

Advancements in the Preparation and Application Research of TMDCs

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Abstract: Two-dimensional transition metal dichalcogenides(TMDCs)have been widely applied in the fields of light, electricity, magnetism, and heat due to their excellent physicochemical properties, including high photoluminescence quantum yield, outstanding thermal conductivity, good mechanical flexibility, and high charge carrier mobility. Tungsten disulfide (WS_2) is a typical TMDCs, and optimizing its crystal structure and achieving high-quality large-area synthesis are of great significance for realizing its large-scale applications. This paper introduces the structure and electronic properties of tungsten disulfide, provides a comprehensive review of its main preparation methods, and summarizes its research progress in various application fields. Finally, the future development directions in the field of two-dimensional materials, including tungsten disulfide, are discussed, emphasizing the importance of further research and development to promote their widespread applications in various fields.

Keywords: Two-dimensional transition metal dichalcogenides; tungsten disulfide; two-dimensional materials.

1. Introduction

Two-dimensional Transition Metal Dichalcogenides (TMDCs) possess unique structural properties and exhibit remarkable advantages. The single-atom thickness confers excellent mechanical flexibility to the material [1], while demonstrating outstanding electrical conductivity on a two-dimensional plane [2], making it a highly sought-after material in electronic devices and nanotechnology [3]. Monolayer materials exhibit superior optical properties, displaying outstanding performance in light absorption and transmission, providing broad application prospects in optoelectronics and sensors, among other fields [4]. Its distinctive two-dimensional structure not only endows it with enormous potential in flexible electronics and nanoelectronics but also provides robust support for the design and synthesis of new materials [5]. Achieving large-scale production is a prerequisite for application. Among these methods, chemical vapor deposition (CVD) is a commonly used and effective approach. It involves introducing precursor gas molecules of tungsten disulfide into a reaction chamber at high temperatures to deposit it on a substrate surface, forming a monolayer structure. Additionally, methods such as solution-based techniques and mechanical exfoliation are widely employed in the preparation of TMDCs. These methods offer feasible pathways for their application in electronics, optics, nanotechnology, and other fields. With continuous technological innovation, the preparation methods of TMDCs are expected to be further optimized, laying a more solid foundation for their widespread applications across various domains in the future.

2. Properties and Structure of TMDCs Materials

The chemical formula of transition metal dichalcogenides can be expressed as MX_2 , where M represents a transition metal atom such as Mo, W and X represents a chalcogen atom. TMDCs have a typical layered structure, with relatively weak

van der Waals forces between layers and strong covalent bonds within each layer. Each monolayer of TMDCs, the transition metal layer, is sandwiched between two chalcogen layers, forming a sandwich-like structure. Classic semiconductor materials like MoS_2 and WS_2 have bandgap widths ranging from 1 eV to 2 eV [6], and the bandgap width gradually increases as the number of layers decreases. When reduced to a monolayer, it transitions from an indirect bandgap structure to a direct bandgap structure [7].

3. Preparation Methods of TMDCs

The application value in the semiconductor field has made the preparation of high-quality and large-area TMDCs a current focus of research [8]. WS_2 is a typical two-dimensional transition metal dichalcogenide, the preparation methods for two-dimensional nanostructured WS_2 can be classified into 'top-down' and 'bottom-up' approaches based on different tungsten sources. The 'top-down' approach typically involves mechanically or liquid-phase exfoliating bulk WS_2 into two-dimensional nanostructured WS_2 , while the 'bottom-up' approach usually employs chemical vapor deposition and hydrothermal methods to synthesize two-dimensional nanostructured WS_2 from small-molecule tungsten precursors through chemical reactions.

3.1. Top-Down Physical Exfoliation Method

The mechanical exfoliation method belongs to the 'top-down' approach. There are relatively weak van der Waals forces between adjacent layers of WS_2 [9]. By mechanically disrupting the interlayer forces, single or few-layer two-dimensional WS_2 nanosheets can be obtained. Dong [10] and others repeatedly peeled off block-like WS_2 using specific tape to obtain well-shaped single-layer and few-layer WS_2 . Characterization revealed a positive correlation between the number of layers and the adhesion time of the tape to the block-like WS_2 . Liu [11] and colleagues attached block-like WS_2 to specific tape, folded it, and adhered it to a polydimethylsiloxane (PDMS) substrate. Peeling off the tape revealed a single-layer WS_2 observed under an optical microscope. The mechanical exfoliation method achieves

two-dimensional nanostructured WS_2 with minimal defects while preserving the crystallinity of block-like WS_2 to the greatest extent [12]. However, this method has low production efficiency, poor controllability, and is not suitable for large-scale production, having certain limitations in practical applications. In 2019, Zhang et al [13] proposed a method inspired by the failure principle of solid lubricants, named as intermediate-assisted mechanical exfoliation (iMAGE). This method cleverly converts vertical pressure into horizontal shear force by adding a force transfer agent as an intermediate for force transmission, opening up the weak

van der Waals forces between layers, and thus achieving the efficient exfoliation of two-dimensional materials. The exfoliation rate is as high as 67%, the yield is up to 0.3gh^{-1} , the energy consumption is as low as $3.01 \times 10^6 \text{Jg}^{-1}$, and the exfoliated material has a large lateral size with ideal integrity. The production speed and energy consumption are improved by one to two orders of magnitude compared to previous results. Moreover, this method is applicable to most two-dimensional materials, providing a constructive guidance for the large-scale high-quality exfoliation preparation of two-dimensional materials.

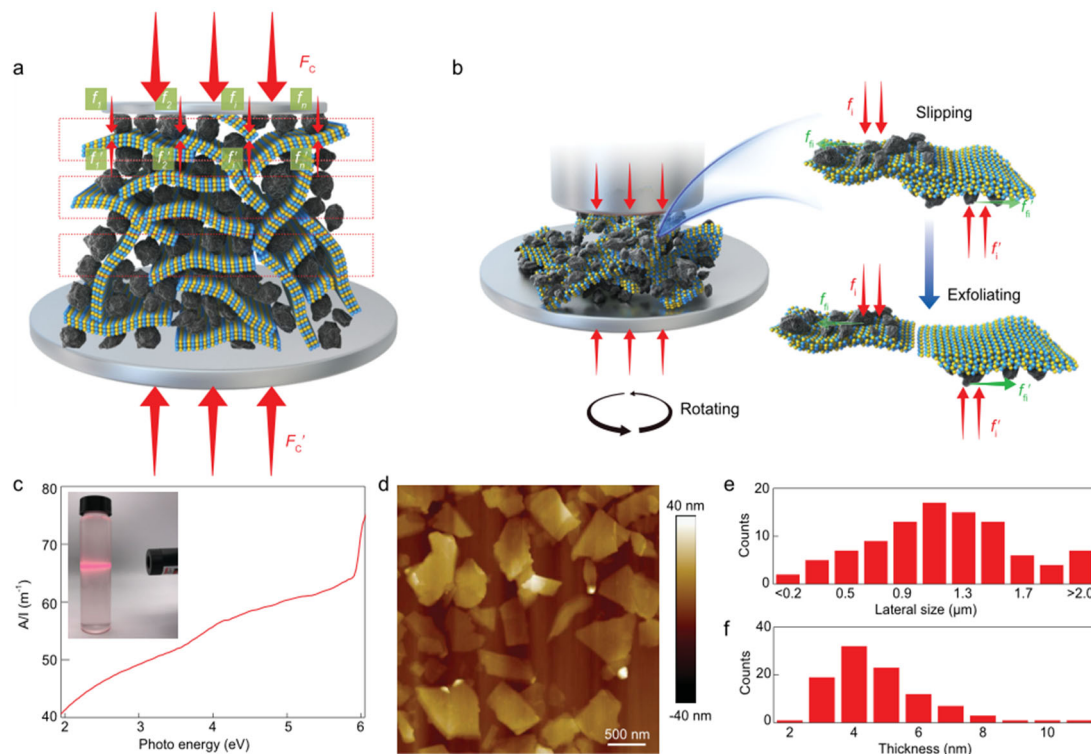


Figure 1. (a b) Schematic diagram of the iMAGE method. (c) Absorption spectrum of exfoliated two-dimensional h-BN dispersed in deionized water. (d e) Statistical analysis of the lateral size and thickness of two-dimensional h-BN [13]

3.2. 3.2 Bottom-Up Hydrothermal Method

The hydrothermal method belongs to the 'bottom-up' preparation approach. Typically, the hydrothermal method involves dissolving raw materials such as sulfur and tungsten sources in water, stirring and mixing them uniformly, transferring the mixture into a sealed pressure vessel, heating it to different temperatures, maintaining the temperature for a certain duration, and finally centrifuging, washing, and drying the reactants to obtain two-dimensional WS_2 [14]. Govindasamy et al [15] used tungsten hexachloride as the tungsten source and thiourea as the sulfur source, reacting them at a hydrothermal temperature of 270°C for 24 hours to obtain two-dimensional WS_2 nanosheets. The porous structure of the two-dimensional WS_2 nanosheets exhibits a huge specific surface area. Moreover, the synthesis of WS_2 with different morphologies can be achieved by controlling the type of added surfactants. Wu et al [16] utilized sodium tungstate and L-cysteine as the tungsten and sulfur sources, respectively, and under a hydrothermal temperature of 200°C , obtained rod-shaped WS_2 assembled from two-dimensional WS_2 nanosheets with a diameter of 420 nm and a length of 2

μm . The hydrothermal method can produce WS_2 with different morphologies and good uniformity by adjusting parameters such as temperature, time, and raw material ratios. Additionally, it does not pollute the environment under closed conditions and does not introduce impurity ions, contributing to the enhancement of WS_2 purity.

Various morphologies of WS_2 nanostructures were prepared through the hydrothermal synthesis method assisted by surfactants. By adding different surfactants, such as cetyltrimethylammonium bromide (CTAB) and polyethylene glycol (PEG), to the reaction solution, the morphology and size of WS_2 were successfully controlled. The addition of CTAB facilitated the formation of nanosheet structures, while the use of PEG resulted in the formation of nanofiber structures. These nanostructures were optimized and purified during the hydrothermal reaction by adjusting the pH, heating, and subsequent washing and drying steps. This work not only provides a new perspective for the synthesis of tungsten disulfide nanostructures but also offers a possible application pathway for the nanostructure synthesis of other transition metal sulfide materials [25].

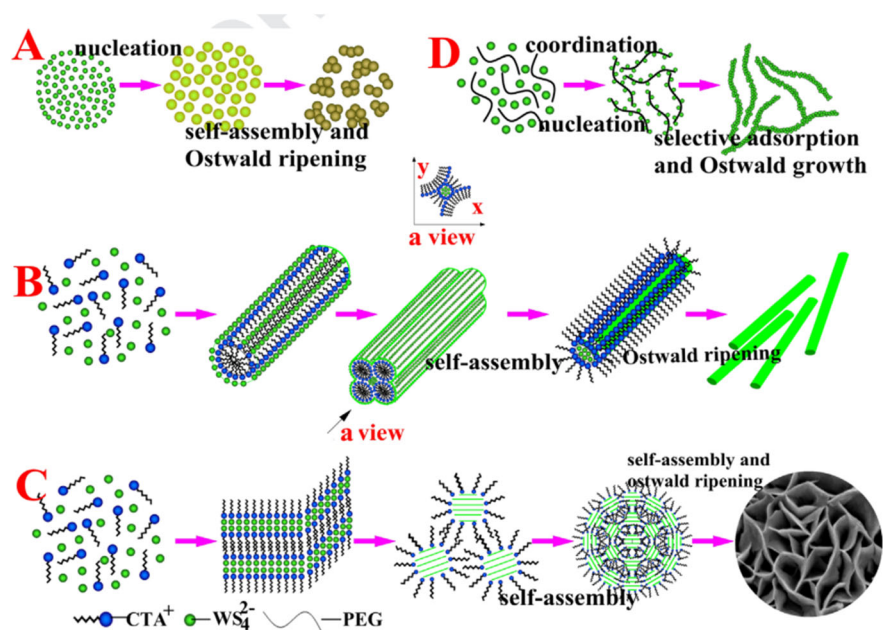


Figure 2. Schematic diagram of WS₂ samples in different morphologies [14]

3.3. Bottom-Up Chemical Vapor Deposition (CVD)

Chemical Vapor Deposition (CVD) is a process where gaseous or vapor-phase substances undergo reactions at the gas-solid interface to generate solid deposits. Due to the challenges in controlling the concentration of solid precursors and the dynamic non-uniform growth in space, achieving large-scale production of TMDCs with good uniformity and repeatability poses significant challenges, greatly hindering their practical applications. Tang et al [17] proposed an improved method called Vertical Chemical Vapor Deposition (VCVD). As the name suggests, this method involves optimizing and modifying the equipment for fabricating thin film materials by transforming the furnace pipeline from a horizontal to a vertical direction. The goal is to achieve the uniform and high-quality growth of two-dimensional film materials by optimizing the concentration of reactants and properly allocating gas flow and temperature within the pipeline. In VCVD, the furnace is vertical, and the airflow is from top to bottom. The vertical design of the furnace and airflow redistributes the temperature field, ensuring uniform gas flow in the space. It eliminates position-dependent growth. The VCVD system uses gaseous H₂S and Ar-bubbled metal precursors instead of traditional solid precursors to overcome the problem of precursor concentration gradients. The vertical design of the furnace and airflow in the VCVD system redistributes the temperature field, ensuring uniform gas flow in the space. Unlike the turbulent and uneven airflow chamber in the precursor gas of the HCVD system, which forms random nucleation sites and leads to unstable growth conditions, the VCVD system maintains a stable and uniform gas flow throughout the growth chamber. The VCVD system addresses issues related to uncontrollable particle size, higher defect density, and uneven distribution caused by factors such as nucleation density, source concentration, and temperature distribution in HCVD, where the airflow chamber is turbulent and non-uniform, forming random nucleation sites and leading to unstable growth conditions. In contrast, the VCVD system maintains a uniform and stable airflow speed throughout the entire growth chamber. The VCVD system resolves the issues of small product particle size, higher defect

density, and uneven distribution caused by uncontrollable factors such as nucleation density, source concentration, and temperature distribution.

Kyung Nam Kang et al [18] focused on the CVD growth technology of WS₂ monolayer films. Continuous WS₂ monolayer films were grown at the millimeter scale using the CVD method, and the influence of H₂ concentration on the growth process was investigated in detail. Innovatively, the phenomenon of SiO₂ substrate etching occurred at low H₂ concentrations, and its causes were discussed. High H₂ concentrations resulted in the etching of the grown WS₂ crystals. These observations not only contribute to understanding the growth mechanism of WS₂ but also provide important chemical reaction insights for optimizing the CVD process. A new growth mode of single-crystal monolayer WS₂ was proposed, and a sequential growth model was established to explain the observed phenomena. These findings are of great significance for understanding and controlling the growth of TMDCs and provide new perspectives and methods for further material development and applications.

3.4. Bottom-Up Atomic Layer Deposition (ALD)

Atomic Layer Deposition (ALD) is a sophisticated thin-film fabrication technique that allows precise control of the thickness and composition of films at the atomic level. In the ALD process, chemical vapor precursors react sequentially, forming a film on the substrate with the addition of one layer of atoms or molecules per reaction cycle. This process precisely regulates the thickness and composition of the film, making it well-suited for the fabrication of nanostructures and high-quality thin film materials, enabling the precise control of material construction at the molecular level.

During the Atomic Layer Deposition (ALD) growth process of WS₂, the growth mechanism is influenced by nucleation density and film thickness. When the film thickness is less than 5.6 nm (8 layers), the lateral growth mechanism predominates, indicating that the WS₂ film mainly expands horizontally along the substrate surface. However, when the film thickness exceeds 20 nm, the vertical growth mechanism begins to dominate, manifesting as growth perpendicular to the substrate surface [19].

Understanding and optimizing the deposition conditions for the growth mechanism have ultimately led to the realization of WS₂ films with larger particle sizes. These films exhibit excellent electronic performance, and the fabricated WS₂-based field-effect transistors (FETs) demonstrate high electron mobility and a high switch current ratio. This is of great significance for the development of various applications such as supercapacitors, batteries, sensors, and catalysts.

4. Application of Two-Dimensional Transition Metal Dichalcogenide WS₂

TMDCs are a type of bipolar semiconductor with n-type and p-type semiconductor characteristics [20]. Heterojunctions formed by stacking layered WS₂, such as graphene and other special two-dimensional materials, exhibit unique physical properties, greatly advancing the development of layered tungsten disulfide in optoelectronics [21], electronic devices [22], the photovoltaic industry [23], and the field of transistors [24]. Yang et al [25] used Ni as a texture promoter for layers, employing the van der Waals rheological method (vdWR) to grow high-quality wafer-scale independent WS₂. By utilizing the hydrophobicity of WS₂ and the hydrophilicity of sapphire, wafer-level transfer of vdWR-grown WS₂ onto different substrates was achieved for the first time using a non-destructive etching technique. Transferring p-type WS₂ at room temperature onto n-type GaN produced high-quality p-n junctions, with a leakage current density of 29.6 μA/cm² at -1V, exhibiting superior performance compared to directly grown WS₂/GaN heterojunctions, significantly expanding the application of WS₂ thin films in electronic and optoelectronic devices.

TMDCs materials have advantages such as high electron mobility and a large on/off ratio. They can be applied in field-effect transistors, and further discussions and explorations of their electrical transport characteristics are conducted. Hwang et al [26] first used two-dimensional WS₂ nanosheets to fabricate field-effect transistors, demonstrating that the existence of the layered WS₂ bandgap leads to high on/off ratios and saturation currents at room temperature. Compared to silicon, WS₂ has a higher electron mobility, making it a potential material for low-energy field-effect transistors. Zheng et al [27] used an ultra-thin Al₂O₃ interfacial layer between metal and WS₂ to reduce the Schottky barrier height (SBH) of the source and drain (S/D) contacts in WS₂ field-effect transistors (FETs). The most significant reduction in SBH was achieved with an Al₂O₃ layer thickness of 1.1 nm. The presence of the Al₂O₃ capping layer significantly increased the conduction current and enhanced the field-effect mobility of WS₂ FETs.

In the field of sensors, the advantages of two-dimensional TMDCs mainly manifest as follows: (1) High specific surface area of the structure can enhance the concentration detection range; (2) High strength and toughness can be used to fabricate flexible sensor devices; (3) Relatively high surface chemical activity can improve the detection sensitivity and recognition of chemical molecules through surface modification; (4) High electron mobility can enhance the response rate of devices, and semiconductor characteristics provide good switching responses for devices. These unique properties endow two-dimensional TMDCs with tremendous potential for ultra-high sensitivity and rapid-response sensors [28]. The electrical signals of FET devices are extremely

sensitive to changes in the surface state of TMDCs. He et al [29] prepared thin films of mechanically exfoliated single-layer or multilayer WS₂ to fabricate FET devices used in NO gas detection. The results indicate that the lowest detection concentration can reach 0.013 mg/m³.

5. Summary

Layered transition metal dichalcogenides (TMDCs) have undergone rapid development in the past decade, and the methods for preparing two-dimensional nanostructured WS₂ have become more diversified, expanding their applications. In this review, we explore various preparation methods for WS₂ in different two-dimensional TMDCs. From mechanical exfoliation to chemical vapor deposition (CVD), each method demonstrates its unique advantages and limitations. Mechanical exfoliation is favored for its simplicity and minimal damage to material structure, but its batch production capability is limited. In contrast, CVD shows tremendous potential in terms of yield and controllability, although it requires more sophisticated process control and comes with higher costs. Future research may focus on reducing costs, improving efficiency, and developing more environmentally friendly preparation methods. The preparation techniques of TMDCs are not only significant in the field of materials science but also lay the foundation for advancements in various application areas such as electronics, energy, catalysis, sensors, and more. With the continuous maturation and optimization of these technologies, WS₂ and its TMDCs-based composite materials are expected to have broader and more profound application prospects in the future.

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