Synthesis of Large-Scale Transition Metal Dichalcogenides for Their Commercialization

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Seoung-Woong Park^{a,b}, Yong Jun Jo^a, Sukang Bae^a, Byung Hee Hong^b, and Seoung-Ki Lee^{a,*}

^aFunctional Composite Materials Research Center, Institute of Advanced Composite Materials, Korea Institute of Science and Technology (KIST), Jeonbuk 55324, Republic of Korea

^bDepartment of Chemistry, Seoul National University, Seoul 08826, Republic of Korea

*Corresponding author E-mail: sklee@kist.re.kr

ABSTRACT

Transition metal dichalcogenides (TMDC) have been identified as excellent platforms for developing the next-generation commercial flexible logic devices and sensors, owing to their outstanding mechanical, optical, and electrical properties. The TMDCs can be used to produce novel form-factors for wearable electronic devices. Typically, synthesis of large-scale TMDC thin film have been achieved by complexity vacuum-based approach. Therefore, it is essential to develop a simple and effective method to boost-up mass production of TMDC thin films on a large scale upon arbitrary substrates. In this regard, the solution-based TMDC synthesis method is advantageous because it proposes a simplification of the fabrication processes and an easy scaling-up of the material with a non-vacuum system. In this review, we summarize the evolution of the solution-based thin-film preparation and synthesis of the TMDCs; subsequently, we discuss the merits and drawbacks of the recently developed methods to form TMDC thin films directly from the deposited precursor. Finally, we discuss the practical applications of the TMDC thin films, which demonstrate the feasibility of their commercialized applications in electronic devices and sensors.

Keywords: Transition metal dichalcogenide, Large-scale synthesis, Solution-based process, Transistor, Sensor, Hydrogen evolution reaction

1. Introduction

Two-dimensional (2D) materials provide a versatile platform for investigating various electronic and optoelectronic phenomena. Since the exfoliated graphene was demonstrated in 2004, 2D materials have been one of the central research topics in the last two decades in the field of material science [1], physics [2], and electronics, [3,4] providing. Various merits and applications of 2D materials have been verified through numerous analytical methods. In the next step, the synthesis of large-area 2D materials for their commercialization has become the focus of subsequent investigations. Bae *et al.* [5] developed the method of scaling-up of graphene, grown up to 30 inches by the chemical vapor deposition (CVD) method. Since then, various progressive strategies have been introduced for the production of high-quality graphene, even by companies, such as Sony [6] and Samsung [7]. The successful scalability of graphene boosted the mass production of other 2D materials, which belong to the family of transition metal dichalcogenide (TMDC) [8]. The TMDCs, which have semiconducting characteristics, are preferred as the target materials for developing the next-generation electronic devices because of their unique properties, such as direct or indirect band gap modulation [9], quantum-confinement [10], transparency [11], and flexibility [12]. Therefore, the uniform synthesis of TMDCs on a large-scale is important to accelerate their mass production [13,14]. Large-area TMDC thin films can be successfully fabricated via CVD, which can be used to grow vertically or horizontally stacked heterostructures [15-17]. However, the CVD-

based synthesis is limited by several factors, such as the requirement of high temperatures ($\approx 1000^\circ\text{C}$), difficulties in modulating the deposited film thickness to a desired value, and long processing time, which cause delay in the material preparation [18]. Recently, solution-phase deposition methods have been reported, which have several technical advantages, such as relatively low processing temperature [19], compatibility with various substrates, including polymer film (e.g. polyimide (PI)) [20], easily controlled layer thickness [20], rapid synthesis, and scalability with the help of existing coating techniques [21]. Recently, the lithography-free approach has been developed to form patterns directly on a TMDC film [22-24]. In this paper, we review an industrially applicable solution-based TMDC synthesis method, involving trial and error of the solution-phase deposition and its underlying mechanisms. Further, we discuss the corresponding applications, such as in transistors, sensors, and diodes, in detail. The achievements of the advanced synthesis method include large-scale fabrication of novel TMDC thin films for industrial applications.

2. Synthesis of TMDC thin films by thermolysis

Solution-phase synthesis of TMDC thin film is generally performed in several steps: the preparation of a precursor solution, deposition of the precursor, and conversion of the precursor's chemical structure. The thickness or uniformity of the synthesized TMDC film can be adjusted by controlling the precursor concentration, solution composition, and coating environment. In this section, we

review the development of various deposition and synthesis methods for fabricating TMDC thin films.

2.1. Two-step thermolysis of the TMDC film

Principles of thermolysis

The solution-deposited TMDC compounds are usually synthesized by thermolysis of a precursor $[A]_{nb}[MX]_{a+nb}$, where A is a cation that facilitates dissolution in the solvent, M is a transition metal, and X is a chalcogen that produces charge balance between A and M to support the precursor structure. MX is the anion in the precursor structure. This MX anion has a high bonding strength, which maintains its structure via the chalcogen bonding.

For example [Fig. 1(a)], synthesis of MoS₂ requires an ammonium thiomolybdate $[(NH_4)_2[Mo_3S_{13} \cdot 2H_2O]]$ precursor and a two-step thermolysis [25]. The precursor dissolves in a solvent as an anion $[Mo_3S_{13}]^{2-}$ and a cation $[NH_4]^{2+}$. In the first step, at temperatures $120 \leq T \leq 360$ °C (where T represents temperature), the $[Mo_3S_{13}]^{2-}$ clusters cleave along an intermolecular bonding weakness to produce sulfur as H₂S. Additionally, as the bond strength of the Mo–Mo bond in Mo₃S₁₃ obtained by a thermal reaction gradually weakens, it decomposes to amorphous MoS₄. Subsequently, for $T \geq 440$ °C, the remaining Mo–S bond breaks to yield a poorly crystallized MoS₂. The second thermolysis reaction produces sulfur as well as emits H₂S gas that escapes from the precursor, thereby producing a sulfur vacancy; therefore, to ensure a stable reaction, H₂ or H₂S gas is injected constantly into the reaction chamber. On completion of the reaction, MoS₂ is synthesized as a bulk structure (rod, wire, and dot) instead of being deposited on a specific substrate [Fig. 1(a), right]. Generally, $[NH_4]_2[Mo_3S_{13}]$ has a high molecular weight; therefore, it is difficult to control the layer thickness, and this drawback impedes the formation of atomically thin TMDC films.

As an alternative precursor, ammonium tetrathiomolybdate (ATM, $[NH_4]_2MoS_4$) is used to facilitate thermal decomposition for the fabrication of the MoS₂ film [18] [Fig. 1(b)]. In the ATM structure, $[NH_4]_2$ is a cation; Mo maintains the bonding as the center of the precursor, and S₄ maintains the precursor structure. Prior to the two-step thermolysis, ATM is deposited on a specific substrate and all residual solvents are removed by heating at 100 °C. Next, amorphous MoS₃ is synthesized at $120 \leq T \leq 360$ °C in the first thermolysis step. In the second thermolysis step, a thin film of MoS₂ is synthesized under an atmosphere of a mixture of Ar and S (i.e., Ar+S), with Ar injected into the chamber at $T \geq 440$ °C. The crystallinity of thermally decomposed MoS₂ can be improved by increasing T to 820 °C during the second thermolysis step [26].

Characteristics

The Raman spectral characteristics are generally used to analyze the intrinsic property of the TMDCs (MoS₂, WS₂, MoSe₂, WSe₂, and etc). Liu et al. [12,27] comparatively analyzed the Raman spectrum of the thermally decomposed MoS₂ films on sapphire substrate, under Ar and Ar+S atmosphere. Figure 1(c) shows two representative Raman absorption peaks, which are ascribed to the E_{2g}¹ and A_{1g} modes of the MoS₂ vibration. The E_{2g}¹ mode reflects the in-plane vibration and A_{1g} mode reflects the out-of-plane vibration of the MoS₂ as the difference in the energy level of electron from Raman absorption. A higher intensity of the Raman peak implies a better quality of the MoS₂ film. Therefore, the sulfur gas aids in the filling of the sulfur vacancy, thereby enhancing the quality of the MoS₂ film during thermolysis. In

Fig. 1(d), the frequency difference between the A_{1g} and E_{2g}¹ modes ($\Delta\omega = \omega_{A_{1g}} - \omega_{E_{2g}^1}$) can be used to identify the number of layers of the synthesized MoS₂ [Fig. 1(d), bottom]. The Raman mode spacing is considerably narrow ($\Delta\omega \approx 25$ cm⁻¹), which indicates that the MoS₂ film is composed of five layers; a mono layer has $\Delta\omega \approx 16.5$ cm⁻¹ [28,29]. As the number of layers of the synthesized MoS₂ approaches one, this synthesized monolayer develops a direct band gap and has optical properties; it absorbs light of a specific wavelength (672 nm). Figure 1(e) shows the photoluminescence (PL) of a tri-layer MoS₂ film, thermally decomposed on a sapphire substrate. The PL peaks also exhibit a stronger intensity when Ar+S gas mixture is injected; the result indicates that a MoS₂ film of better quality is formed. Next, X-ray photoelectron spectroscopy (XPS) analysis was conducted to identify the chemical composition of the thermally decomposed MoS₂ film [Fig. 1(f)]. The Mo 3d shows two peaks at 229.3 and 232.5 eV, which are attributed to Mo 3d_{5/2} and S 2s peaks, indicating that the chemical composition of the MoS₂ film exists during the 2H phase formation. The S 2p peaks, shown in the inset, indicate the intramolecular bonding of divalent sulfide ions (S²⁻). Accordingly, the two distinguished peaks are observed approximately at 163.3 and 162 eV, corresponding to the S 2p_{1/2} and S 2p_{3/2} orbital splits. As a result, it is possible to verify the intrinsic chemical composition of MoS₂ through the thermolysis of $[NH_4]_2MoS_4$. Additionally, the thickness modulation of a synthesized MoS₂ film can be demonstrated by adjusting the concentration of the ATM precursor [20]. Figure 1(f) shows the atomic force microscopy (AFM) image of a MoS₂ thin film, synthesized through a two-step thermolysis reaction with different concentrations of ATM precursor. Thus, a MoS₂ thin film, with one (0.65 nm) to a few layers (3.2 nm), can be synthesized by a two-step thermolysis method.

2.2. Synthesis of TMDC films on a large scale

To synthesize a TMDC film from a solution on an arbitrary substrate (e.g., SiO₂/Si and sapphire), it is important to monitor the precursor deposition since it determines the scale, thickness, and patterning of the TMDC films. Here, we first describe the dip coating deposition method, which is proposed by Liu *et al.* [27]. In this method, $(NH_4)_2MoS_4$ is dissolved in dimethylformamide (DMF) to form a precursor solution. A SiO₂ substrate that is prepared via the oxygen treatment is immersed into the $(NH_4)_2MoS_4$ solution. Next, the substrate is pulled out slowly (0.5 mm s⁻¹) from the solution. The deposition yield of $(NH_4)_2MoS_4$ film is determined by the precursor–substrate wettability and separation speed. The process is very simple; however, controlling the thickness of the precursor layer is difficult; thus, this method is not suitable for the mass production of TMDC films.

Figure 2(a) illustrates the spin-coating strategy to obtain wafer-scale MoS₂ thin films through the dissolution of $(NH_4)_2MoS_4$ in *N*-methylpyrrolidone (NMP) [30]. Spin coating is widely used to deposit photoresists during the semiconductor manufacturing; the coating thickness can be controlled easily by varying the rotation speed. Therefore, using the spin coating method, the precursor film thickness can be controlled by varying the concentration of the solution and rotating speed, thereby yielding precisely tuned mono-/bi-/tri-layers of the thermally decomposed MoS₂ film. Spin coating is advantageous for thickness control; however, only one solvent is used; therefore, the wetting of a substrate is low. As a result, the viscosity or surface tension

Figure 1. (a) Schematic of the chemical composition of bulk-type MoS₂ formation from (NH₄)₂[Mo₃S₁₃]. (Reprinted with permission from [18] (A. Giri *et al.*, Adv. Mater. 30, 1707577 (2018)), © 2020, John Wiley and Sons). Optical microscope image of rod-type MoS₂ (right). (Reprinted with permission from [43] (Z. Huang *et al.*, Angew. Chem. Int. Ed. Engl. 54, 15181 (2015)), © 2020, Elsevier). (b) Schematic representation of the synthesis of thin-film MoS₂ via two-step thermolysis from (NH₄)₂[MoS₄]. (Reprinted with permission from [44] (T. Zhang *et al.*, Chem. Asian J. 11, 1392-2398 (2016)), © 2020, John Wiley and Sons). Optical microscopic image of synthesized MoS₂ thin film on SiO₂/Si substrate (right). (c) Raman spectra of two-step thermally decomposed MoS₂ under Ar or Ar+S atmosphere. (d) Energies of the two characteristic peaks: Variation of the spacing between E_{2g} and A_{1g} with number of MoS₂ layers. (e) PL intensity of the thermally decomposed triple layered MoS₂ film. (f) XPS spectra of the thermally decomposed MoS₂ film: Mo 3d and S 2s peaks. (Reprinted with permission from [27] (Liu *et al.*, Nano Letters 12, 1538-1544 (2012)), © 2020, American Chemical Society). (g) Surface topographic images (insets) and cross-sectional height profile of the thermally decomposed MoS₂ with thickness modulation by adjusting (NH₄)₂[Mo₃S₁₃] concentration. (Reprinted with permission from [20] (H. Yang *et al.*, Nanoscale 7, 9311-9319 (2015)), © 2020, Royal Society of Chemistry).

of a precursor cannot be controlled easily. Therefore, this method is useful only to synthesize TMDC films on a relatively small scale.

Yang *et al.* [20] proposed a solution engineering that can easily control the wetting of precursors in the solution with the substrate.

The DMF-based (NH₄)₂MoS₄ solution is reformulated additionally with two types of amino alcohol-based solvents. Before the spin coating, an oxygen plasma surface treatment is applied to increase the wettability of the precursor solution with the substrate. The quality of

Figure 2. (a) Schematic representation of spin coating based 4 inch scaled MoS_2 thin-film synthesis. (Reprinted with permission from [30] (A.S. Gergo *et al.*, *Adv. Funct. Mater.* 24, 7461-7466 (2014)), © 2020, John Wiley and Sons). (b) Optical microscope images of the spin coated $(\text{NH}_4)_2\text{MoS}_4$ films using different compositions of the solvent. (Reprinted with permission from [20] (Yang *et al.*, *Nanoscale* 7, 9311-9319 (2015)), © 2020, Royal Society of Chemistry). (c), (d) Schematic diagram of the polymer-assisted spin coated $(\text{NH}_4)_2\text{MoS}_4$ film and its thermal decomposition on a 6-inch scaled SiO_2/Si wafer. (Reprinted with permission from [21] (Yang *et al.*, *Chem. Mater.* 29, 5772-5776 (2017)), © 2020, American Chemical Society). (e) Schematic illustration and photographs of the roll-to-roll based 20-inch scaled MoS_2 thin-film synthesis: solution coating and thermal decomposition. (Reprinted with permission from [32] (Y. Lim *et al.*, *Adv. Mater.* 30, 1705270 (2018)), © 2020, John Wiley and Sons).

the spin-coated precursor film is gradually improved owing to the additive solvent [Fig. 2(b), left to right]. During the spin coating of the precursor, the additive solvent promotes the solvation of $(\text{NH}_4)_2\text{MoS}_4$ with balanced viscosity and surface tension. An optimized solvent mixture of DMF:n-butylamine:2-aminoethanol = 4.5:4.5:1 (v/v/v, where v represents volume) generates a uniform spin-coating of the precursor, without pinholes or dewetted regions. Ionescu *et al.* [31] reported a spin coating technique, wherein the $(\text{NH}_4)_2\text{MoS}_4$ precursor is dissolved into a dimethyl sulfoxide (DMSO):ethylenediaminetetraacetic acid (EDTA) co-solvent. During the spin coating, the DMSO increases the wettability between the $(\text{NH}_4)_2\text{MoS}_4$ precursor and SiO_2 substrate, and

EDTA stabilizes the precursor by chelation. Another method of improving the synthetic area of the MoS_2 thin film is the polymer-assisted precursor deposition technique, which was engineered by Yang *et al.* [21]. A linear polymer matrix (poly ethyleneimine, PEI) [Fig. 2(c)] allows the viscosity modulation of $(\text{NH}_4)_2\text{MoS}_4$ precursor with full coverage of the spin-coated MoS_2 on a 6-inch SiO_2/Si wafer [Fig. 2(d)]. The film thickness can be tuned by adjusting the concentration of the $(\text{NH}_4)_2\text{MoS}_4$ precursor.

Although the solution-engineered precursor deposition method increases the film area, this method has several drawbacks, such as low production yield, differences in the crystal growth depending on the

Figure 3. (a) Schematic diagram representing the synthesis of self-assembled WSe₂/MoS₂ wires. (b), (c) Images of cross-aligned WSe₂/MoS₂ wires showing their growth directions. (d), (e) Optical microscopy images of different angles of WSe₂/MoS₂ wires: 90° and 45°. (Reprinted with permission from [22] (Lee *et al.*, Adv. Mater. 31, 1904194 (2019)), © 2020, John Wiley and Sons). (f) Illustration of MoS₂ and WS₂ pattern formation, including spin coating, photothermal decomposition, and rinsing. (g) Photograph of the patterned MoS₂ and WS₂ supported on a 2-inch SiO₂/Si wafer. (Reprinted with permission from [23] (Park *et al.*, ACS Nano 14, 8485-8494 (2020)), © 2020, American Chemical Society).

substrate, and high production cost. Owing to these limitations, Lim *et al.* [32] developed a synthetic method of producing 20-inch-scale MoS₂ thin films using a roll-to-roll process [Fig 2(e)]. They suggested that spray coating of the (NH₄)₂MoS₄ precursor on a Ni foil can improve the production yield and crystallinity [33]. The precursor deposited film is heated in a furnace at 800 °C under Ar or H₂ atmosphere to thermally decompose the (NH₄)₂MoS₄ precursor. This method significantly increases the production of the MoS₂ thin films on a large scale. A high yield can be achieved by controlling the various process parameters.

Synthesis of direct-patterned TMDC films

To use a TMDC thin film in a practical electronic device, the fabricated film should be isolated to form a source-drain array. Therefore, a TMDC pattern is typically fabricated via the additional photolithography or oxygen plasma treatment-based mask process. To simplify this process, the precursor deposition and synthesis methods have been developed to form TMDC patterns directly, without the

additional patterning step. Lee *et al.* [34] demonstrated the direct pattern formation in the TMDC precursor film through a dip coating method for the synthesis of WS₂ or MoS₂ wires. In this process, a piece of SiO₂, Si, or quartz wafer is soaked in (NH₄)₂MoS₄ (or ammonium tetrathiotungstate, (NH₄)₂WS₄) solution in de-ionized water. Next, the SiO₂, Si, or quartz wafer is lifted in the upward direction, and the precursor is precipitated simultaneously in the form of a periodic wire. This method can yield both homostructured WS₂-MoS₂ wires and WS₂/MoS₂ heterostructured wires, under optimized parameters, such as proper pH and concentration of the aqueous precursor, required humidity and evaporation speed in the environment. The addition of isopropyl alcohol can tune the solvent's evaporation speed, thereby modulating the thickness of the precipitated precursor layer.

Later, Lee *et al.* [22] developed cross-aligned WSe₂/MoS₂ heterostructures through partial pinning of the solution to the substrate, which generates a regular and repetitive circular convection flow, i.e., Marangoni flow, during the precursor feeding [Fig. 3(a)]. The precursor nuclei in the solution continuously adhere to the SiO₂/Si substrate;

Table I. Comparison between the different methods of solution-processed TMDC thin film synthesis.

Precursor Deposition	Precursor Solution	Annealing Method	Synthetic Area	Heterostructure	Reference
Dip coating (full cover)	DMF	Thermolysis (furnace)	1 × 1 cm ²	X	[27]
Spin coating (full cover)	NMP	Thermolysis (furnace)	2 inch	X	[30]
Spin coating (full cover)	DMF+Additive	Thermolysis (furnace)	2 inch	X	[20]
Spin coating (full cover)	DMF+DMSO	Thermolysis (furnace)	4 inch	X	[31]
Spin coating (full cover)	DMF+PEI	Thermolysis (furnace)	6 inch	X	[21]
Roll-to-Roll (full cover)	ethylene glycol	Thermolysis (furnace)	20 inch	X	[32]
Dip coating (pattern)	DI water	Thermolysis (furnace)	1 × 1 cm ²	O	[34]
Dip coating (pattern)	DMF	Thermolysis (furnace)	1 × 1 cm ²	O	[22]
Spin coating (full cover)	DMF+Additive	Locally Thermolysis (pulsed laser)	4 inch	O	[23]

therefore, vertically (directionally) heterostructured TMDC wires can be precipitated [Figs. 3(b) and 3(c)]. Such a direct method to form precursor patterns is useful to fabricate a specific heterojunction or to form patterns on a single material without using an additional patterning process. The fabricated cross-aligned wires show different cross-angles of 45° and 90°; this arrangement is advantageous for producing stacked TMDCs to develop integrated electronic devices [Figs. 3(d) and 3(e)].

Park *et al.* [23] have recently developed a novel process that can freely form TMDC patterns through a pulsed laser annealing method. Using the precursor deposition method of Yang *et al.* [20], a precursor is initially deposited on a 4-inch TMDC thin film by spin coating. Next, a pulsed-laser source of wavelength 1.06 μm is irradiated on the precursor to achieve photothermolysis [Figs. 3(f) and 3(g)]. As a result, a fine WS₂ or MoS₂ homostructure is formed with a WS₂ or MoS₂ vertical heterostructure pattern. This method allows the synthesis of a large-area patterned TMDC film only with a single-step heat treatment at room temperature and pressure in a shortened process time. Further, the fabrication is accomplished without the additional processes by easily blocking the external oxygen in a chalcogen gas (S, Se) rich atmosphere, wherein the gas is derived from the TMDC precursor. Details on the aforementioned synthesis methods are summarized in Table I.

3. Applications of TMDCs

TMDC thin films obtained from a solution (e.g., MoS₂, WS₂, WSe₂) can be synthesized on a large scale using simple thermal decomposition processes and therefore have a variety of applications in electronic devices. In this section, we review the electronic devices and sensors that have been developed by using the solution-based synthesis methods.

3.1. Field-effect transistors (FETs)

One of the key characteristics of a TMDC thin film is its semiconducting property. A TMDC thin film has a tunable band gap depending on the number of its layers [35,36]. Liu *et al.* [27] first reported the fabrication of an FET from the solution-based thermally decomposed MoS₂ thin films. The synthesized triple layered MoS₂ film has the property of n-type behavior and shows good field-effect electron mobility (4.7 cm² V⁻¹s⁻¹). The variation of the electron mobility, depending on the number of layers of the solution-synthesized MoS₂ film, is systemically investigated by Lee and co-workers [34]. Figure 4(a) shows a comparison of the transfer curves (*I*_{DS} vs *V*_{GS}) associated with the thickness modulation of the ion-gel gated MoS₂ wires. The transfer characteristics show that the current increases with increasing thickness of the wires (3 to 32 nm). In the case of a thick MoS₂ wire (32 nm) exhibits symmetric ambipolar behavior, indicating that enhanced electron and Hole mobility was observed. Figure 4(b) shows the variation of the mobility with the MoS₂ film thickness. The statistically evaluated average effective mobility is approximately 100 cm² V⁻¹s⁻¹, as observed from Fig. 4(b). These results are due to the fact that, as the thickness of the MoS₂ films increase, their vulnerability to carrier scattering decreases, which in turn increases their carrier mobility [37,38]. Several solution-synthesized MoS₂ thin films have been applied to FETs. However, they have low average effective carrier mobility, [20,31] and are therefore not suitable for commercialization. The performance of the solution-processed MoS₂ FETs are summarized in Table II.

3.2. Photodetectors

Shifting the perspective to the optoelectronic properties of the solution-based MoS₂ thin films, Lim *et al.* [33] developed a thermally decomposed MoS₂-based visible light photodetector on a 4-inch

Figure 4. (a), (b) Transfer curves (I_{DS} vs V_{GS}) of the ion-gel gated MoS_2 /graphene hybrid FETs, depending on the thickness of the wires in the channel and their effective charge mobility. (Reprinted with permission from [34] (Lee *et al.*, Adv. Mater. 27, 4142-4149 (2015)), © 2020, John Wiley and Sons). (c), (d) Time-resolved photocurrent response of the thermally decomposed MoS_2 on PI film (Reprinted with permission from [33] (Y. Lim *et al.*, Adv. Mater. 28, 5025-5030 (2016)), © 2020, John Wiley and Sons). (e), (f) Polarization curves of a series of samples: Pt/C, bulk MoS_2 , hydrothermal MoS_2 , and photothermally decomposed MoS_2 . (Reprinted with permission from [39] (Deng *et al.*, J. Mater. Chem. A. 4, 6824-6830 (2016)), © Royal Society of Chemistry).

Table II. Comparison of the performance of the FETs, produced by solution based-TMDC synthesis.

Materials	Annealing Method	On/ Off Ratio	Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$).	Directly Patterning	Reference
MoS_2	Thermolysis (furnace)	$\sim 10^5$	~ 4.7	X	[27]
MoS_2 WS_2	Thermolysis (furnace)	$\sim 10^6$	~ 100	O	[34]
MoS_2	Thermolysis (furnace)	$\sim 10^4$	~ 0.24	X	[20]
MoS_2	Thermolysis (furnace)	$\sim 10^8$	~ 0.1	X	[31]
MoS_2 WS_2	Locally Thermolysis (pulsed laser)	$\sim 10^3$	~ 6.4	O	[23]

SiO_2/Si wafer. They focused on the spatial distribution of the large-scale MoS_2 thin film with 100 devices (10 rows $\times$ 10 columns). The result of the homogeneous photoresponse is displayed in Fig. 4(e), which indicates that the device yielded a periodically varying photocurrent under a halogen lamp irradiation with a tunable power,

regardless of the bias voltages (1, 5, 10, 15, and 20 V). For a fixed photocurrent at a bias voltage of 20 V, the illumination power increases from 7.0 to 12.5 mW cm^{-2} ; this observation implies that the photocurrent is proportional to the illumination power, owing to an increase in the carrier-generation rate. Thus, the photocurrent of a

Figure 5. (a) Relative resistance variation and gauge factor of the MoS₂-based strain gauge in the range of 0.5–3.0%. (b) Mechanical stability of MoS₂-based strain gauge up to 1000 cycles with different strain levels. (c) Operation of the MoS₂-based 3-axis strain gauge rosette with sensing ability from unknown directions. (Reprinted with permission from [23] (Park *et al.*, ACS Nano 14, 8485–8494 (2020)), © 2020, American Chemical Society). (d) Time-resolved trajectory mapping of the MoS₂-based haptic sensor using a stylus pen movement. (Reprinted with permission from [24] (Park *et al.*, Nano Energy 78, 105266 (2020)), © 2020, American Chemical Society).

photodetector is linearly dependent on the illumination power.

Furthermore, Lee *et al.* [22] recently demonstrated a solution-based cross-aligned WSe₂/MoS₂ *p-n* junction structured photodiode and detector. The analyzed photo responsivity of the fabricated device is $\sim 5.39 \text{ A W}^{-1}$, which is higher than that of the previously reported TMDC-based optoelectronic devices that are made up of monolayer homo- and heterojunctions. Park *et al.* [23] demonstrated a *p-n* diode with vertically stacked solution-processed WS₂/MoS₂ thin films prepared by irradiating (NH₄)₂WS₄/MoS₂ films with an ultra-short laser pulse ($\sim 100 \text{ ps}$) to cause selective thermolysis of (NH₄)₂WS₄, since it shows ~ 60 times higher absorbance than the MoS₂ film during the laser annealing ($1.06 \mu\text{m}$). The process converts (NH₄)₂WS₄ to a WS₂ film with high crystallinity despite the instant formatting on the MoS₂ lattice. This *p-n* diode that uses WS₂/MoS₂ produces good electrical rectification with a forward-to-reverse current ratio of $\sim 10^3$.

3.3. Hydrogen evolution reactor (HER)

Another solution-based TMDC application has attracted considerable attention in the field of catalysis. Deng *et al.* [39] developed hydrogen evolution reaction (HER) catalysts from the one-step photothermal decomposition of PI and MoS₂ precursor by using a continuous-wave laser to ensure strong heating. The laser-irradiated sample must include a composite of laser-induced graphene and MoS₂

nanoparticles; the composite significantly influences the HER activity by increasing the specific area and producing heat-induced surface defects. The results of the linear sweep voltammetry measurements, showing the polarization curves of bulk MoS₂, hydrothermal MoS₂, MoS₂/C hybrids, and Pt/C, are shown in Fig. 4(e). The MoS₂/C hybrids exhibit a higher overpotential (216 mV) and a lower Tafel slope (64 mV dec^{-1}) than other samples [Fig. 4(f)]. Hasani *et al.* [40] demonstrated a solar-driven HER sensor having a heterojunction formed by thermally decomposed n-type MoS₂ on a p-type Si. This sensor shows the highest catalytic activity with the lowest Tafel slope of 65 mV dec^{-1} , when an appropriate MoS₂ thin-film thickness (16.8 nm) is used.

3.4. Strain and haptic sensors

The previously reported methods of TMDC-based strain sensor fabrication used thin films grown using CVD, with several subsequent photolithography steps to pattern the strain gauge [41,42]. Park *et al.* [23] demonstrated the direct pattern formation of a MoS₂-based strain gauge and proposed that a lithography-free approach can be applied to develop a three-axis strain gauge rosette. The application of an external force on the MoS₂ strain gauge causes strain-induced deformation of the conductive pathways, which changes the electrical conductivity of the material [Fig. 5(a)]. Notably, the relationship between the conductivity and strain is linear, and the gauge operates reversibly,

without hysteresis, at a strain $< 1.67\%$. Therefore, the range of the strain is restricted to the linear regime ($\approx 1.5\%$), and the mechanical response of the strain gauge shows a stable response over 1000 repeated cycles [Fig. 5(b)]. When mounted on a human wrist, this three-axis strain gauge rosette can simultaneously respond in unknown X° and Y° directions [Fig. 5(c)]. The time-resolved resistance response of the rosette shows an omnidirectional sensing ability.

Direct-pattern formation by photothermal decomposition is used to fabricate self-powering haptic sensors that use an MoS_2 active layer. Park *et al.* [24] fabricated large-scale patterned MoS_2 thin films and developed strain induced crumpled MoS_2 . The crumpled MoS_2 has distinct characteristics compared to the pristine MoS_2 . A widening in the MoS_2 lattice and a decrease in the orbital overlap increase the work function of the sensor; these changes increase the charge-transfer effect during the generation of self-powering signal, i.e., the triboelectric current generation. Hence, the haptic sensor is self-powered and includes a triboelectric touchpad on a latex glove. The 4×4 arrayed, crumpled MoS_2 haptic touch sensor has a time-dependent mapping trajectory, according to the movement of a stylus [Fig. 5(d)].

4. Summary

This review covers a wide range of large-scale, inexpensive, and simple methods for synthesizing TMDC thin films from solutions with direct-pattern formation, in addition to elucidating their practical applications. Various precursor deposition methods have been developed to increase the film area and modulate the solution composition, which yields the appropriate coating conditions for large-scale fabrication. Thus, the thickness of the TMDC film is easily modulated by adjusting the precursor concentration. Notably, direct formation of the TMDC patterns is also achieved using the solution-phase precipitation and photothermal decomposition. These processes yield vertically stacked TMDC-based heterostructures, without complex processing steps. The synthesis of TMDCs from solutions can be practically applied to readily fabricate devices, such as FETs, photo-detectors, HER catalysts, diodes, and mechanical sensors.

However, the TMDC thin film synthesis method covered in this review is still problematic to be applied to high performance electronic devices because of the small TMDC grain size. Therefore, the development of another methodology for the mass production of highly crystallinity of TMDC thin films is crucial for their applications in the semiconductor industry and researches.

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