

Doped, Two-Dimensional, Semiconducting Transition Metal Dichalcogenides in Low-Concentration Regime

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Abstract: Doping semiconductors is crucial for controlling their carrier concentration and enabling their application in devices such as diodes and transistors. Furthermore, incorporating magnetic dopants can induce magnetic properties in semiconductors, paving the way for spintronic devices without an external magnetic field. This review highlights recent advances in growing doped, two-dimensional (2D) transition metal dichalcogenide (TMDC) semiconductors through various methods, like chemical vapor deposition, molecular beam epitaxy, chemical vapor transport, and flux methods. It also discusses approaches for achieving n- and p-type doping in 2D TMDC semiconductors. Notably, recent progress in doping 2D TMDC semiconductors to induce ferromagnetism and the development of quantum emitters is covered. Experimental techniques for achieving uniform doping in chemical vapor deposition and chemical vapor transport methods are discussed, along with the challenges, opportunities, and potential solutions for growing uniformly doped 2D TMDC semiconductors.

Keywords: chemical vapor transport; transition metal dichalcogenide; doping; magnetism



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1. Introduction

To scale down transistors requires not only a short distance between the source and the drain electrodes but also thin-layered channels [1–3]. These requirements create opportunities for 2D semiconductors to drive the continuation of the scaling process, thanks to their one-atom-thick nature, without dangling bonds [4–6]. TMDCs are a 2D material family emerging as a prototype to explore nanoscale transistors [1–3]. Interestingly, the reduced screening effect in TMDCs leads to strongly bound excitons that persist at room temperature [7–10], initiating studies on exciton physics at high temperatures, including Bose-Einstein condensation [8,11–13]. Furthermore, the absence of dangling bonds at the interface promotes the formation of new periodic potentials by twisting two mono layers of TMDCs [14–19]. Manipulating electron interactions within these potentials allows for control over the distance between periodic potentials by adjusting the twist angle, facilitating the study of strong correlation physics [16–18,20]. Exotic physics phenomena exist in such systems, including magnetism, superconductivity, Wigner crystals, and the integral and fractional quantum anomalous Hall effect [14,17–19,21–25].

Crucial aspects of using TMDCs are their controllable properties through dopants, for instance, the carrier type (e.g., n-type and p-type) [26–32]. They are essential for the realization of transistors that are based on doped TMDCs. The modulation of charge carriers can be realized by surface functionalization [33] using chalcogen atoms [34,35], as well as the substitution and intercalation of dopants in host materials [34,35]. However,

this review focuses on substitutional doping in TMDCs, particularly at the transition metal sites [34,36–38]. For well-known TMDCs such as MX_2 ($\text{M} = \text{Mo}, \text{W}; \text{X} = \text{S}, \text{Se}$), the elements Nb [27,39], Ta [40], and V [41–43] serve as p-type dopants, while Re [44–46] is an n-type dopant. Notably, V, Fe, and Co can induce magnetic properties in TMDCs [36,41,47–49], with V being a widely explored dopant [36,37,50,51].

For example, V-doped WSe_2 exhibits both ferromagnetic and semiconducting features at low doping levels ($<0.5\%$) at room temperature. Such doped magnetic TMDCs are referred to as diluted magnetic semiconductors (DMSs) [36,41,47]. The physical properties of TMDC DMSs are highly sensitive to doping concentration. For instance, the ferromagnetic feature in V-doped WSe_2 manifests at doping levels ranging from 0.1% to 0.5%, while retaining its semiconducting nature. In contrast, at higher doping concentrations, the system tends to enter a degenerative state, diminishing the ferromagnetic characteristic [36,41,50]. Therefore, precisely controlling the doping concentration is crucial for tuning the magnetic properties of TMDCs [36,42,52]. Despite these advances, significant challenges remain, such as the limited uniformity of dopants within the host materials.

In this review, we present the current state-of-the-art properties of doped TMDCs, particularly substitutional doping at transition metal sites. We also briefly introduce growth techniques, such as chemical vapor deposition (CVD), for synthesizing atomically thin TMDCs, and chemical vapor transport (CVT), for the bulk growth of doped TMDCs. Additionally, we compare the physical properties and dopant distributions in TMDCs and discuss the current challenges and opportunities associated with doped TMDs.

2. Growth Approaches for Doped TMDCs

Pristine and doped TMDCs are typically synthesized in two forms: large-area monolayer and bulk single crystals. The former is synthesized by CVD [4,29,31,32,39,53], molecular organic chemical vapor deposition [54,55], and molecular beam epitaxy [56–59], while the latter is obtained through chemical vapor transport and flux methods [60–66].

In the CVD method for TMDC synthesis, transition metals (both the host and the dopants) are sourced in solid and gas phases [41,43] (Figure 1a). When solid sources are used, the material is prepared on a substrate in a thin film form, which can be achieved through spin-coating or e-beam evaporation. Figure 1a shows a schematic of the CVD growth of V-doped WSe_2 [36,43,50], in which V and W precursors were prepared in solution and spin-coated onto a SiO_2/Si substrate. This substrate was then loaded into a two-zone tube furnace, with the hot zone set to $\sim 600\text{--}900^\circ\text{C}$. The Se source was placed in the cool zone ($\sim 230^\circ\text{C}$). At this temperature, Se gas reacts with the decomposed metal oxides in the hot zone, resulting in the formation of monolayers of pristine and doped TMDCs (e.g., V-doped WSe_2). In the case of gas sources, the precursors evaporate during the reaction (Figure 1b) [36,43]. For instance, MoO_3 and V precursors were evaporated and reacted with an S vapor, leading to the formation of V-doped MoS_2 monolayers on an SiO_2/Si substrate. An advantage of using the gas source approach is that the dopant distribution is more uniform [53].

In the chemical vapor transport (CVT) method, the sources are solid. Each element (transition metal, dopant, and chalcogen) is in its purest form. These elements are measured stoichiometrically to their atomic weights, ground together, well-mixed, and sealed in quartz ampules in a strong vacuum (Figure 1c). This method involves vapor transport via a volatile substance called a transport agent, which is non-reactive and easily removed from the bulk crystals after growth. The transport agent is crucial for CVT growth; the type and amount of the transport agent play a critical role in TMDC growth [50,60,67–69]. Chlorine, bromine, and iodine are well-known transport agents, with iodine being the most widely used for the growth of TMDCs [67–69]. The optimal amount of iodine, $4\text{--}6\text{ mg/cm}^3$, worked best in our synthesis of pristine and doped TMDCs. Excess iodine can lead to either quartz ampoule explosions at higher temperatures due to overpressure or cause lattice defects (such as stacking faults) with a low yield (tiny crystals or no crystal) [60,70]. The

steps followed in our laboratory for the CVT growth of V-doped WSe₂ will be explained in detail in a later section.

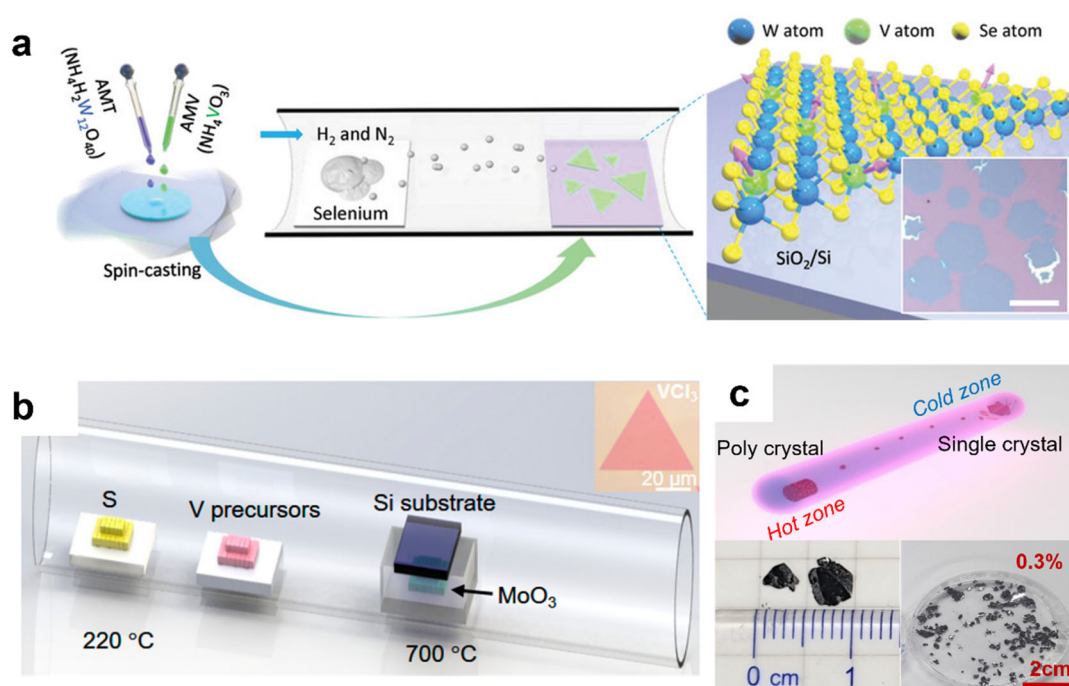


Figure 1. Synthesis of V-doped TMDs by CVD and CVT methods. (a) Schematic of synthesis by mixing liquid precursors (W and V). The inset shows an optical image of CVD-grown V-doped WSe₂ monolayer. Scale bar, 50 μm . The randomly oriented purple arrows indicate spins originated from V atoms. This figure was adapted with permission from Ref. [36]. 2020, WILEY-VCH GmbH & Co. kGaA, Weinheim, Germany. (b) Schematic showing solid growth of TMDs by solid precursors (V-doped MoS₂). This figure was reprinted with permission from Ref. [43]. 2021, American Chemical Society, Washington, DC, USA. (c) Schematic showing CVT growth of TMDs; (top) hot zone kept at higher temperatures than cold zone, where single crystal grows. Single crystals of V-doped WSe₂ (bottom). This figure was adapted with permission from Ref. [50]. 2021, American Chemical Society, Washington, DC, USA.

2.1. Structural Properties

To understand the influence of dopants on the atomic structures of TMDCs, it is crucial to determine their atomic structure after doping. Due to their atomically thin nature, scanning transmission electron microscopy (STEM) allows us to observe the arrangement of atoms on the nanoscale. The STEM technique analyzes the transmitted electrons through an extremely thin sample, creating various intensity profiles based on the elemental wave functions. As a result, the atoms can be identified by their contrast differences in the micrograph. Figure 2a shows the STEM micrographs of pristine and V-doped WSe₂ [50]. The brighter spots correspond to W atoms (shown in cyan color in the simulated model), while the Se atoms appear as darker spots (yellow color in the simulated model) compared to W. At the Se spots, the electron beam was transmitted through two Se atoms. Moreover, native Se vacancies can be identified as darker spots at equivalent Se locations. In contrast, the V-doped WSe₂ sample shows the V dopants as darker spots at locations equivalent to the W atoms, confirming substitutional doping at the W sites. These V spots appear darker than W due to the V atoms being lighter compared to the W atoms. In addition, the experimental intensity profiles of these elements agree with the simulated intensity profiles, further confirming the atomic structure and the substitutional V dopants in WSe₂. In other examples, Re and V substitutional doping in MoS₂ (Figure 2b) reflects a similar phenomenon as the V-doped WSe₂, except that the Re spots appear brighter than the Mo

atoms since Re is heavier than Mo [41]. It is worth noting that Se vacancies persist in both the pristine and the doped TMDCs [36,41,50].

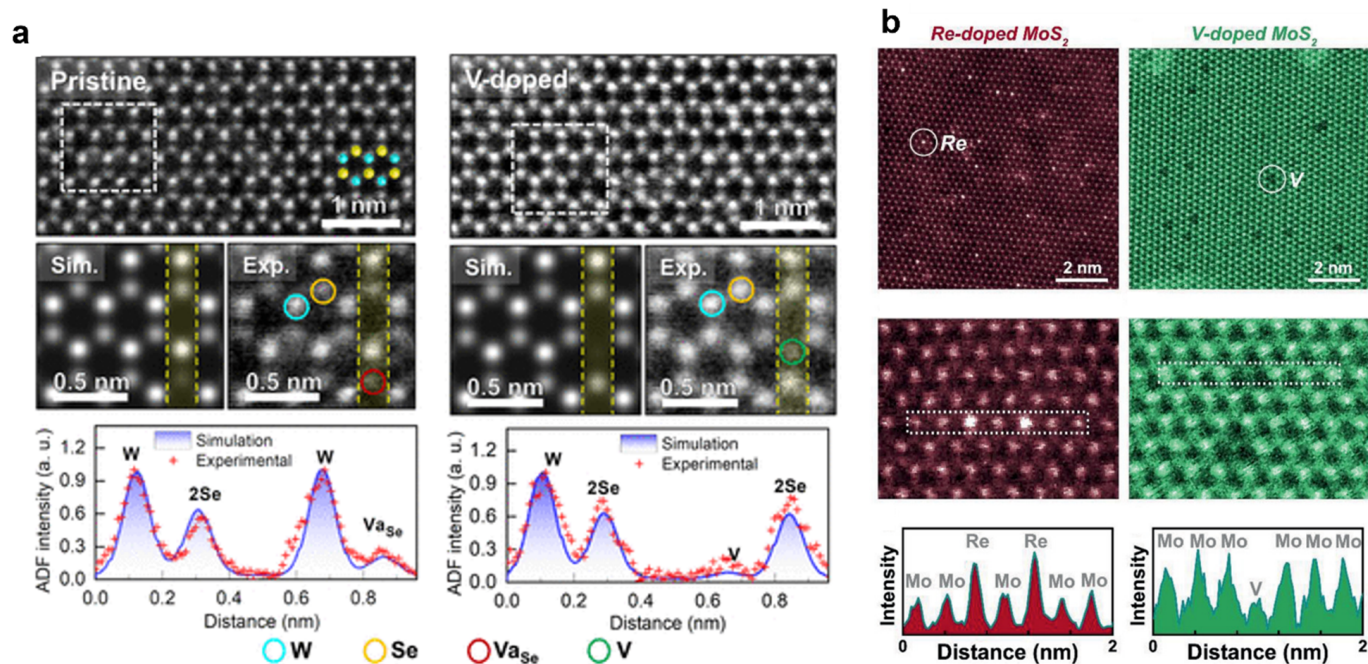


Figure 2. Structural properties of TMDs. (a) ADF-STEM micrograph of pristine and V-doped WSe₂ monolayers: the hexagonal configuration with six atomic sites for W (high intensity, cyan) and Se (low intensity, yellow) atoms, including Se vacancy (red), and the low intensity spot (green) corresponds to V at W sites, indicating V atom substitution. This figure was adapted with permission from Ref. [50]. 2021, American Chemical Society, Washington, DC, USA. (b) STEM images of Re- and V-doped MoS₂: high intensity spots correspond to Re sites in MoS₂, whereas dark spots to V sites. This figure was reprinted with permission from Ref. [41]. 2021, Wiley-VCH GmbH, Weinheim, Germany.

2.2. Electronic Transport Properties of p- and n-Type Doped TMDCs

Materials' properties can be predicted by density functional theory (DFT) calculations. Figure 3a shows the band structure of pristine (dark green) and V-doped WS₂ (red) [42]. A supercell (a large cell containing multiple unit cells) was used to examine the effect of doping at various dopant concentrations. For instance, an 8×8 supercell with one V atom is equivalent to 1.56% of V in the stoichiometric formula $V_xW_{1-x}S_2$ ($x = 0.028$). Pristine WS₂ is a semiconductor, with its Fermi level lying approximately in the middle of the band gap. In contrast, the V-doped WS₂ formed an acceptor state ~ 50 meV below the conduction band, shifting the Fermi level closer to the valence band, indicating that V is a p-type dopant for WS₂. Additionally, strong hybridization of the band induces a state significantly manifested at the top of the valence band. In contrast, the Re dopant induced a donor state below the conduction band (~ 0.3 eV) (Figure 3b), indicating that Re is an n-type dopant [71]. In this band calculation, a 7×7 supercell was used, with a Re doping concentration equivalent to 2%. As the Re doping concentration increased, the doping state shifted closer to the conduction band edge, indicating that the doping state is strongly dependent on the doping concentration and host material.

Figure 3c shows the band structure of V-doped WSe₂, calculated using an 8×8 supercell. The empty state of the V atom, which was located on top of the valence band in the case of WS₂, shifted below the valence band in WSe₂. A charge transfer occurred between the valence band and the empty state of WSe₂, causing the Fermi level to shift inside the valence band of WSe₂. Thus, V-doped WSe₂ exhibits a strong p-type behavior in TMDCs [51]. The strong hybridization band and the Fermi level location inside the valence band are prominent aspects of understanding the long-range magnetic interactions in V-doped WSe₂ [51].

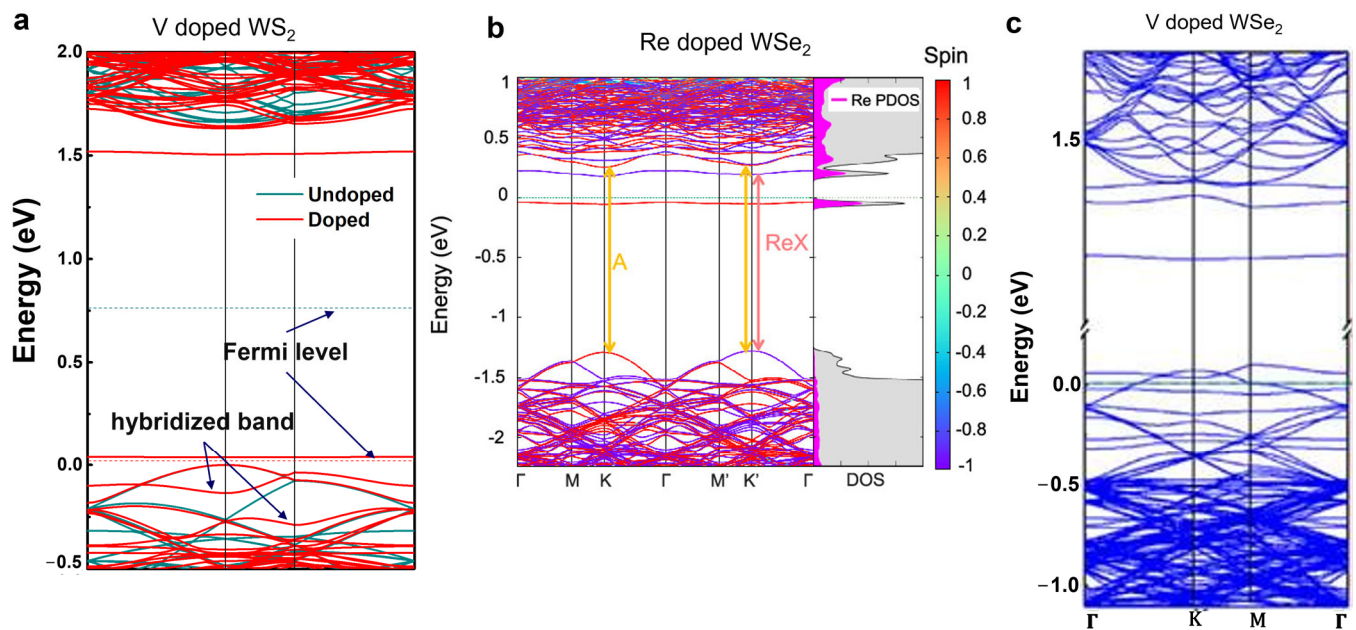


Figure 3. Electronic band structure of pristine and doped TMDs. (a) The band structures of pristine and V-doped WS₂, as V doping Fermi level shifted deeper into the valence band with hole injection. This figure was adapted with permission from Ref. [42]. 2021, Wiley-VCH GmbH, Weinheim, Germany. (b,c) DFT band structures of Re- and V- doped WSe₂. These figures were reprinted with permissions from Refs. [51,71]. 2019, AIP publishing, Melville, New York, NY, USA and 2021, American Chemical Society, Washington, DC, USA.

The doping of TMDCs can significantly enhance device performance: p-type doping improves stability, while n-type doping enhances mobility [72]. These effects can be investigated by fabricating and characterizing doped TMDC-based, field-effect transistor (FET) devices (Figure 4). Unlike the FET configuration of bulk semiconductors, 2D TMDC semiconductors depend not only on carrier types but also on the electrode materials. In addition, the influence of intrinsic neutral defects in TMDCs remain unclear. Therefore, it is necessary to compare pristine and doped materials with the same electrode materials. In this review, we will not discuss the effects of electrode materials; readers are encouraged to refer to particular references for more information [4,53,73–81].

Figure 4a shows the source–drain current (I_{ds}) versus the gate bias (V_g) of pristine and Re-doped WS₂ [41]. No significant change was observed between the two curves. Since the donor state induced by the Re dopants lay far from the conduction band (~ 300 meV), significantly higher than the thermal excitation energy at room temperature (~ 25 meV), we can conclude that this Re-doping had a negligible effect. In contrast, Re-doping in WSe₂ revealed an n-type behavior. The on-current increases and the threshold gate voltage (e.g., the gate voltage that induces a zero source–drain current) shifted towards negative V_g with the increasing Re-doping concentration (Figure 4b). Figure 4c shows the I_{ds} – V_g characteristics of pristine and V-doped WSe₂. The pristine WSe₂ exhibited a p-type behavior with a threshold voltage of -50 V. As the V-doping concentration increased, the threshold voltage shifted toward positive values. The on-current at the negative gate voltages also increased. With further increases in the V concentration, the ability to control the carrier density via the gate shrank and the off-current was concealed due to the presence of a greater number of holes. Similarly, the Nb-doped MoS₂ showed a p-type feature, while the pristine MoS₂ exhibited an n-type behavior (Figure 4d). Both the type of dopant and its concentration, as well as the dopant distribution, had significant influences on the properties of the doped TMDCs. Notably, the dopant distribution varied with the growth method used. Dopants are more uniformly distributed in the materials grown by the CVT method compared to those grown by CVD. For example, the I_{ds} – V_g characteristics of 1%

V-doped WSe₂ grown by CVT resemble those of 10% V-doped WSe₂ grown by the CVD method. We address this issue in detail in a later section.

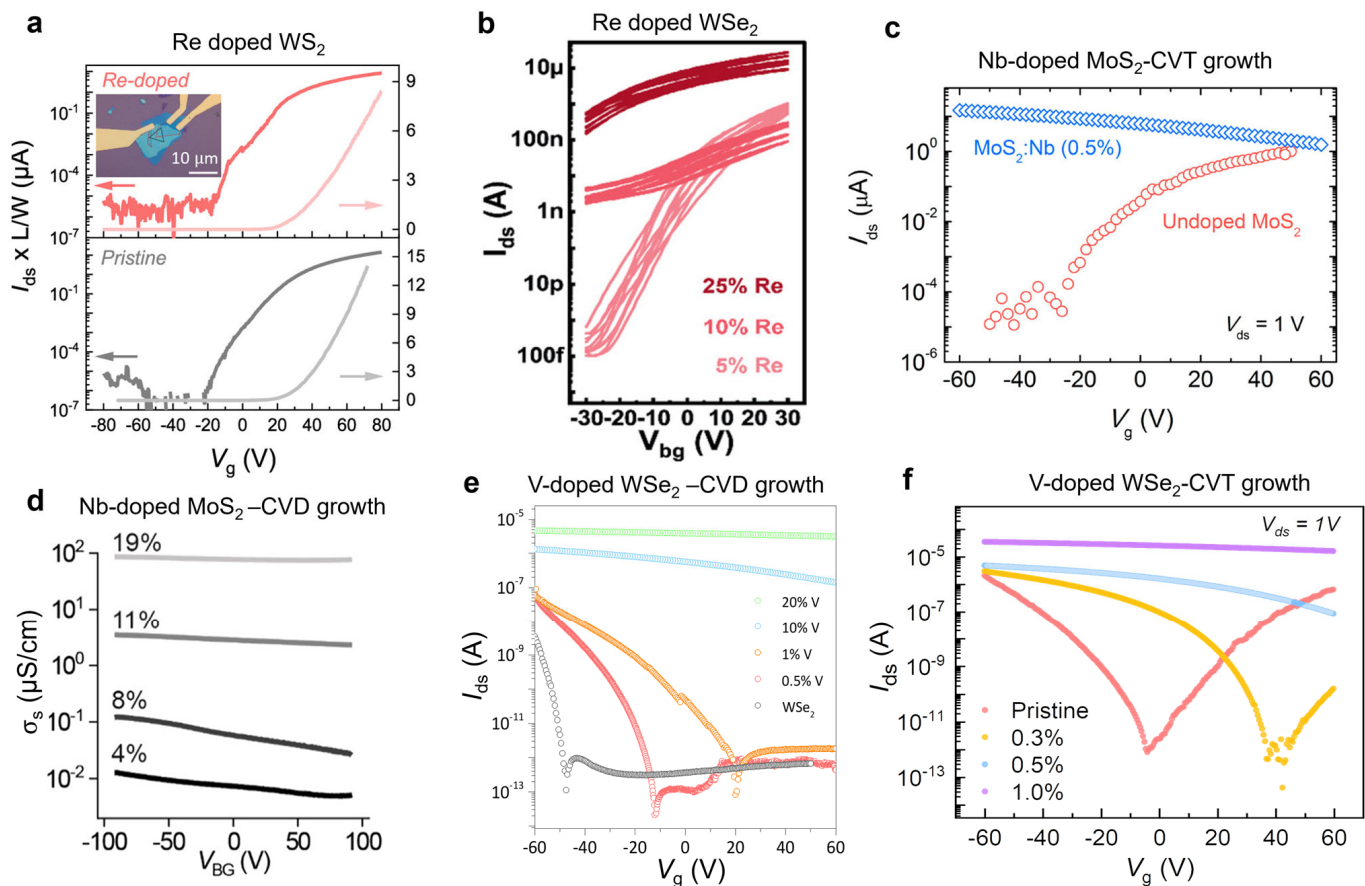


Figure 4. Electronic transport properties. Tunable electrical properties of pristine and doped TMDs grown by CVD and CVT. (a) Typical transport curves of pristine and Re-doped WS₂ monolayer FETs (inset, optical image of the device). This figure was adapted with permission from Ref. [71]. 2021, American Chemical Society, Washington, DC, USA. (b) Transport properties of Re-doped WSe₂, as concentration increases from 5% to 25% the system enters degenerate state from non-degenerate state. This figure was reprinted with permission from Ref. [41]. 2021, Wiley-VCH GmbH, Weinheim, Germany. (c,d) Typical transport curves of pristine and Nb-doped MoS₂. These figures were reprinted with permission from Refs. [27,31]. 2014 & 2020, respectively, American Chemical Society, Washington, DC, USA. (e,f) Transport characteristics of pristine and V-doped WSe₂. These figures were adapted with permission from Refs. [36,50]. 2020, WILEY-VCH GmbH & Co. kGaA, Weinheim, Germany and 2021, American Chemical Society, Washington, DC, USA, respectively.

Furthermore, the doped TMDC channels in Gate-All-Around, Field-Effect Transistors (GAAFETs) present a promising material choice for advancement in semiconductor technology [82,83]. These 2D TMDC materials exhibit excellent electrical properties, particularly a high carrier mobility, which is critical for efficient transistor performance. Doping introduces impurities that increase charge carrier density, enhancing conductivity and reducing power consumption [84,85].

Doped TMDCs improve electrostatic control by optimizing band structure and reducing short-channel effects [85]. Additionally, they allow engineers to tailor the electrostatic properties, reducing band-to-band tunnelling and improving efficiency in low-power applications [85]. However, challenges in doping control and integration with existing technologies remain. Despite these challenges, doped TMDCs in GAAFETs benefitted from enhanced gate control, making them strongly promising candidates for future semiconductor technologies [83].

2.3. Magnetic Properties of Doped TMDCs

Magnetism in 2D TMDC semiconductors is an intriguing research area of condensed matter physics due to its potential applications in low power spintronics, quantum computing, and fundamental quantum physics. These materials, also referred to as diluted magnetic semiconductors, present an opportunity for developing spintronic and quantum devices with enhanced functionality and performance. Antiferromagnetic semiconductors are naturally abundant because antiferromagnetic coupling is a conventional ground state that minimizes energy through the Pauli exclusion principle. In some cases, a ferromagnetic state can also acquire a ground state with minimal energy. However, in such compounds, energy is lost during the state conversion from two degenerate antiferromagnetic states to a non-degenerate ferromagnetic state. As a result, the exchange energy in ferromagnetic semiconductors is usually weaker, leading to low Curie temperatures. CrSBr is such an example of an intrinsic ferromagnetic semiconductor with the highest Curie temperature (T_C) ~ 140 K [86,87].

One approach to developing ferromagnetic semiconductors is to dope these 2D TMDC semiconductors with magnetic elements to induce the magnetic properties. To retain the gate-tunable properties, the doping concentration should be low enough to allow the modulation of the magnetic properties via a gate bias, yet high enough to form long-range magnetic order in real space. To achieve both of these requirements, the Zener band-type structure should be utilized instead of the impurity band-type structure [88]. Although this idea is simple, the best achievement in this research field is Mn-doped GaAs, which has a Curie temperature of ~ 172 K [89,90]. When heavily doped or alloyed in low-band gap semiconductors, such as GaFeSb [91,92] and FeInSb [93,94], TMDC semiconductors exhibit Curie temperatures at room temperature, but their ability to control magnetic properties via a gate bias is quite limited [95].

In this context, the strong hybridization at the edge of the valence band with a free hole, induced by the electron transfer from W to V, makes V a crucial dopant for WSe₂ [51]. These features lead to strong ferromagnetic exchange interactions and T_C s at room temperature. The control of ferromagnetic domains via a gate bias at room temperature was first demonstrated in 0.1% V-doped WSe₂ (CVD grown) on a conventional SiO₂/Si substrate (Figure 5a) [36]. Magnetic force microscopy (MFM) was used in this experiment. Ferromagnetic domains were identified by detecting the magnetic force between the tip and the stray fields induced by the ferromagnetic domains in the material using a two-path technique [36]. Figure 5b shows micrographs of the topology, the phase contrast from the first-path scan (tapping mode phase), and the phase contrast from the second-path scan (MFM phase contrast). The topology image displays a short dendrite shape of a monolayer (with edges belonging to a multilayer), and no contrast difference is observed in the tapping mode image. However, the phase contrast from the second-path scan reveals the magnetic domains in the monolayer, with multilayer features at the edges of the flake. Furthermore, these magnetic domains can be controlled by applying a gate bias (Figure 5c). At room temperature, the domains exhibit a higher contrast under a positive bias (10 V) and disappear when a negative bias (−10 V) is applied, indicating tunability by an applied bias. To check the tunability of the T_C in the ferromagnetic material, the sample was cooled to low temperatures under a negative voltage (−10 V). Ferromagnetic domains appeared at temperatures below 150 K, suggesting that the T_C shifts to lower temperatures with a negative bias. Additionally, ferromagnetic features were also confirmed by electrical transport measurements [96].

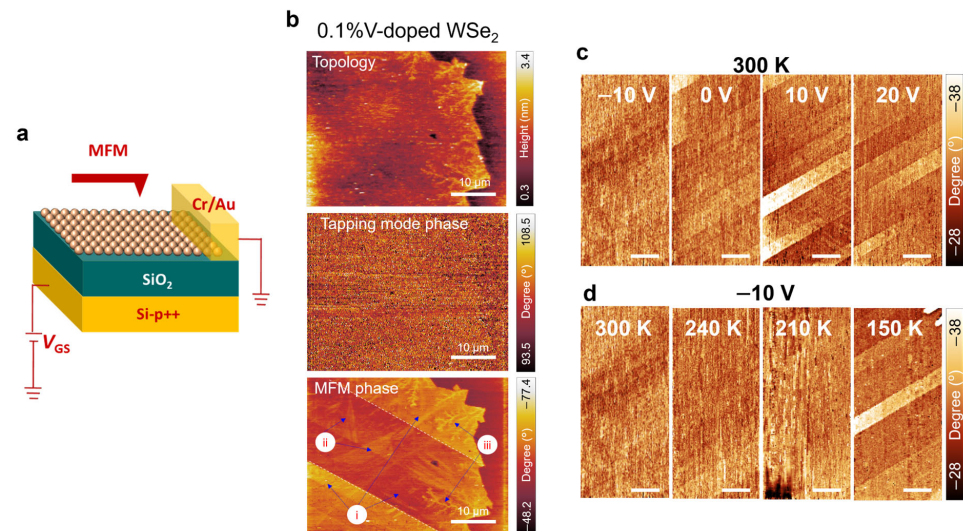


Figure 5. Magnetic properties of V-doped WSe₂. (a) Schematic of the experimental setup for gate-dependent magnetic force microscopy (MFM) measurements. (b) Topology, tapping mode phase, and MFM phase of 0.1%V-doped WSe₂. The **bottom** figures showing various types of domains observed, (i) large domains with clear boundaries (white dotted line), (ii) dendritic patterns in monolayer flake, and (iii) multilayer dendrites. (c) Gate-tunable properties at room temperature. (d) Temperature-dependent magnetic properties at −10 V. This figure was reprinted with permission from Ref. [36]. 2020, WILEY-VCH GmbH & Co. kGaA, Weinheim, Germany.

3. Dopant Distributions in TMDCs

Although the modulation of TMDC properties by dopants has been demonstrated, the main challenge lies in controlling dopant uniformity over a large area. Figure 6a shows the photoluminescence (PL) mapping of a monolayer V-doped WSe₂ grown by CVD. Since V is a strong p-dopant, the PL intensity of the WSe₂ excitons decreases significantly with the increasing V concentration. The PL mapping micrograph reveals variations in intensity, indicating a non-uniform distribution of V in the WSe₂ flake. In contrast, the V-doped WSe₂ monolayer, exfoliated from a single crystal grown by CVT, exhibits relatively high uniformity, at least on the microscale (Figure 6b) [36,50]. Nevertheless, variations in the doping concentration were observed in crystals synthesized by different methods. A recent study on V-doped MoS₂ demonstrated that V atoms can be homogeneously distributed by controlling the vapor sources (Figure 6c) [43], although further research is needed to optimize the conditions for uniform dopant distribution.

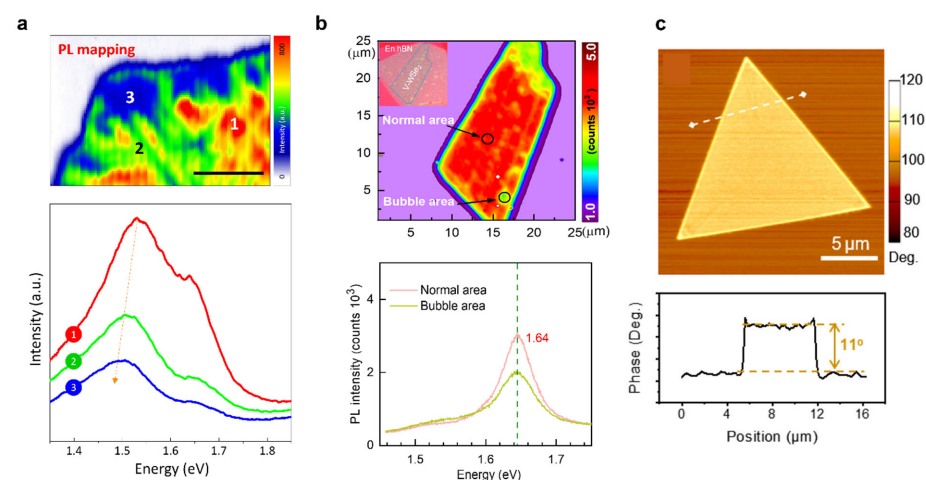


Figure 6. Uniform dopant distribution in TMDCs, illustrated by photoluminescence (PL) mapping of samples. (a,b) PL mapping (top) and the corresponding spectra (bottom) at various spots of V-doped

WSe₂. These figures were reprinted with permissions from Refs. [36,50]. 2020, WILEY-VCH GmbH & Co. kGaA, Weinheim, Germany and 2021, American Chemical Society, Washington, USA. (c) PL mapping of V-doped MoS₂ (**top**), the line drawn from substrate to flake indicating phase of the PL spectra (**bottom**). This figure was adapted with permission from Ref. [43]. 2021, American Chemical Society, Washington, USA.

4. V-Doped WSe₂ Grown by Using CVT Method

In this section, we will describe the details of our CVT method for growing V-doped WSe₂ in our laboratory. These samples have been synthesized, and we have explored their properties, with regard to room-temperature ferromagnetic semiconductors, for over five years [36,37,50,51]. We observed variations in the doping concentration in single crystals, with values ranging up to 50% (e.g., a nominal value of 0.5% (V_xW_{1-x}Se₂)). We found that using a vortex mixer significantly improves the uniformity of the synthesized powder before the single crystal growth step.

4.1. Selection of Ampule and Cleaning

The controlled growth of TMDCs in the CVT method involves sealed ampules made from suitable glass, selected based on the reaction temperature. For TMDCs, synthesis occurs at temperatures ranging from 900 °C to 1100 °C. Therefore, fused quartz is a suitable choice for the ampules, as it remains stable up to 1100 °C (Hanjin Quartz, Seoul, South Korea), even when exposed to the corrosive substances used in TMDC single crystal synthesis.

Prior to beginning the synthesis, it is essential to thoroughly clean all the tools and the quartz ampules to prevent unintended contamination, which can significantly impact the materials' properties, particularly in low-doping concentrations. In our laboratory, we clean the mortar-pestle (used for grinding materials), pellet-maker, vials, and ampules with acetone and IPA, followed by drying them in an oven at 80–100 °C for 12–15 h.

4.2. Step 1: Weighing, Mixing Powders, Vacuum Sealing, and Solid-State Reaction

Single the crystals of TMDCs are typically synthesized from powdered transition metals and chalcogens, the formation of TMDC compounds involves reactions between a stoichiometric mixture of a transition metal and chalcogen elements within a vacuum-sealed ampoule. We used high-purity elements from Alfa Aesar and Sigma Aldrich: purities ranging from 99.99% to 99.999%. These elements are ground into fine powders separately (Figure 5a) and weighed stoichiometrically using weighing paper to minimize material loss and prevent contamination. At this stage, the equivalent of 1–2% of the samples' weight in chalcogen to was added to compensate for chalcogen loss during preparation and to minimize chalcogen vacancies.

The powders were then transferred into vials and mixed using a vortex mixer (Figure 7b) for 2–3 min, to ensure the uniform mixing of the reactant elements. This mixture was then carefully transferred into a pellet maker, where pellets were formed by pressing at 9–10 MPa (Figure 7c). This helps to reduce material loss during vacuum sealing. The pellets were then transferred into a pre-cleaned quartz ampule and sealed with a vacuum of $\sim 10^{-3}$ Torr in a short ampule (10–11 cm), as shown in Figure 7d. The sealed ampule was then transferred to a box furnace (Figure 7e). The raising temperature was raised at a rate of 60 °C/h, held at 900 °C for 48 h, and then cooled to room temperature for approximately 32 h. This temperature profile is shown in Figure 7e. The pre-reaction process yields the growth of polycrystal TMDs.

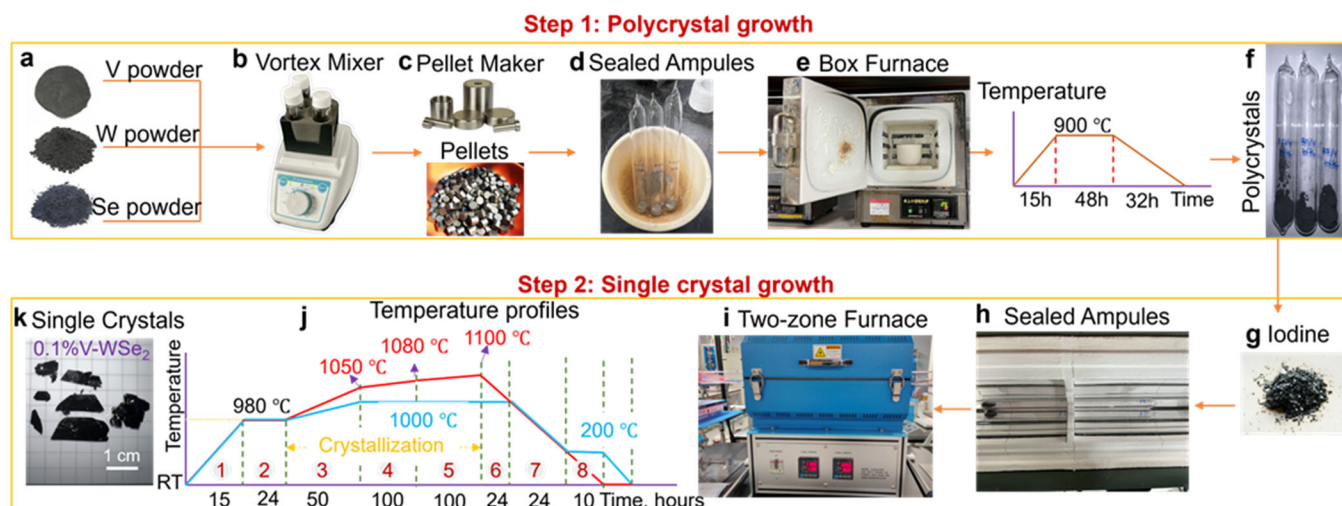


Figure 7. Chemical vapor transport (CVT) growth of doped transition metal dichalcogenides (TMDs) in bulk, involving two steps: polycrystal growth followed by single crystal growth. Step 1: (a) Weighed powders (W, V, and Se) for V-doped WSe₂, (b) mixed with a vortex mixer (b), (c) pressed into pellets at 10 MPa, (d) sealed under vacuum in a quartz ampule (~10 cm long), (e) heated in a box furnace at 900 °C for 2 days, and (f) collected as pre-reacted polycrystals for the next step. Step 2: (g) Iodine was added to polycrystals, sealed under vacuum in a longer quartz ampule (~24 cm) (h), and placed in a two-zone furnace (i) with temperature profiles shown in (j). Single crystals of V-doped WSe₂, on a centimeter scale, were then collected (k).

4.3. Step 2: Single Crystal Growth

The polycrystals obtained in the previous step were carefully removed from the ampules and either transferred into a pellet maker to make pellets under mild pressure ($\ll 0.1$ MPa) or transferred directly into a pre-cleaned quartz ampule. At this stage, a transport agent was added to the ampule before sealing; based on the ampule volume, approximately 5–6 mg/cm³ of iodine (optimized) was added. The ampule was then sealed under a 10^{-3} Torr vacuum. The iodine loss during sealing was negligible, as we used long ampules (23–24 cm). The transport agent, temperature, and temperature gradient are critical for growing high-quality crystals. We optimized the temperature gradient for a two-zone furnace.

Stage 2 in Figure 7 shows the sealed ampoules placed in a two-zone furnace, with the zones namely being the source zone (maintained at a higher temperature) and the growth zone (at a lower temperature). Since the TMDCs' compounds were already pre-reacted at 900 °C, a higher temperature of >950 °C is recommended for single crystal growth. We raised the temperature to 980 °C for WSe₂ in 15 h (1), then held it at 980 °C for 24 h to ensure uniform vaporization throughout the CVT tube (2). For crystallization (3), the temperature was gradually increased to 1050 °C in the source zone and 1000 °C in the growth zone over approximately 50 h, creating a gradient (Δ) = 50 °C. The growth zone temperature was kept constant at 1000 °C, while further (4) increasing the source zone temperature to 1080 °C over 100 h enhances vapor transport, leading to crystallization.

Additionally, (5) raising the source zone temperature to 1100 °C or 1110 °C over the following 100 h resulted in larger crystals with higher crystallinity. Afterward, the source zone was cooled to the growth zone's temperature over one day (6). Both zones were then cooled to 200 °C over 24 h at the same cooling rates (7). Finally, (8) the growth zone was maintained at 200 °C while the source zone was cooled to room temperature. This reverse gradient helps diffuse iodine from the grown crystals back to the source zone.

4.4. Extraction of Crystals from Ampoules and Removing Transport Agent

After CVT growth, the ampoule was carefully removed from the furnace. It must be opened inside a fume hood or a glovebox, especially in cases involving air-sensitive

materials. The crystals should be carefully extracted from the ampoule and transferred to vials. The remaining iodine on the grown crystals can be removed in two ways: by rinsing in organic solutions or by heating in a vacuum oven. We heated the crystals in a vacuum oven for several hours at 80–100 °C.

5. Challenges and Opportunities with Doped TMDCs

5.1. Searching for Universal n- and p-Type Dopants

V, Nb, and Ta are three common p-type dopants for TMDCs. Stronger p-type doping is also useful for improving contact resistance. Ti, Zr, and Hf are potential candidates for this purpose. In contrast, there are fewer studies on strong n-type dopants. While Re is an n-type dopant, it is considered weak because its doping state is relatively far from the conduction band. Therefore, developing new n-type dopants remains an open area of research.

5.2. Uniformity Controls the Dopant Distributions

As discussed above, dopants are randomly distributed within host materials. Therefore, developing methods to synthesize uniformly doped TMDCs is crucial. The CVT approach, with its thermodynamically controlled growth at higher doping levels, presents challenges in achieving uniformity. In contrast, methods like CVD, MOCVD, and MBE may give better opportunities for controlling uniformity. Developing new precursors for these approaches is a key task for chemists and materials scientists.

5.3. Understanding the Mechanism of Long-Range Magnetic Order in Magnetic, Doped TMDs

The results of this study provide concrete evidence regarding a room-temperature, long-range, ferromagnetic semiconductor in V-doped WSe₂, below a 0.5% V-doping concentration, equivalent to ~5 nm of the dopant distance. The mechanism behind establishing a long-range, ferromagnetic order at room temperature over such a long distance is of great interest for investigation. The intriguing question of why magnetic order is established at higher temperatures in 2D TMDCs compared to bulk materials remains unresolved. It has been observed that magnetic order also occurs in twisted bilayer TMDCs, where the periodic potential is ~10 nm [17], but this order is only observed at low temperatures.

5.4. Designing Different Doping Types for Diverse Applications

The advantage of the two-dimensional form of TMDCs contributes to the high-efficiency quantum emitters [97–102]. Nevertheless, the origin of quantum emitters in TMDCs induced by strain remains unknown. Dopants that create mid-gap states in TMDCs can induce single-quantum emitters. By selecting a suitable dopant in TMDCs paves the way to introduce new quantum emitters. This research direction is intriguing, and it is not straightforward to determine which dopants will be most effective for this purpose. Mid-gap states can also be useful for designing the photovoltaic cells that exceed the Queiser-Schottky limit [103–106]. The atomic-thin nature of TMDCs is advantageous for tunneling junctions, which can help overcome the low-efficiency charge transport in quantum dots.

A critical area of research for enhancing the impact of TMDCs in diverse applications is the quest for universal n- and p-dopants for MoS₂, WS₂, MoSe₂, and WSe₂. Universal dopants are expected to provide consistent doping behaviors across different TMDCs, making it easier to tune their electrical characteristics for various applications. These dopants must be feasible and scalable for industrial applications, have electronic states that align well with the host TMDC's band structure to provide the desired type of carrier, be thermally stable to retain their properties under operating temperatures and conditions, and chemically bond well within the host lattice to avoid significant disruption or defect formation.

6. Conclusions

The experimental growth of doped 2D TMDC semiconductors offers potential advancements for future applications in electronics, spintronics, and quantum computing. Synthesis techniques, such as CVD and CVT, allow for precise doping control, enabling tunable properties like ferromagnetism and enhanced semiconducting characteristics. Doping TMDCs also enables the development of next-generation nanoscale transistors and quantum emitters. However, challenges such as achieving a uniform dopant distribution over a large area of monolayer still persists. In low-doping regimes, CVD-grown materials often exhibit non-uniformity, highlighting the need for refined growth techniques, like those used in CVT. Further research into doping processes, new dopant combinations, and the structural and electronic properties of doped TMDCs is essential for advancing TMDC-based technologies and creating more efficient, scalable devices.

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