicknesses. All the MoS$_2$TFs samples are capable of catalyzing the reduction of CO$_2$ into methane (CH$_4$), ethylene (C$_2$H$_4$), acetaldehyde (CH$_3$CHO), and acetone (C$_3$H$_6$O). Methane and acetaldehyde were identified as the first and second major products, respectively. In addition, small amounts of ethane and acetone were also detected. The corresponding gas production yield and quantum efficiencies (QE) of all MoS$_2$TF samples are summarized in Tables 2 and 3, respectively.
Table 2. Production yields and QEs of MoS\(_2\) TFs synthesized at various reaction temperatures.

| MoS\(_2\) TFs | Apparent Production Yield (nmol/cm\(^2\)) | QE (%) |
|---------------|-------------------------------------------|--------|
|               | CH\(_4\) | C\(_2\)H\(_4\) | CH\(_3\)CHO | C\(_3\)H\(_6\)O | Total | MoS\(_2\) TFs | Total (%) |
| Blank test    | 0.14    | 0.07       | 0.78       | 0.48         | 1.47   | Blank test | none  |
| T = 500 °C    | 0.83    | 0.22       | 0.96       | 0.08         | 2.09   | T = 500 °C | 0.000029 |
| T = 700 °C    | 0.86    | 0.39       | 1.77       | 0.14         | 3.16   | T = 700 °C | 0.000045 |
| T = 900 °C    | 1.38    | 0.86       | 2.35       | 0.20         | 4.79   | T = 900 °C | 0.000068 |

Note: The gas products from the blank test have been subtracted from all gas product values pertaining to the samples.

Table 3. Production yields and QEs of MoS\(_2\) TFs with various thicknesses.

| MoS\(_2\) TFs | Apparent Production Yield (nmol/cm\(^2\)) | QE (%) |
|---------------|-------------------------------------------|--------|
|               | CH\(_4\) | C\(_2\)H\(_4\) | CH\(_3\)CHO | C\(_3\)H\(_6\)O | Total | MoS\(_2\) TFs | Total (%) |
| Blank test    | 0.14    | 0.07       | 0.78       | 0.48         | 1.47   | Blank test | none  |
| t = 7 nm      | 0.95    | 0.34       | 0.69       | 0.15         | 2.13   | t = 7 nm  | 0.000030 |
| t = 17 nm     | 0.94    | 0.47       | 1.41       | 0.25         | 3.07   | t = 17 nm | 0.000044 |
| t = 25 nm     | 1.38    | 0.86       | 2.34       | 0.21         | 4.79   | t = 25 nm | 0.000068 |
| t = 50 nm     | 1.10    | 0.75       | 2.16       | 0.15         | 4.16   | t = 50 nm | 0.000059 |

Note: The gas products from the blank test have been subtracted from all gas product values pertaining to the samples.

The QE of the MoS\(_2\) TFs was determined as the ratio of the effective electrons used for gas production, such as the CH\(_4\) molecule, to the total input photon flux, and it was calculated by the following equation \([36,37]\):

\[
\text{QE}\% = \frac{\text{Effective electrons}}{\text{Total photons}} \times 100\% = \frac{8 \times Y \times N}{\Theta \times T \times S} \times 100\% (1)
\]

where ‘Y’ is the product yield of CH\(_4\) (mol), ‘N’ is Avogadro’s number (6.022 \(\times 10^{23}\) mol\(^{-1}\)), ‘\(\Theta\)’ is the photon flux (2.46 \(\times 10^{17}\) cm\(^{-2}\) s\(^{-1}\)), ‘T’ is the reaction time (s), and ‘S’ is the area of illumination (cm\(^2\)). The area under illumination (S) of the MoS\(_2\) TF samples is 2 cm\(^2\). For example, the QE\% of CH\(_4\) for 25 nm MoS\(_2\) TFs after 24 h of PC-CO\(_2\)RR can be calculated as

\[
\text{QE} = \frac{8 \times 1.38 \times 10^{-9} \times 6.022 \times 10^{23}}{2.46 \times 10^{17} \times 24 \times 3600 \times 2} \times 100\% = 0.000016\%.
\]

Based on the same calculation method, the QE\%s of C\(_2\)H\(_4\), CH\(_3\)CHO, and C\(_3\)H\(_6\)O for the 25 nm MoS\(_2\) TFs were calculated to be 0.000015%, 0.000033%, and 0.0000047%, respectively.

The total QE of all gas products for MoS\(_2\) TFs is 0.000068%, and it is calculated by the following equation:

\[
\text{Total QE}\% = \text{QE}\%\ of\ CH_4 + \text{QE}\%\ of\ C_2H_4 + \text{QE}\%\ of\ CH_3CHO + \text{QE}\%\ of\ C_3H_6O. (2)}
\]

Figure 9b shows that the 25 nm MoS\(_2\) TFs prepared at a reaction temperature of 900 °C can convert the highest amount of CO\(_2\) into the four gas products (total amount of gas products is 4.79 nmol/cm\(^2\)), which is followed by the samples produced at a reaction temperature of 700 °C (3.16 nmol/cm\(^2\)), and these in turn are followed by the MoS\(_2\) TF samples synthesized at a reaction temperature of 500 °C (2.09 nmol/cm\(^2\)). The resulting total QEs for the MoS\(_2\) TF samples produced at reaction temperatures of 500, 700, and 900 °C were 0.000029%, 0.000045%, and 0.000068%, respectively. In Figure 9c, we observe that as the thickness of MoS\(_2\) TFs increased from 7 to 25 nm, the gas production yield and total QE exhibited a gradually increasing trend (2.13 to 4.79 nmol/cm\(^2\) and 0.000030 to 0.000068%). However, when the film thickness increased to 50 nm, the gas production yield and QE showed a downward trend (4.16 nmol/cm\(^2\) and 0.000059%). These results indicate that the 25 nm MoS\(_2\) TFs exhibited the highest photocatalytic activity.

2.4. Photocatalytic Mechanism

From the above-mentioned CO\(_2\) reduction activities of different MoS\(_2\) TF photocatalysts, we can conclude that the crystallinity and thickness of MoS\(_2\) TFs play an important role in determining their photocatalytic activity.
role in the PC-CO$_2$RR processes. We will try to understand the underlying photocatalytic mechanism from the following aspects, as illustrated in Figure 10.

Figure 10. Schematic illustration of the proposed mechanism of ultra-thin film MoS$_2$ photocatalysts for visible light-driven CO$_2$ reduction.

2.4.1. Size Effect

In case 1 as illustrated in Figure 10, the typical process of PC-CO$_2$RR on a semiconductor-based photocatalyst has been schematically depicted. Briefly, the PC-CO$_2$RR process consists of five consecutive steps: light absorption, charge separation, CO$_2$ adsorption, surface redox reaction, and product desorption [38,39]. These five steps can be further divided into two theoretical categories, that is, photophysics (the first two steps) and photochemistry (the next three steps). For the purpose of understanding the performance of the catalysts we have synthesized, we will mainly focus on understanding the relationship between photophysics and the activity of our photocatalysts. The first step shows that it is necessary to analyze the ability of photocatalysts to absorb photons and consequently generate electron–hole pairs, which is acutely affected by factors such as the energy band gap (E$_g$) and thickness of the photocatalyst. The second step hinges on the ability of photocatalysts to effectively separate the photogenerated electrons and holes, which is directly related to charge recombination phenomena. The crystallinity and surface properties of photocatalysts all tangibly affect charge recombination. Therefore, in order to improve the overall photocatalytic efficiency, it is necessary to increase the optical absorption of the incoming visible light radiation, to generate electron–hole pairs with vigor, efficiently separate the photo-generated charge carriers, and suppress their recombination, as shown in Figure 10.

It is worth noting that the utilization of the so-called “nanosizing strategy” has proven to be very beneficial toward improving the performance of visible light-driven photocatalysts [10,40]. For instance, Ta$_3$N$_5$ nanoparticles with a particle size of 30–50 nm exhibited higher photocatalytic activity for H$_2$ evolution, as compared to traditional bulk Ta$_3$N$_5$ particles (300–500 nm) [40]. A photocatalyst with a smaller particle size has the advantage of a higher surface area, which also increases the density of surface catalytic sites. However, it usually results in lower crystallinity and may reduce catalytic activity. Moreover, in particle type photocatalysts with a three-dimensional geometry, calculative complications are caused by particle size reduction, such as crystal facet and morphology change. This makes it a challenging task to lucidly explain the actual catalytic mechanism. Therefore, we propose the utilization of thin-film type photocatalysts with a two-dimensional geometry to isolate the “thickness effect” and avoid the above problems for the study of specific catalytic mechanisms study.
2.4.2. Effect of Optical Absorption

According to past reports [32,41], by controlling the number of layers of MoS2, not only can the bandgap be fine-tuned, but the light absorption performance can also be optimized. In a previous study, Atwater’s group reported that the sub-15 nm thick TMD flakes created by mechanical exfoliation, have near-unity optical absorption [41]. Their calculated and measured absorption spectra showed that the ultra-thin (14–17 nm) MoS2 flakes on an Ag back reflector have the highest broadband absorption. According to our experimental data, the energy bandgap of MoS2TF samples with different thicknesses is about 1.7 to 1.6 eV and there is not too much variation in these values (Figure 6e). However, there are obvious differences in the optical absorption of MoS2TF samples with different thicknesses (Figure 5b). The ultra-thin MoS2TFs on sapphire with a thickness of 25 nm exhibited the highest optical absorption. This result is similar to the optical absorption capacity of MoS2 flakes reported in literature. Therefore, we believe that the sufficient optical absorption of visible light radiation by films having an optimized thickness of 25 nm (sample (case II)), which exhibits better photocatalytic activity than 7 or 17 nm MoS2TFs samples (case III), as shown in Figure 10.

2.4.3. Effect of Grain Size

According to our experimental data, the grain size of MoS2TFs samples with different thicknesses is about 7 to 25 nm. In addition, a point to be noted is that the 25 nm MoS2TF sample has almost the same thickness as the grain size. The 50 nm MoS2TF sample has grain boundaries because the grain size is only 25 nm. Therefore, we propose a possible reason to explain why the 25 nm MoS2TFs sample (case II) has better photocatalytic activity than 50 nm MoS2TFs samples (case IV), as shown in Figure 10. It is well known that the grain boundary of semiconductors is the primary site of charge recombination, and changes therein significantly affect the charge transport [42,43]. Based on this knowledge, we think it is reasonable that the grain size of ultra-thin MoS2TFs samples is similar to film thickness (case II: D is similar to t), which can promote the internal photogenerated carriers to migrate to the surface and efficiently drive the catalytic reaction (case II). On the contrary, the grain size of thick MoS2TFs samples is smaller than the film thickness (case IV: D is smaller than t), resulting in the formation of grain boundaries inside the film and the subsequent suppression of the probability of photogenerated carrier transfer to the surface. We studied two additional thick MoS2TFs samples and measured their grain size and catalytic activity to support this scientific point (Supporting Figures S2 and S3 and Supporting Table S1). The results clearly indicate that when the thickness is continuously increased (from 40 to 60 nm) without increasing the grain size (maintained at around 20 nm), the photocatalytic activity does not increase dramatically. In our current TFs process, the biggest grain size of MoS2TFs with a thickness of 7 to 60 nm is about 20 nm, and the 25 nm MoS2TFs sample has the best photocatalytic activity of about 4.79 nmol/cm². Therefore, we believe that in addition to light absorption, the grain boundary inside the photocatalyst is another important factor that significantly affects the catalytic activity.

2.4.4. Stability Test

In order to test the stability of our MoS2TFs, this model catalyst was reused in a fresh reactor for three successive cycles. According to Supporting Figure S4, the total gas production yield slightly decreases over time, and the reduced ratio was calculated to be about 10% after three cycles. The slight decrease in the activity after the three cycles might be due to the inactivation or poisoning of the catalytic sites on the basal plane MoS2TFs. In addition, we also found a slight change in the production ratio of methane and acetaldehyde (methane production is increased and acetaldehyde formation is decreased). The results indicated that when reducing the catalytic sites on the MoS2TFs surface, the catalytic activity and the reaction pathway of the product will be consequently altered. The detailed reaction mechanism is still unclear, and further investigation is needed.
In addition to optical absorption and the grain size of the MoS\(_2\) TFs, other related phenomena worth studying further include measuring the photocarrier recombination losses, surface reaction investigations, product analysis, and isotopic labeling. For recombination, it is worth noting that traditionally, time-resolved absorption and PL spectroscopies can successfully study the dynamic behavior of photocarriers in photocatalysis [44,45]. However, when the thickness increases, neither our as-prepared MoS\(_2\) film nor the MoS\(_2\) flake [29] have any obvious PL emission. Therefore, this tool cannot be used to understand the behavior of carrier recombination in the case of our MoS\(_2\) TFs. Other alternative tools need to be selected and developed, such as advanced space-resolved techniques [46]. For surface reactions, the relationship between the surface of TMD catalysts and the surface reaction pathways has still not been clearly understood. It is necessary to use in situ catalytic tools to study the surface reactions on the catalyst surface, such as ambient pressure X-ray photoelectron spectroscopy for CO\(_2\) adsorption [47] and infrared absorption spectroscopy for surface species [48]. For product analysis, the accurate measurement of gas products relies heavily on the sensitivity and number of gas analysis detectors (such as gas chromatography-thermal conductivity detector (GC-TCD) and chromatography-flame ionization detector (GC-FID)) [49]. In most cases, only one gas detector is used, which often leads to inaccuracies in the overall gaseous product evaluation. For instance, H\(_2\) could also be one of the products of CO\(_2\) reduction, and its detection requires GC-TCD. Not only that, the H\(_2\) production rate should also be factored into the quantum efficiency calculations. The complete analysis of the products of CO\(_2\) reduction with the appropriate equipment is one of the directions that certainly must not be overlooked. While isotopic labeling technology may be a slightly more expensive alternative to confirm the accuracy of the products and product-specific active sites [50], it is certainly a project well worth being further investigated.

3. Materials and Methods

3.1. Sample Preparation

Uniform MoS\(_2\) TFs on (0001) sapphire substrate with different thicknesses were prepared by two-step post-sulfurization of vacuum-deposited molybdenum trioxide (MoO\(_3\)) films. Initially, a c-face sapphire substrate was cleaned with ethanol, acetone, and DI water for 5 min, respectively. Then, the clear substrates were subjected to O\(_2\) plasma treatment for 10 min prior to the deposition of the MoO\(_3\) film. The precursor MoO\(_3\) powder was supplied by Alfa Aesar with 99.95% purity, which was deposited on the top of sapphire substrate as a thin film, using thermal evaporation. In this process, the desired thickness of the film to be deposited can be closely monitored using a quartz crystal microbalance (QCM) by measuring the change in frequency of a quartz crystal resonator. The deposition rate was maintained in the range of 0.1 to 0.2 kÅs\(^{-1}\). Thereafter, all samples were placed into a chemical vapor deposition (CVD) system to perform the post-sulfurization process. Before introducing H\(_2\)S gas into the system, the MoO\(_3\) films were annealed at 500 °C for 1 h under vacuum in an Ar-H\(_2\) environment (4:1), with the aim of reducing them into MoO\(_2\). Finally, the CVD growth process was performed at atmospheric pressure with 100 sccm of Ar and an H\(_2\)-H\(_2\)S mixture (flow rate 1:4). The post-sulfurization process was performed at 1000 °C at the rate of 30 °C min\(^{-1}\), and this condition was maintained for 30 mins to ensure successful sulfurization of the MoS\(_2\) TFs.

3.2. Characterization

The as-grown MoS\(_2\) TFs on sapphire substrates were systematically characterized by the following microscopy and spectroscopy-based tools. Firstly, the thickness and surface roughness of MoS\(_2\) TFs was examined using the tapping mode of atomic force microscopy (AFM) with a scanning rate of 0.5 Hz and 10 \(\mu\)m scanning area using a Bruker Dimension Icon Atomic Force Microscope. The Raman and photoluminescence (PL) spectra were recorded on a Jobin-Yvon LabRAM H800 system with a 532 nm Nd:YAG laser as the excitation source and a spot size of \(\approx 1 \mu\)m. In addition, the optical absorbance of
the MoS$_2$TFs was measured by a UV-Vis-NIR spectrophotometer (JASCO V-670). The optical band gap of the MoS$_2$TFs was determined using Tauc plots. After that, the crystal structure and grain size of the MoS$_2$TFs was determined using a Bruker D2 PHASER X-ray diffractometer.

3.3. Photocatalytic Activity Measurement

The gaseous product species generated by all the MoS$_2$TF photocatalysts after the PC-CO$_2$RR process were analyzed by gas chromatography (GC), on an Agilent 6890 system using a glass PLOT column (RT-Q-BOND), and a flame ionization detector (FID).

4. Conclusions

In summary, the lab-grown MoS$_2$TFs on sapphire with thickness from 7 to 50 nm were used as a model catalyst and the photocatalytic CO$_2$ reduction activities of thickness dependent MoS$_2$TFs were systematically investigated. The MoS$_2$TFs with 25 nm thickness exhibited the highest photocatalytic activities under visible light irradiation, corresponding to a gas production yield of 4.79 nmol/cm$^2$ with a QE of 0.000068%. It is demonstrated that 25 nm MoS$_2$TFs have the best ratio of light absorption and grain size, as compared to films of other thicknesses. We also proposed a systematic photocatalytic mechanism to relate the dependence of the thickness of TMD based photocatalysts, on their eventual catalytic mechanism. This study provides a novel outlook towards the development of high-efficiency two-dimensional material catalysts for the efficient reduction of CO$_2$ into other useful chemical species.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/catal11111295/s1, Figure S1: The total gas products of two kinds of blank test conditions for photocatalysis: 1.47 nmol/cm$^2$ for blank test-1 and 0.27 nmol/cm$^2$ for blank test-2, respectively, Figure S2: XRD pattern of the MoS$_2$TFs on sapphire with different thicknesses: (a) $t = 40$ nm and (b) $t = 60$ nm, Table S1: The calculated grain size of MoS$_2$TFs on sapphire from (002) peak using Scherrer’s formula, Figure S3: The PC-CO$_2$RR activity of MoS$_2$TFs on sapphire with thickness increasing from 40 to 60 nm, Figure S4: The stability study of the photocatalytic CO$_2$ reduction over the MoS$_2$TFs with 25 nm thickness.

Author Contributions: Y.-F.H. conceived and designed the experiments. K.-W.L. and F.R.Z.F. carried out the thin-film deposition and material characterizations. K.-W.L., F.R.Z.F., Y.-F.H., S.-H.T., S.-W.K. and C.-H.W. performed the GC experimental setup, calibration, photocatalytic activity, and data analysis. Y.-F.H., V.A.M. and K.-H.C. co-wrote the manuscript. K.-H.C. and L.-C.C. supervised the project. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by the Ministry of Science and Technology, Taiwan (Grant Numbers: 108-2119-M-002-030, 109-2123-M-002-004, 110-2123-M-002-006, and 108-2112-M-001-046-MY2) and by Academia Sinica (Grant Number AS-iMATE-110-34). Y.-F.H. acknowledges support from IAMS Junior Fellowship by Institute of Atomic and Molecular Sciences, Academia Sinica, Taiwan.

Conflicts of Interest: The authors declare no conflict of interest.

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