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Review Monolayer transition metal disulfide: Synthesis, characterization and applications



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1. Introduction

In the past few years, considerable attention has been paid to graphene, composed of a single layer of carbon atoms in a two dimensional (2D) honeycomb lattice, exhibiting extraordinary electronic, optical and mechanical properties [1-3]. The discovery of graphene encourages the continuous exploration of other kinds of 2D nanomaterials, for example, 2D TMDCs [4-6]. TMDCs can be described by the formula of MX₂, in which M could be the transition metal molybdenum (Mo) or tungsten (W), and X could be the chalcogen sulfur (S) or selenium (Se). The layers of MX₂ consist of hexagonal structures, with Mo and S atoms alternately located at the hexagon corners. There are three structural polytypes of MX_2 layered-structure: 2H (hexagonal symmetry, trigonal prismatic coordination, two layers in each repeat unit), 3R (rhombohedral symmetry, trigonal prismatic coordination, three layers in each repeat unit) and 1T (tetragonal symmetry, octahedral coordination, one layer in each repeat unit), with the interlayer spacing is \sim 0.7 nm [7]. Originally, 3D MX₂ compounds are among the most interesting classes of materials, because of their extraordinary performance in semi-conductivity, superconductivity [8], charge density wave [9], and so on. The potential application could be found in the areas including lubrication [10], catalysis [11], photovoltaics [12], supercapacitors [13] and rechargeable battery system [14,15]. Recent researches have already confirmed that an indirect band gap in bulk MX₂ materials could be dramatically tuned to a direct band

ABSTRACT

Two-dimensional transition metal dichalcogenides (2D TMDCs) has aroused tremendous attention in recent years, because of their remarkable properties originated from their unique structure. In this review we report the synthesis, characterization and applications of monolayer MoS₂ and WS₂. © 2016 Chinese Materials Research Society. Production and hosting by Elsevier B.V. This is an open access

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gap, when scaled down to monolayer. Therefore, unlike semimetal graphene with a zero band gap, 2D MX₂, including MoS₂, WSe₂ and WS₂, exhibits a direct band gap [16]. For example, monolayer MoS₂ exhibits a direct band gap of \sim 1.6 eV, and the unusual electronic structure and the unique optical properties are attributed to the characteristics of the D-electron orbitals of MoS₂ [16,17]. As it is scaled down to monolayer, the maximum of the valence band at the Γ point shifts downward to the K point of the Brillouin zone [18–20], leading to special semiconductor properties [7,21,22]. The On/Off ratio of monolayer MoS₂-based field effect transistor (FET) was reported to be close to 10⁸ at room temperature [23]. Furthermore, the single-layer MoS₂ transistor shows better electric and photoresponse performance compared to graphene-based devices [24]. 2D MX₂ have also been employed in many other applications such as catalysis [6,25], optical devices [26], solid lubricants [27], batteries [28], biological systems [29-32] and so on. With such attractive properties and promising potential applications, various efforts have been contributed to prepare single-layer MX₂ materials. Methods such as mechanical exfoliation [33,34], liquid exfoliation [35,36], electrochemical Li-intercalation, exfoliation and chemical vapor deposition (CVD) [18,20] have been reported to approach controllable monolayer MX₂ synthesis. However, the access towards reliable monolayer synthesis is still need to be explored and consummated.

2. Synthesis

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To fully explore the potential applications of 2D MX₂ on device fabrication, it is essential to realize reliable approaches towards atomic

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2D MX₂ synthesis. So far, various methods have been employed to the synthesis of 2D MX₂ materials. These methods can be divided into two sorts: physical methods and chemical methods. The most common physical method is mechanical exfoliation, which is an easy and simple method to obtain monolayer sample. CVD method is so far the most practical method toward monolayer MX₂ synthesis. Hereon, we focus on these two methods to introduce the synthesis of mono-layer MX₂.

2.1. Mechanical cleavage

Since Novoselov et al. successfully exfoliated various singlelayer 2D materials from the layered bulk materials such as graphite, BN and MoS_2 [2,37], mechanical exfoliation method has become a widely-used way to obtain 2D monolayers. The key procedure of mechanical exfoliation method is to rub a fresh bulk material surface against a target surface [38]. The obtained singlelayer structure could be confirmed by various characterization methods, such as optical microscopy, Raman spectrometer, photoluminescence, atomic force microscopy (AFM) and so on. The obtained single-layer nanostructure has the same crystal structure as that in their bulk form, as well as its stability. It could survive on the target surface under ambient conditions for several weeks. which is enough to study their physical and chemical properties by the electronic and optical devices. Mechanical exfoliation has been among the most popular routine methods applied to the synthesis of 2D nanostructures [39–41]. Fig. 1a shows the optical image of thin MoS₂ films deposited on the SiO₂/Si substrate via mechanical exfoliation method [40]. The AFM height profile across the selected area in Fig. 1a demonstrates the different thickness along the blue line, referring to the different layer number in the mechanical-cleavage flakes, as shown in Fig. 1b. Mechanical



Fig. 1. (a) The optical image of the mechanical-cleavaged MoS₂ thin films deposited on the SiO₂/Si substrate [40]. (b) The AFM height image taken from the area indicated by dotted lines in figure (a). The height profile in green reveals the different thickness across the deposited thin film [40]. (c) Schematic diagram of the CVD system applied for the synthesis of monolayer WS₂ under ambient pressure [42]. (d) Optical image of as-synthesized WS₂ on SiO₂ (300 nm)/Si substrate, the inset presents a fine-shaped triangular monolayer WS₂ [42]. (e) AFM image of an as-synthesized triangular WS₂. The height profile demonstrates the thickness of the domain is ~0.92 nm [42].

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