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Two-dimensional MoS_2: Properties, preparation, and applications

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Abstract

Graphene-like two-dimensional (2D) transition metal dichalcogenides (TMDCs) have been attracting a wide range of research interests. Molybdenum disulfide (MoS_2) is one of the most typical TMDCs. Its particular direct band gap of 1.8 eV in monolayer and layer dependence of band structure tackle the gapless problems of graphene, thus making it scientific and industrial importance. In this Review, we attempt to provide the latest development of optical and electronic properties, synthesis approaches, and potential applications of 2D MoS_2. A roadmap towards fabricating hybrid structures based on MoS_2 and graphene is highlighted, proposing ways to enhance properties of the individual component and broaden the range of functional applications in various fields, including flexible electronics, energy storage and harvesting as well as electrochemical catalysis.

Keywords: Two-dimensional; Transition metal dichalcogenides; Molybdenum disulfide; Chemical vapor deposition; van der Waals heterostructure

1. Introduction

Graphene, which is a typical two-dimensional (2D) layered material, has experienced its brilliant age since it was first mechanically exfoliated from three-dimensional (3D) graphite in 2004 [1]. Many strikingly highlighted properties, such as its high transparency (97.7% transmittance in the visible spectrum), high thermal conductivity at room temperature (3×10^3 W/m K), high electrical conductivity (~$10^4\ \Omega^{-1}\ cm^{-1}$), high Young's modulus (1.1 TPa) and high specific surface area (2630 m^2/g) have been identified in monolayer graphene [2,3]. All these extraordinary properties benefit graphene for various applications, including transparent electrodes [4], energy storage [5], solar cells [6,7], wearable devices [8] and catalysis [9]. Graphene is defined as a semi-metallic material because of its special π−π* band structure. The conduction band and valence band are symmetrical about Dirac point, so its electronic properties near K point can be described with Dirac equation, not Schrodinger equation. The Fermi surface is just the intersection point of the conduction band and valence band, making graphene to be a zero gap material [1]. This unique structure gives graphene extremely outstanding electrical property, while limits its applications in logical circuits for low-power electronic switching.

Recently, researchers have been refocusing on other graphene-like 2D materials, aiming at overcoming the shortage of graphene and broadening its range of applications [10,11]. 3D bulk materials possess similar traits to obtain their corresponding 2D layered materials [12]. The melting temperature of these materials is higher than 1000 °C, and they should be both chemically inert and surface stable at room temperature. Generally, 2D insulating and semiconducting materials are more likely to be obtained due to the intrinsic chemical activity of most metallic materials. Graphite, hBN and molybdenum disulfide (MoS_2) stand out in this

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competition, which are all widely used as lubricants at first. hBN is electrical insulator and widely used as gate dielectrics in capacitors [13]. Due to the widespread in nature as molybdenite, MoS_2 has been one of the most studied layered transition metal dichalcogenides (TMDCs). Monolayer MoS_2 is a semiconductor with a direct bandgap of 1.8 eV [10]. This property of MoS_2 is inspiring, which will largely compensate the weakness of gapless graphene, thus making it possible for 2D materials to be used in the next generation switching and optoelectronic devices. Thus far, MoS_2 has achieved primary progress in the following fields, including energy conversion [14] and storage [15] and hydrogen evolution reaction (HER) [16]. Additionally, MoS_2 with odd number of layers could produce oscillating piezoelectric voltage and current outputs, indicating its potential applications in powering nanodevices and stretchable electronics [17].

In this Review, taking MoS_2 as a benchmark material, we attempt to give a basic outlook of the large family of 2D TMDCs, highlighting their interesting physical properties that are most relevant in device applications and systematically introducing the recent process in the preparation methods, including exfoliation and chemical vapor deposition (CVD). Finally we delineate and categorize a series of emerging applications of MoS_2, such as field-effect transistors (FETs), memory devices, photodetectors, solar cells, electrocatalysts for HER, and lithium ion batteries.

2. Properties

TMDCs, whose generalized formula is MX_2 (M = Transition metal (Ti, Zr, Hf, V, Nb, Ta, Mo, W, Tc, Re, Co, Rh, Ir, Ni, Pd, Pt), X = Chalcogen (S, Se, Te)), have a large family of materials and their electronic characters could be semiconducting, metallic and superconducting [12]. We focus on the most widely and stable existing semiconducting MoS_2 for introduction. In the single layer of MoS_2 films, Mo (+4) and S (−2) are arranged to a sandwich structure by covalent bonds in a sequence of S−Mo−S [18], whereas the sandwich layers are interacted by relatively weak van der Waals forces (Fig. 1a). Generally, each layer has a thickness of ~0.65 nm. Monolayer MoS_2 with trigonal prismatic polytype is found to be semiconducting (referred to as 2H), while that with octahedral crystal symmetry configuration (referred to as 1T) is metallic (Fig. 1b) [19]. Very similarly to graphene, MoS_2 is mechanically flexible with a Young's modulus of 0.33 ± 0.07 TPa [20].

2.1. Raman spectra

Raman spectra is a convenient characterization method to illustrate the evolution of structural parameters in layered materials in changing from the 3D bulk blocks to the 2D van der Waals bonded constructions, which has been popularly used to study the quality and layer number of graphene. Similarly, early in 2010, Changgu Lee's group has been systematically characterized single- and few-layer MoS_2 by Raman spectra [21]. Generally, two typical Raman peak, E^1_{2g} and A_{1g} are investigated to reflect the crystal structure of MoS_2. E^1_{2g} and A_{1g} are indicators of in-plane and out-of-plane vibration modes of S atoms, respectively (Fig. 1c) [21]. From bulk to monolayer, three changing rules are collected. First, E^1_{2g} exhibits a regularly blue-shifted while A_{1g} shows an opposite red-shifted. E^1_{2g} and A_{1g} locate at the ~384 cm^{-1} and 405 cm^{-1} for single layer MoS_2 (Fig. 1d, f). Second, the peak frequency difference between E^1_{2g} and A_{1g} shows a clear decreasing trend as a function of layer number (Fig. 1d, f) [21]. The frequency spacing is about 25 cm^{-1} and 19 cm^{-1} for bulk and monolayer MoS_2, respectively. Third, two peak intensities almost increase linearly up to four layers with increasing layer thickness, while decrease for thicker MoS_2 (Fig. 1e) [21]. Yongjie Zhan's group has also reported the intensity ratio between E^1_{2g} and silicon (Si) substrate is

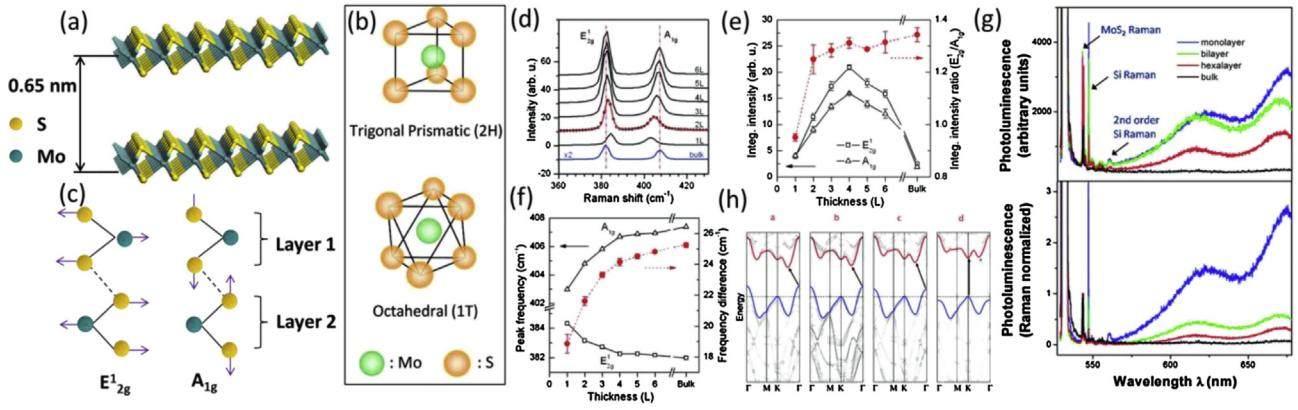

Fig. 1. Crystal structure and optical properties of MoS_2. (a) Chemical structure of two layers of MoS_2. (b) Two polytypes of single layer MoS_2: trigonal prismatic (1H) and octahedral (1T). (c) Schematic illustrations of the two typical Raman-active phonon modes (E^1_{2g}, A_{1g}). (d) Raman spectra of thin (nL) and bulk MoS_2 films. (e) Frequencies of E^1_{2g} and A_{1g} Raman modes (left vertical axis) and their difference (right vertical axis) corresponding to layer thickness. (f) Thickness dependence of integrated intensity (left vertical axis) and ratio of integrated intensity (right vertical axis) for the two Raman modes. (g) PL and Raman spectra of MoS_2 monolayer, bilayer, hexalayer, and bulk sample. (h) Calculated band structures of bulk MoS_2, quadrilayer MoS_2, bilayer MoS_2, and monolayer MoS_2 (from left to right, a~d). The solid arrows indicate the lowest energy transitions. Panel b reprinted with permission from Ref. [19]. Copyright 2011 American Chemical Society. Panel a, c ~ f reproduced and reprinted with permission from Ref. [21]. Copyright 2010 American Chemical Society. Panel g, h reprinted with permission from Ref. [23]. Copyright 2010 American Chemical Society.