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Recent Progress on Two-Dimensional Materials

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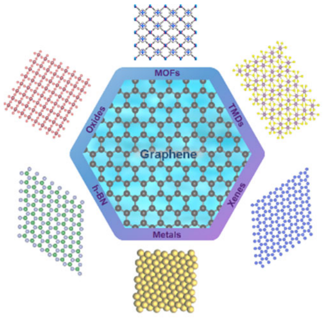

Abstract: Research on two-dimensional (2D) materials has been explosively increasing in last seventeen years in varying subjects including condensed matter physics, electronic engineering, materials science, and chemistry since the mechanical exfoliation of graphene in 2004. Starting from graphene, 2D materials now have become a big family with numerous members and diverse categories. The unique structural features and physicochemical properties of 2D materials make them one class of the most appealing candidates for a wide range of potential applications. In particular, we have seen some major breakthroughs made in the field of 2D materials in last five years not only in developing novel synthetic methods and exploring new structures/properties but also in identifying innovative applications and pushing forward commercialisation. In this review, we provide a critical summary on the recent progress made in the field of 2D materials with a particular focus on last five years. After a brief background introduction, we first discuss the major synthetic methods for 2D materials, including the mechanical exfoliation, liquid exfoliation, vapor phase deposition, and wet-chemical synthesis as well as phase engineering of 2D materials belonging to the field of phase engineering of nanomaterials (PEN). We then introduce the superconducting/optical/magnetic properties and chirality of 2D materials along with newly emerging magic angle 2D superlattices. Following that, the promising applications of 2D materials in electronics, optoelectronics, catalysis, energy storage, solar cells, biomedicine, sensors, environments, *etc*. are described sequentially. Thereafter, we present the theoretic calculations and simulations of 2D materials. Finally, after concluding the current progress, we provide some personal discussions on the existing challenges and future outlooks in this rapidly developing field.

Key Words: Two-dimensional materials; Transition metal dichalcogenides; Phase engineering of nanomaterials; Electronics; Optoelectronics; Catalysis; Energy storage and conversion

CONTENTS

1 Introduction

The first report on the mechanical cleavage of atomically thin single-crystalline carbon film, namely graphene, and its extraordinary transport properties by Geim, Novoselov and co-workers [1] in 2004 had ignited the resurgence of a class of fascinating functional nanomaterials, *i.e.*, two-dimensional (2D) materials [2–10]. 2D materials now have been recognized as a type of nanomaterials which have a sheet-like morphology featuring with a large lateral size from hundreds of nanometers to tens of micrometers or even larger but a thickness in single or few atomic layer [2,3]. Such a unique structural feature of 2D materials endows them with various unconventional physical, chemical, optical, electronic and magnetic properties as compared to their bulk, zero-dimensional (0D) and one-dimensional (1D) counterparts [2]. Owing to their unusual properties, 2D materials have been proven to be one of the most promising candidates for numerous potential applications like electronics [11–14], optoelectronics [15–20], catalysis [21–26], energy storage [27–34], solar cells [35–38], biomedicine [39–45], sensors [46–49], environments [50–54], *etc*. Driven by their unusual properties and promising applications, a large number of novel 2D materials beyond graphene, such as transition metal dichalcogenides (TMDs including MoS_2, $MoSe_2$, $MoTe_2$, WS_2, WSe_2, ReS_2, TaS_2, *etc*.) [55,56], hexanol boron nitride (h-BN) [57,58], graphyne [59,60], noble metal dichalcogenides (NMDs: $PdSe_2$, $PtSe_2$, PtS_2, *etc*.) [61,62], elemental 2D materials (e.g., black phosphorus (BP), tellurium, silicene, germanene, borophene, *etc*.) [63–65], layered metal oxides [66,67], layered double hydroxides (LDHs) [68,69], graphitic carbon nitride (*g*-C_3N_4) [70,71], MXenes [72], metals [73], organics/polymers [74,75], metal-organic frameworks (MOFs) [76,77], covalent-organic frameworks (COFs) [78,79], organic-inorganic hybrid perovskites [80–82], and transition metal halides [83,84], have been synthesized by various synthetic methods in the last decade. It is worth pointing out that the number of materials in the family of 2D materials is still continuously growing every year.

On the basis of the previous research works, the last five years have witnessed some major breakthroughs made in the field of 2D materials in all aspects. Firstly, a large number of novel 2D materials have been reported, including NMDs [85–87], tellurium [88,89], selenium [90], and so on. Secondly, some novel methods have been developed for synthesis of 2D materials with higher quality, larger size, or better control, such as oxygen plasma- or Au-enhanced mechanical exfoliation [91,92], organic intercalation-assisted liquid exfoliation of layered materials (e.g., BP, TMDs, InSe, *etc*.) [93–95], salt-assisted chemical vapor deposition (CVD) growth of a library of 2D thin layers [96,97], CVD growth of wafer-scale high-quality 2D thin films [98,99], pulsed laser deposition (PLD) of BP thin films [100], vapor phase synthesis of high-purity 1T'-phase 2D TMD crystals [101], and liquid metal-assisted synthesis of metal oxide nanosheets [102]. Thirdly, some new promising applications of 2D materials have been demonstrated, such as integrated circuits based on wafer-scale 2D thin films [103] and infrared imaging sensor systems based on graphene [104]. More importantly, some newly emerging research directions have been extensively explored on 2D materials in recent years. For example, the phase engineering of nanomaterials (PEN) including 2D materials has been recognized as a promising way to fine tune their physicochemical properties and enhance their performances in addition to other conventional structural characteristics, such as size, thickness, defects, vacancies, and interlayer spacing [105,106]. As another typical example, by simply stacking two 2D graphene in a specific magic angle, namely magic angle 2D superlattices, the properties of graphene can be tuned from a conductor to a superconductor or insulator [107,108]. Inspired by the unexpected properties of magic angle graphene superlattices, magic angle 2D superlattices have become one of the most interesting materials to explore new properties in condensed matter physics.

Although many review articles related to 2D materials have been published previously, most of them were published in several years ago or even earlier, and most of them focused on a selected type 2D materials (e.g., graphene, graphyne, TMDs, MOFs, elemental ones, metals, MXenes, *etc*.) [4,55,73], or specific application (e.g., electronics, optoelectronics, energy storage, electrocatalysis, sensors, biomedicine, *etc*.) [27,31,39]. Bearing this mind, offering a comprehensive review article to cover all of the 2D materials from all aspects with highlights on recent progress in this growing field is of great significance for its further development. To this end, this review aims to critically summarize the recent progress on 2D materials with particular focus on the last five years. Following a brief background introduction, the major synthetic methods for 2D materials, including the mechanical exfoliation, liquid exfoliation, vapour phase deposition, and wet-chemical synthesis as well as phase engineering of 2D materials are first discussed. The superconducting, optical, magnetic properties and chirality of 2D materials along with newly emerging magic angle 2D superlattices are then introduced. Thereafter, we summarize the great potential of 2D materials in various applications like electronics, optoelectronics, catalysis, energy storage, solar cells, biomedicine, sensors, environments, *etc*. Following that, recent progress on the theoretic calculations and simulations of 2D materials is also discussed. Finally, we conclude this Review by summarizing the current process and offering some personal insights on the existing challenges and future opportunities in this promising field.

2 Synthetic methods

2.1 Mechanical exfoliation

Mechanical exfoliation has been recognized as an efficient method to obtain fresh atomically flat surface of layered materials [109,110]. In 2004, a new tape-based exfoliation method developed in Geim's group was used to prepare monolayer and few-layer graphene from graphite [1,111]. As one of the most popular "top-down" strategy to date, this mechanical exfoliation technique has been widely used to get a large number of 2D crystals, such as MoS_2 [112,113], WS_2 [114], SnS_2 [115] and BP [115,116]. The exfoliated 2D materials are ideal samples to study their intrinsic electronic [117,118], optical [119] and mechanical properties. However, there are a few shortcomings for the conventional mechanical exfoliation. Firstly, the sample size of exfoliated 2D materials is usually in the range of few to tens of micrometers. Secondly, the yield is quite low. With the discovery of new layered materials, novel mechanical methods are desired to prepare high-quality, large-area 2D materials with relatively high efficiency.

Although the exfoliation processes are generally simple, some scientific questions were not well understood at the beginning.