A Novel Carbon-Assisted Chemical Vapor Deposition Growth of Large-Area Uniform Monolayer MoS$_2$ and WS$_2$

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Abstract: Monolayer MoS$_2$ can be used for various applications such as flexible optoelectronics and electronics due to its exceptional optical and electronic properties. For these applications, large-area synthesis of high-quality monolayer MoS$_2$ is highly desirable. However, the conventional chemical vapor deposition (CVD) method using MoO$_3$ and S powder has shown limitations in synthesizing high-quality monolayer MoS$_2$ over a large area on a substrate. In this study, we present a novel carbon cloth-assisted CVD method for large-area uniform synthesis of high-quality monolayer MoS$_2$. While the conventional CVD method produces thick MoS$_2$ films in the center of the substrate and forms MoS$_2$ monolayers at the edge of the thick MoS$_2$ films, our carbon cloth-assisted CVD method uniformly grows high-quality monolayer MoS$_2$ in the center of the substrate. The as-synthesized monolayer MoS$_2$ was characterized in detail by Raman/phololuminescence spectroscopy, atomic force microscopy, and transmission electron microscopy. We reveal the growth process of monolayer MoS$_2$ initiated from MoS$_2$ seeds by synthesizing monolayer MoS$_2$ with varying reaction times. In addition, we show that the CVD method employing carbon powder also produces uniform monolayer MoS$_2$ without forming thick MoS$_2$ films in the center of the substrate. This confirms that the large-area growth of monolayer MoS$_2$ using the carbon cloth-assisted CVD method is mainly due to reducing properties of the carbon material, rather than the effect of covering the carbon cloth. Furthermore, we demonstrate that our carbon cloth-assisted CVD method is generally applicable to large-area uniform synthesis of other monolayer transition metal dichalcogenides, including monolayer WS$_2$.

Keywords: carbon-assisted CVD; growth mechanism; monolayer; MoS$_2$; WS$_2$

1. Introduction

Two-dimensional (2D) materials have attracted much attention due to their novel physical and chemical properties [1–5]. Graphene, the most studied 2D material, is thin, flexible, remarkably strong, and has exceptionally high electron mobility and thermal conductivity, allowing for a wide range of novel applications [1,2,6]. However, graphene has a zero bandgap, which results in very low on-off ratios in its applications of electronic devices such as transistors [4,5,7]. On the other hand, unlike graphene, transition metal dichalcogenides (TMDCs) have been extensively studied as new 2D layered materials because they have a sizable bandgap and interesting electronic and optical properties [3–5,7]. MoS$_2$, a family of TMDCs, has been used as a building block for 2D field-effect transistors due to its high carrier mobility and excellent on-off ratios [8–10]. In addition, due to its exceptional physicochemical properties, 2D MoS$_2$ has been extensively used for novel 2D electronics, flexible optoelectronics, and efficient catalysis [11–15]. When MoS$_2$ is thinned down to a monolayer, its electronic structure and physical symmetries are radically altered, resulting in new physical behavior such as indirect to direct bandgap transitions [16–18]. In addition, monolayer MoS$_2$ exhibits strong light–matter interactions due to its planar exciton confinement effect [16,19,20]. To increase the potential use of monolayer MoS$_2$ in
various applications, it is highly desirable to develop methods for preparing monolayer MoS$_2$ [8,10,11,15,21,22]. The most well-known mechanical exfoliation method is suitable for producing high-quality single crystalline MoS$_2$ flakes, but it cannot control the number of layers of the flakes and is unscaleable for mass production [23–26]. In contrast, the chemical vapor deposition (CVD) method can control the number of MoS$_2$ layers and enables wafer-scale synthesis [27–29]. However, the conventional CVD method using MoO$_3$ and S powder has a problem in that thick MoS$_2$ films are formed in the center of the substrate and only MoS$_2$ monolayers are generated at the edge of the thick MoS$_2$ films [30–34].

This problem is related to the growth mechanism of MoS$_2$ in the conventional CVD method. The growth of MoS$_2$ is mainly achieved by the reaction of S with suboxide MoO$_{3-x}$ species produced from MoO$_3$ powder [35–37]. MoO$_{3-x}$ is highly volatile and improves the reaction kinetics for the formation of monolayer MoS$_2$ [35,37]. Monolayer MoS$_2$ can be effectively formed when the degree of MoO$_{3-x}$ formation is sufficiently high, whereas thick MoS$_2$ films are generated when the degree of MoO$_{3-x}$ formation is low. Therefore, keeping the degree of MoO$_{3-x}$ formation high in the reaction process is a key condition for large-area uniform growth of high-quality monolayer MoS$_2$ without forming thick MoS$_2$ films. To achieve the large-area growth of monolayer MoS$_2$, various methods have been reported, including confined-space CVD, reverse-flow chemical vapor deposition (CVD), and metal organic CVD, etc. [38–44].

In this study, we report a novel carbon cloth-assisted CVD method that uniformly produces high-quality monolayer MoS$_2$ over a large area on a substrate without forming thick MoS$_2$ films. As-synthesized monolayer MoS$_2$ was characterized in detail by Raman/photoluminescence (PL) spectroscopy, atomic force microscopy (AFM), and transmission electron microscopy (TEM). We reveal the detailed growth process of monolayer MoS$_2$ initiated from MoS$_2$ seeds by conducting a series of experiments with varying reaction times. In addition, we show that the CVD method employing carbon powder instead of carbon cloth also enables large-area growth of monolayer MoS$_2$, confirming the large-area growth of monolayer MoS$_2$ by the carbon cloth-assisted CVD method is mainly due to reducing properties of the carbon material, rather than the effect of covering the carbon cloth. Furthermore, we confirm that the carbon cloth-assisted CVD method can be used for the synthesis of other monolayer TMDCs such as monolayer WS$_2$.

2. Materials and Methods

2.1. Conventional CVD Method for MoS$_2$ and WS$_2$ Synthesis

MoS$_2$ was synthesized by a CVD method using a two-zone horizontal hot-wall tube furnace equipped with a mass flow controller and a vacuum pump (Edwards Vacuum, west Sussex, United Kingdom). The synthetic scheme is illustrated in Figure 1a. In a 1-inch diameter quartz tube, S powder (0.1 g, Sigma–Aldrich, St. Louis, MO, USA, 99.999%) in an alumina boat was placed upstream, and MoO$_3$ powder (0.03 g, Sigma-Aldrich, 99.5%) in an alumina boat was put downstream. The growth promoter solution that was prepared by supersaturating NaCl in ethanol was dropped on a clean 300-nm SiO$_2$/Si substrate and maintained at 740 °C for 20 min. After the end of the reaction, the furnace lid was opened to cool the furnace rapidly to room temperature.
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Figure 1. Conventional chemical vapor deposition (CVD) growth of MoS$_2$. (a) Schematic illustration of the experimental setup for the conventional CVD growth of MoS$_2$. (b) Optical image of the MoS$_2$ synthesized on an SiO$_2$/Si substrate using the conventional CVD method. (c) Magnified optical image of the region A in (b). (d) Magnified optical image of the region B in (b). (e) Magnified optical image of the dotted red rectangle in (d). (f) Magnified image of the dotted blue rectangle in (d). (g) Atomic force microscopy (AFM) height image of monolayer MoS$_2$ synthesized using the conventional CVD method. (h) Height line profiles along the dotted red line in (g). (i) Raman and (j) photoluminescence (PL) spectra of monolayer MoS$_2$. (k,l) Raman maps of the E$_{2g}$ mode and A$_{1g}$ mode of MoS$_2$, respectively. (m) PL map of monolayer MoS$_2$.

For the synthesis of monolayer WS$_2$, S powder (0.3 g, Sigma–Aldrich, 99.999%) and WO$_3$ powder (0.05 g, Sigma–Aldrich, 99.9%) were used as precursors. The c-cut sapphire substrate was placed face down on an alumina boat containing WO$_3$ powder. After the quartz tube was evacuated to 5-mTorr or less, Ar and H$_2$ gases flowed at a rate of 140 sccm and 20 sccm, respectively, and the chamber pressure was maintained at $\approx$ 1.6 Torr. The WO$_3$ powder was heated to 950 °C for 30 min at a rate of $\approx$30.8 °C/min and kept at 950 °C for 20 min. The S powder was heated to 210 °C for 32 min at a rate of $\approx$5.8 °C min$^{-1}$ and maintained at 210 °C for 18 min.

2.2. Carbon Cloth-Assisted CVD Method for Monolayer MoS$_2$ and WS$_2$ Synthesis

The synthesis conditions of the carbon cloth-assisted CVD method are the same as those of the conventional CVD method described above, except that carbon cloth is placed on top of MoO$_3$ and WO$_3$ powder in an alumina boat for the synthesis of monolayer MoS$_2$ and WS$_2$, respectively.

2.3. Carbon Powder-Assisted CVD Method for Monolayer MoS$_2$ Synthesis

The synthesis conditions of the carbon powder-assisted CVD method are the same as those of the conventional CVD synthesis method described above, except that activated carbon powder is mixed with MoO$_3$ powder. The mixing ratios of MoO$_3$ powder to activated carbon powder used in each experiment were 1:1, 1:2, 1:3, 1:4, 1:5, and 1:10, respectively.
2.4. Characterization

Raman spectra and maps were obtained using a 532-nm laser with 100 µW focused through a 100× objective at room temperature. Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDS) data were taken at 5 kV using a JSM-7900F (JEOL) microscope operating from 1 to 15 kV (JEOL Ltd., Tokyo, Japan). AFM measurement was performed in noncontact mode on an Anton–Paar Tosca 400 AFM instrument (Anton Paar, Sumida, Austria). TEM measurements were performed using a JEM-2100F microscope (JEOL Ltd., Tokyo, Japan).

3. Results and Discussion

3.1. Thick MoS$_2$ Films and Monolayer MoS$_2$ Synthesized Using the Conventional CVD Method

Figure 1a shows a schematic illustration of the experimental setup for the conventional CVD method in which solid powders (MoO$_3$ and S powder) are used as precursors for MoS$_2$ synthesis. Figure 1b shows an optical image of MoS$_2$ synthesized on a 300-nm SiO$_2$/Si substrate using the conventional CVD method. Figure 1c is a magnified optical image of region A in Figure 1b, showing the MoS$_2$ grown in the form of a thick film in the center of the substrate. Figure 1d is a magnified optical image of region B in Figure 1b, showing the edge region of the thick MoS$_2$ films. Figure 1e,f show magnified optical images of the dotted red rectangle and dotted blue rectangle in Figure 1d, respectively, confirming the partial formation of monolayer MoS$_2$ at the edge of the thick MoS$_2$ film. Additional data on the optical characterization of the MoS$_2$ grown using the conventional CVD method are shown in Supplementary Materials Figure S1. The growth of such thick MoS$_2$ films and partial formation of monolayer MoS$_2$ have been commonly observed in MoS$_2$ growth by the conventional CVD method using MoO$_3$ and S powder as precursors [30–34]. An AFM height image of monolayer MoS$_2$ shows small particles grown nonuniformly on the surface of monolayer MoS$_2$ (Figure 1g). The line profile obtained along the dotted red line in Figure 1g shows that the thickness of the synthesized monolayer MoS$_2$ is ~0.72 nm, which is consistent with the reported thickness of monolayer MoS$_2$ [19,46]. Raman and photoluminescence (PL) analyses were performed on the as-synthesized monolayer MoS$_2$. The Raman spectrum of monolayer MoS$_2$ shows that the frequency difference between the E$_{12g}$ mode located at 382 cm$^{-1}$ and the A$_{1g}$ mode located at 403 cm$^{-1}$ was approximately 21 cm$^{-1}$ (Figure 1i), which is consistent with that of the reported monolayer MoS$_2$ [31]. Due to the direct bandgap of monolayer MoS$_2$, the PL spectrum of MoS$_2$ shows a strong A exciton peak at 1.84 eV (Figure 1j) [19,47]. Raman and PL maps show that monolayer MoS$_2$ exhibited nonuniform Raman and PL peak intensities, confirming that monolayer MoS$_2$ had nonuniform optical and electronic properties (Figure 1k–m). Even when H$_2$ was used as a carrier gas with Ar for the MoS$_2$ synthesis, thick MoS$_2$ films were formed in the center of the substrate and some flakes of monolayer MoS$_2$ were partially formed at the edge of the thick films (Figure S2).

3.2. Monolayer MoS$_2$ Synthesized Using Carbon Cloth-Assisted CVD Method

Figure 2a shows a schematic illustration of the carbon cloth-assisted CVD growth of monolayer MoS$_2$. The experimental conditions were the same as those of the conventional CVD synthesis growth, except that the MoO$_3$ powder contained in the alumina boat was covered with carbon cloth. Unlike the conventional CVD method, this carbon cloth-assisted CVD method enables the growth of monolayer MoS$_2$ without forming thick films in the center of the substrate. Figure 2b is an optical image showing MoS$_2$ grown on a 300-nm SiO$_2$/Si substrate by the carbon cloth-assisted CVD method, confirming that there were no thick films in the center of the substrate. Figure 2c–e show the low-magnification and high-magnification optical images for regions A, B, and C in Figure 2b, respectively, confirming that monolayer MoS$_2$ grew relatively uniformly throughout the substrate without forming thick MoS$_2$ films in the center of the substrate. Additional data on the optical characterization of the MoS$_2$ grown using the carbon-assisted CVD method are shown in Figures S3 and S4. In addition, we observed that the size of the monolayer MoS$_2$
decreased when we moved from region A to region C in Figure 2b. The change in the size of the monolayer MoS\textsubscript{2} can be explained as follows; on regions A and B located upstream, a sufficient amount of S vapor reacts with MoO\textsubscript{3-x} to form large monolayer MoS\textsubscript{2}, whereas on region C located downstream, the amount of S vapor reaching region C is relatively small, resulting in relatively limited reactions with S vapor and MoO\textsubscript{3-x}.

Figure 2. Carbon cloth-assisted CVD growth of monolayer MoS\textsubscript{2}. (a) Schematic illustration of the experimental setup for carbon cloth-assisted CVD growth of monolayer MoS\textsubscript{2}. (b) Optical image of monolayer MoS\textsubscript{2} grown on an SiO\textsubscript{2}/Si substrate. Low-magnification and high-magnification optical images of (c) region A, (d) region B, and (e) region C in (b).

To investigate the mechanisms of the carbon cloth-assisted CVD growth of monolayer MoS\textsubscript{2}, materials formed on carbon cloth during the growth were analyzed. Figure 3a,b show low-magnification and high-magnification SEM images of carbon cloth obtained after the carbon cloth-assisted CVD growth, respectively, confirming that the surface of the carbon cloth was entirely covered with nanoplates with a size of two to three microns. Raman analysis confirms that these nanoplates consisted of MoS\textsubscript{2} and MoO\textsubscript{2} (Figure 3c) [48]. In addition, EDS analysis shows that the nanoplates were composed of Mo, S, and O, and the proportion of O was very large compared to the proportion of S (Figure 3d), which confirms that the nanoplates were mostly composed of MoO\textsubscript{2} and were partially composed of MoS\textsubscript{2}. MoO\textsubscript{2} is a byproduct that is frequently formed in the conventional CVD growth of MoS\textsubscript{2} using MoO\textsubscript{3} and S powder as precursors. MoO\textsubscript{2} is nonvolatile and has a high melting point, so it remains once it is formed on the substrate. One of the important roles of carbon cloth in carbon cloth-assisted CVD growth is to prevent MoO\textsubscript{2} from forming on the SiO\textsubscript{2}/Si substrate by allowing MoO\textsubscript{2} to form on the carbon cloth (Figure S5). Another role of carbon cloth is to improve the reaction kinetics for MoS\textsubscript{2} growth by facilitating the formation of suboxide MoO\textsubscript{3-x} species formed from MoO\textsubscript{3} as carbon acts as a reducing agent.
Figure 3. MoO$_2$-MoS$_2$ nanoplates grown on carbon cloth after carbon cloth-assisted CVD growth. (a,b) Low-magnification and high-magnification scanning electron microscopy (SEM) images of MoO$_2$-MoS$_2$ nanoplates grown on carbon cloth after the carbon cloth-assisted CVD growth. (c) Raman spectrum of MoO$_2$-MoS$_2$ nanoplates. (d) SEM–energy-dispersive X-ray spectroscopy (SEM–EDS) data of MoO$_2$-MoS$_2$ nanoplates.

Figure 4a is an AFM image of the monolayer MoS$_2$ synthesized using the carbon cloth-assisted CVD method, which shows that the surface of monolayer MoS$_2$ was clean without any particles, unlike monolayer MoS$_2$ synthesized using the conventional CVD method. The line profile obtained along the dotted red line in Figure 4a shows that the thickness of the synthesized monolayer MoS$_2$ was ~0.988 nm, which is consistent with the reported thickness of monolayer MoS$_2$ (Figure 4b) [19,46]. Additional AFM data of monolayer MoS$_2$ are shown in Figure S6. Figure 4c shows an optical image of monolayer MoS$_2$ grown on an SiO$_2$/Si substrate. The Raman spectrum (Curve 1) of monolayer MoS$_2$ taken at point 1 shows the Raman peaks of the E$_{12g}$ mode located at 380 cm$^{-1}$ and the A$_{1g}$ mode located at 401 cm$^{-1}$ (Figure 4d) [31]. Curve 2 in Figure 4d shows the Raman spectrum obtained from the substrate at point 2. The PL spectrum (Curve 1) of monolayer MoS$_2$ shows a strong peak at 1.84 eV (Figure 4e), which is consistent with the A exciton peak due to the direct bandgap of monolayer MoS$_2$ [19,47]. Curve 2 in Figure 4e is the PL spectrum obtained from the substrate at point 2. Raman and PL maps of MoS$_2$ show that monolayer MoS$_2$ exhibited uniform Raman and PL peak intensities, confirming that monolayer MoS$_2$ had a uniform chemical composition and electronic structure (Figure 4f–h). Figure 4i shows a TEM image of monolayer MoS$_2$. The high-resolution TEM (HRTEM) image (Figure 4j) and
corresponding selected area electron diffraction (SAED) patterns (Figure 4k) with [001] zone
axis confirm the hexagonal lattice structure with the lattice spacing of 0.278 nm assigned to
the (100) planes of MoS$_2$. In addition, TEM–EDS analysis shows that the monolayer MoS$_2$
consisted of Mo and S, and the ratio of Mo to S elements was 1:2 (Figure 4l). The Cu peak
originated from the TEM grid, and the Cr peak came from the pole pieces of the TEM.

Figure 4. Detailed analysis of monolayer MoS$_2$ synthesized by CVD growth using carbon cloth. (a) AFM image of monolayer
MoS$_2$. (b) Height line profile along the dotted red line in (a). (c) Optical image of monolayer MoS$_2$. (d) Raman spectra taken
at points 1 and 2 of (c). (e) PL spectra taken at points 1 and 2 of (c). (f,g) Raman maps of the $E_{2g}$ mode and $A_{1g}$ mode of
MoS$_2$, respectively. (h) PL map of monolayer MoS$_2$. (i) Low-magnification transmission electron microscopy (TEM) image
of monolayer MoS$_2$. (j) High-resolution TEM (HRTEM) image of monolayer MoS$_2$. (k) Selected area electron diffraction
(SAED) patterns of monolayer MoS$_2$. (l) TEM–energy-dispersive X-ray spectroscopy (TEM–EDS) data of monolayer MoS$_2$.

Figure 5 shows the growth process of monolayer MoS$_2$ depending on the reaction
time in carbon cloth-assisted CVD growth. The reaction time was set to 5, 15, 20, and
25 min, respectively. Figure 5a–d show the low-magnification and high-magnification
optical images of MoS$_2$ flakes synthesized at each reaction time. At the reaction time of five
minutes, small round-shaped MoS$_2$ seeds were formed (Figure 5a). At the reaction times
of 15 and 20 min, triangular monolayer MoS$_2$ was generated, and its size increased with
increasing reaction time (Figure 5b,c). Size distribution of monolayer MoS$_2$ synthesized
at reaction times of 5 min, 15 min, and 20 min is shown in Figure S7. At the reaction time
of 25 min, monolayer MoS$_2$ films were formed (Figure 5d). The growth of monolayer
MoS$_2$ depending on the reaction time can be explained as follows. In the initial stage of
the reaction (reaction time: five minutes), S vapor and MoO$_3$ vapor are supplied on the
substrate to form small MoS$_2$ seeds. As the reaction time increases (reaction time: 15 and
20 min), MoS$_2$ seeds form on the substrate and grow to form triangular monolayer MoS$_2$,
and as the reaction time increases, the size of the monolayer MoS$_2$ increases. When the
reaction time is further increased (reaction time: 25 min), S vapor and MoO$_{3-x}$ vapor are continuously supplied to grow triangular monolayer MoS$_2$ to form monolayer MoS$_2$ films. Figure 5e shows the Raman spectra of MoS$_2$ synthesized at each reaction time, confirming that the flakes and films synthesized at all reaction times were composed of MoS$_2$. Figure 5f shows the PL spectra of MoS$_2$ formed at each reaction time, confirming that all MoS$_2$, except for the MoS$_2$ seeds formed at the reaction time of five minutes, exhibited a strong A exciton peak at 1.84 eV, indicating that the as-synthesized MoS$_2$ flakes and layers were monolayers. We believe that the variation of the PL peak position originated from the variation of strain or defects of the as-synthesized monolayer MoS$_2$ [49].

Figure 5. Growth process of monolayer MoS$_2$ in the carbon cloth-assisted CVD growth. Low-magnification and high-magnification optical images of monolayer MoS$_2$ synthesized at reaction times of (a) 5 min, (b) 15 min, (c) 20 min, and (d) 25 min, respectively. (e) Raman and (f) PL spectra of monolayer MoS$_2$ synthesized at reaction times of 5 min, 15 min, 20 min, and 25 min, respectively.

3.3. Monolayer MoS$_2$ Synthesized Using the Carbon Powder-Assisted CVD Method

The MoS$_2$ synthesis was conducted using the carbon powder-assisted CVD method to determine whether the large-area growth of monolayer MoS$_2$ without forming thick MoS$_2$ films is because carbon acts as a reducing agent or because carbon cloth physically covers the MoO$_3$ precursor. For carbon powder-assisted CVD synthesis, experiments were conducted by mixing MoO$_3$ powder and carbon powder in ratios of 1:1, 1:2, 1:3, 1:4, 1:5, and 1:10, respectively.

Figure 6a–f shows low-magnification and high-magnification optical images of monolayer MoS$_2$ synthesized with various mixing ratios of carbon powder to MoO$_3$ powder, confirming that monolayer MoS$_2$ was grown on the substrate over the large area without forming thick films in the center of the substrate. We demonstrated that the carbon material, acting as a reducing agent, plays an important role in the large-area uniform synthesis of monolayer MoS$_2$. When the mixing ratio of MoO$_3$ powder to carbon powder was 1:1, the MoS$_2$ had a nonequilateral triangle shape, which means that MoS$_2$ has low crystallinity (Figure 6a). This is because when the ratio of carbon powder is low, the degree of the
formation of suboxide MoO$_{3-x}$ species formed during the reaction process is low, so the reaction kinetics deteriorate. When the mixing ratio of the MoO$_3$ powder to the carbon powder was from 1:2 to 1:10, MoS$_2$ with an equilateral triangle shape and high crystallinity was formed. Among them, the largest monolayer MoS$_2$ was obtained when the mixing ratio of MoO$_3$ powder to carbon powder was 1:5 (Figure 6e). When the mixing ratio of the MoO$_3$ powder to the carbon powder was further changed to 1:10, the size of the monolayer MoS$_2$ became small (Figure 6f).

![Figure 6](image_url)

**Figure 6.** Carbon powder-assisted CVD growth of monolayer MoS$_2$. Low-magnification and high-magnification optical images of monolayer MoS$_2$ synthesized depending on the mixing ratio of carbon powder to MoO$_3$ powder; (a) 1:1, (b) 1:2, (c) 1:3, (d) 1:4, (e) 1:5, and (f) 1:10, respectively. (g) Raman and (h) PL spectra of monolayer MoS$_2$ synthesized using the carbon powder-assisted CVD method.

The Raman spectra confirm that all synthesized flakes exhibited Raman peaks at the $E_{12g}$ mode and the $A_{1g}$ mode of MoS$_2$ (Figure 6g). Figure 6h shows the PL spectra of the MoS$_2$ synthesized with various mixing ratios of carbon powder to MoO$_3$ powder. As the ratio of carbon powder increased, monolayer MoS$_2$ with higher crystallinity was produced, which showed higher PL intensity. The PL spectra of the MoS$_2$ show strong A exciton peaks at 1.84 eV when the mixing ratio of MoO$_3$ powder to carbon powder was 1:4 and 1:5, confirming that the as-synthesized MoS$_2$ flakes were high-quality MoS$_2$ monolayers. However, when the ratio of carbon powder to MoO$_3$ powder is too high, MoO$_3$ is reduced to suboxide MoO$_{3-x}$ species and further reduced to form MoO$_2$ or Mo, which rather hinders the growth of monolayer MoS$_2$. Thus, under this condition, the size of the monolayer MoS$_2$ became smaller again and the PL intensity decreased.

We performed the synthesis of monolayer MoS$_2$ using graphite powder mixed with MoO$_3$ powder (Figure S8). Like the activated carbon powder-assisted CVD method, the graphite powder-assisted CVD method led to the synthesis of monolayer MoS$_2$ over a large area on the substrate. These results confirm that the reducing property of carbon is the main factor inducing the large-area growth of monolayer MoS$_2$. 
3.4. Growth Mechanism of Monolayer MoS\(_2\) in the Carbon-Assisted CVD Growth

During the carbon-assisted CVD growth of monolayer MoS\(_2\), MoO\(_3\) is reduced by carbon to form volatile suboxide MoO\(_{3-x}\) species, which are further sulfurized to form MoS\(_2\) on an SiO\(_2\)/Si substrate. The proposed reaction mechanism is as follows [50,51].

\[
2\text{MoO}_3 + x\text{C} \rightarrow 2\text{MoO}_{3-x} + x\text{CO}_2
\]

\[
2\text{MoO}_{3-x} + (7 - x)\text{S} \rightarrow 2\text{MoS}_2 + (3 - x)\text{SO}_2
\]

In this paper, we showed that the reaction kinetics for the growth of monolayer MoS\(_2\) can be improved by using carbon materials. When no carbon materials were used, thick MoS\(_2\) films were formed in most areas on the substrate and Figure S1), whereas when carbon materials were used, monolayer MoS\(_2\) was formed in most areas on the substrate (Figure 2, Figure 6 and Figure S3). Thus, we believe that the carbon materials improve the reaction kinetics for the growth of monolayer MoS\(_2\) and suppress the formation of thick MoS\(_2\) films.

The generally accepted mechanism for the growth of monolayer MoS\(_2\) involves the nucleation of tiny suboxide MoO\(_{3-x}\) seeds on the substrate surface followed by subsequent sulfurization of these seeds and subsequent growth of monolayer MoS\(_2\) [50]. Thus, suboxide MoO\(_{3-x}\) species play a key role in the growth of monolayer MoS\(_2\). By using carbon cloth or carbon powder, we effectively increased the degree of the formation of suboxide MoO\(_{3-x}\) species, leading to the growth of monolayer MoS\(_2\) in most areas on the substrate. On the other hand, the formation of thick MoS\(_2\) films can be achieved by either the direct nucleation of nonvolatile MoO\(_3\) or MoO\(_2\) clusters on the substrate followed by subsequent sulfurization.

3.5. Application to Other TMDCs

In addition, to confirm that the carbon cloth-assisted CVD method applies to the synthesis of other monolayer TMDCs, we performed the synthesis of monolayer WS\(_2\) using the conventional CVD method and the carbon cloth-assisted CVD method, respectively. Figure 7a is an optical image of the monolayer WS\(_2\) synthesized using the conventional CVD method. The size of the monolayer WS\(_2\) was as small as four microns, and its shape was not an equilateral triangle. Raman and PL mappings at the 2LA mode and A\(_{1g}\) mode of WS\(_2\) show that the monolayer WS\(_2\) exhibited nonuniform Raman and PL peak intensities, confirming that the monolayer WS\(_2\) had nonuniform optical and electronic properties (Figure 7b–d). Figure 7e is an optical image of monolayer WS\(_2\) synthesized using the carbon cloth-assisted CVD method. The size of the monolayer WS\(_2\) was approximately 13.5 microns, and its shape was an equilateral triangle. Raman and PL mappings at the 2LA mode and A\(_{1g}\) mode of WS\(_2\) show that the monolayer WS\(_2\) exhibited uniform Raman and PL peak intensities, confirming that monolayer WS\(_2\) had a uniform chemical composition and electronic structure (Figure 7f–h). Figure 7i shows an AFM image of the monolayer WS\(_2\) synthesized using the carbon cloth-assisted CVD method, confirming that the surface of the monolayer WS\(_2\) was clean without any particles. The line profile shows that the thickness of the monolayer WS\(_2\) was \(\sim 0.69\) nm, which is consistent with the reported thickness of the monolayer WS\(_2\) (Figure 7j) [52,53].

The growth of high-quality monolayer WS\(_2\) by the carbon cloth-assisted CVD method can be explained as follows. For the synthesis of monolayer WS\(_2\), WO\(_3\) powder was used as a precursor. The WO\(_3\) has a significantly high melting point (1473 °C) and its vapor pressure is very low at the reaction temperature (950 °C). Thus, the conventional CVD method produces small monolayer flakes of WS\(_2\) with very low coverage on the substrate (Figure S9). When carbon cloth is placed on top of WO\(_3\) powder, carbon acts as a reducing agent and increases the degree of the formation of suboxide WO\(_{3-x}\) species to improve the reaction kinetics for the formation of monolayer WS\(_2\). Thus, under this condition, triangular monolayer WS\(_2\) with increased size forms uniformly on the substrate.
Consequently, we confirmed that the carbon cloth-assisted CVD method is generally applicable to the synthesis of high-quality monolayer WS$_2$.

**Figure 7.** Conventional CVD growth and carbon cloth-assisted CVD growth of monolayer WS$_2$. (a) Optical image of monolayer WS$_2$ synthesized using the conventional CVD method. (b,c) Raman maps of monolayer WS$_2$ synthesized using the conventional CVD method, taken at the 2LA mode and the A$_{1g}$ mode of WS$_2$, respectively. (d) PL map of monolayer WS$_2$ synthesized using the conventional CVD method. (e) Optical image of monolayer WS$_2$ synthesized using the carbon cloth-assisted CVD method. (f,g) Raman maps of monolayer WS$_2$ synthesized using the carbon cloth-assisted CVD method, taken at the 2LA mode and A$_{1g}$ mode of WS$_2$, respectively. (h) PL map of monolayer WS$_2$ synthesized using the carbon cloth-assisted method. (i,j) AFM image and height line profiles of monolayer WS$_2$ synthesized using carbon cloth-assisted CVD method.

### 4. Conclusions

We developed a novel carbon-assisted CVD method for large-area uniform growth of high-quality monolayer MoS$_2$. Using the carbon cloth-assisted CVD method, we synthesized high-quality monolayer MoS$_2$ uniformly over a large area on the substrate without forming thick MoS$_2$ films. Through detailed analyses of the carbon cloth that was used in the reaction and experiments with varying reaction times, we revealed the mechanisms for the large-area growth of high-quality monolayer MoS$_2$. In addition, we showed that the carbon powder-assisted CVD method also produces high-quality monolayer MoS$_2$ over a large area on the substrate. This confirms that the uniform large-area growth of MoS$_2$ using the carbon cloth-assisted CVD method is mainly due to the reducing properties of the carbon material. Furthermore, we demonstrated that the carbon cloth-assisted CVD method can be generally used to synthesize monolayer WS$_2$.

**Supplementary Materials:** The following are available online at [https://www.mdpi.com/article/10.3390/nano11092423/s1](https://www.mdpi.com/article/10.3390/nano11092423/s1), Figure S1: Additional optical characterization of the MoS$_2$ grown using the conventional CVD method, Figure S2: MoS$_2$ synthesized by the CVD method using H$_2$ as a carrier gas with Ar, Figure S3: Additional optical characterization of the MoS$_2$ grown using the carbon cloth-assisted CVD method, Figure S4: MoS$_2$ flakes grown using the carbon cloth-assisted...
CVD growth, Figure S5: MoO$_2$-MoS$_2$ nanoplates grown after the carbon cloth-assisted CVD growth and after the conventional CVD growth, Figure S6: Additional AFM data of monolayer MoS$_2$ synthesized using the carbon cloth-assisted CVD method, Figure S7: Size distribution of monolayer MoS$_2$ synthesized at reaction times of 5 min, 15 min, and 20 min using the carbon cloth-assisted CVD method, respectively, Figure S8: Graphite powder-assisted CVD growth of monolayer MoS$_2$, Figure S9: Monolayer WS$_2$ synthesized on a c-cut sapphire substrate using the conventional CVD method and the carbon cloth-assisted CVD method.

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