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Introductory Chapter: 2D Materials

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1. Overview

Two-dimensional (2D) materials are a class of nanomaterials that have two dimensions (XY plane) outside of the nanometric size range and atomic-scale thicknesses (Z dimension). The first well-known 2D material is graphene consisting of a single layer of carbon atoms arranged in a hexagonal lattice. To compare with 0D material (fullerene) and 1D material (carbon nanotube), the researches related to 2D material (graphene) have grown up quickly over other carbon allotropes as shown in **Figure 1**. Based on Scopus database (search by keyword “graphene” on March 18, 2019), publications on graphene increased from 3772 papers in 2010 to 21,439 papers in 2018. The total number of graphene-related publications is 132,628 documents. However, it is not only 2D graphene that has been widely applied in a large variety of potential applications but also other 2D materials such as tungsten disulfide, molybdenum disulfide, and silicon nitride open up new opportunities for the future devices. In this chapter, synthesis and applications of these 2D materials have been introduced and presented in brief.

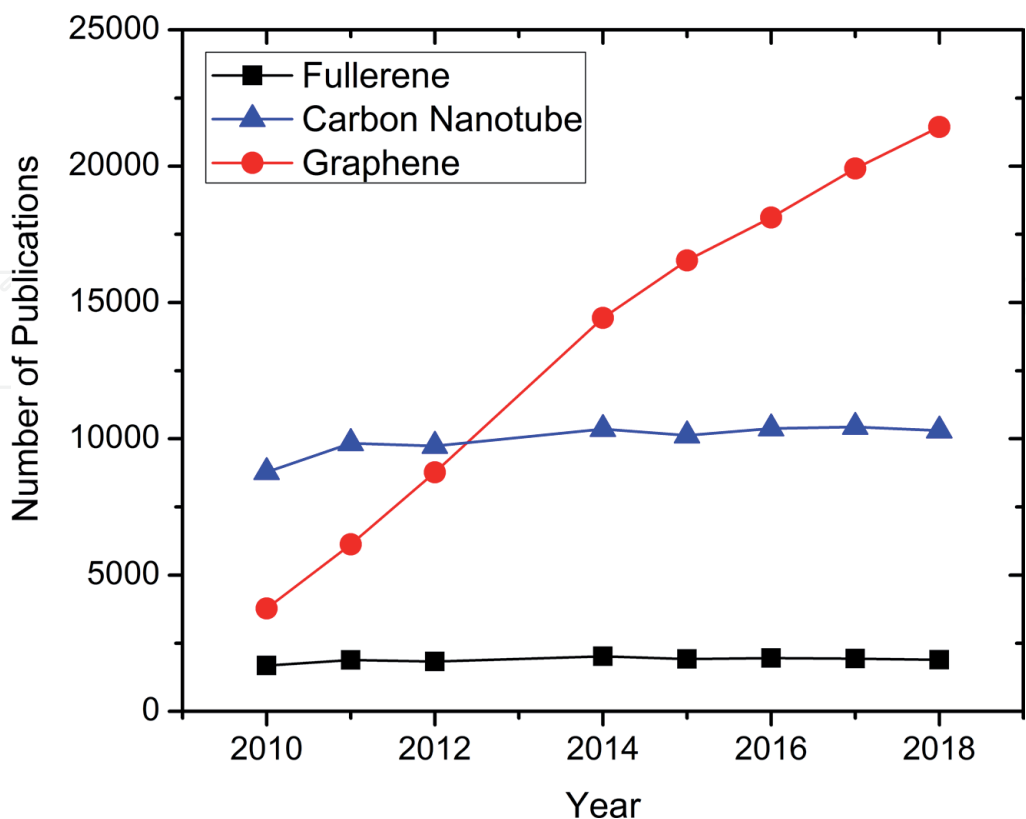


Figure 1. Number of publications versus publication years based on Scopus database (search by keyword “fullerene,” “carbon nanotube,” and “graphene” on March 18, 2019).

2. Synthesis methods of 2D materials

2.1 Graphene

Graphene can be synthesized by several methods depending on the required quality and quantity. (I) Chemical exfoliation method by modified Hummers method [1] is one of the popular methods for graphene oxide growth based on suitable oxidizing agents from graphite oxide. This method offers a large amount of graphene products and is of low cost. (II) Electrochemical exfoliation method is based on formation of graphene product from graphite rod or highly orientated pyrolytic graphite (HOPG) by using electricity for exfoliation of the graphite rod or HOPG immersed into electrolyte solutions [2]. (III) Chemical vapor deposition (CVD) method provides high-quality graphene products with controllable graphene layers over a large-scale area [3, 4]. Usually, methane (CH_4) and acetylene (C_2H_2) were used as carbon source for graphene growths on copper (Cu) or nickel (Ni) foam under high temperature around 1000°C .

2.2 Tungsten disulfide (WS_2)

The synthesis of tungsten disulfide (WS_2) can be done by three main methods, namely hydrothermal method, atomic layer deposition (ALD), and CVD. A simple hydrothermal method was used to form WS_2/C composite using $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and CH_3CSNH_2 as raw materials, polyethylene glycol as dispersant, and glucose as the carbon source under annealing at a low temperature in argon atmosphere [5]. ALD was employed to form mono-, bi-, and multilayer WS_2 nanosheets by controlling the number of cycles of ALD WO_3 with plasma enhancement using WH_2 (iPrCp)₂ and oxygen [6]. The synthesis process of large-area WS_2 films based on CVD can be described as follows [7]: (I) the Na_2WO_4 precursor coated on SiO_2/Si substrate was loaded into quartz tube of CVD process. (II) Argon was flowed into the quartz tube until temperature reached 850°C . (III) A liquid phase of dimethyl disulfide ($(\text{CH}_3)_2\text{S}_2$, DMDs) was introduced with a bubbling system for 30 min to form the WS_2 film.

2.3 Molybdenum disulfide (MoS_2)

MoS_2 can be synthesized by using mechanical and chemical methods. For example, single-layer and multilayer MoS_2 nanosheets were formed by using adhesive Scotch tape from transition metal dichalcogenide (TMD) materials [8]. MoS_2 nanosheets were synthesized from NaBH_4 as a reductant by chemical exfoliation [9] and liquid-phase exfoliation method with N-methyl-2-pyrrolidone (NMP) solvents [10]. Moreover, MoS_2 can be prepared via hydrothermal method, ALD, and CVD. For example, MoS_2 nanospheres were formed with $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ dissolved in DDW by hydrothermal method [11]. MoS_2 atomic layers were synthesized from MoO_3 and pure sulfur in a vapor-phase-deposition process with a reaction temperature of 850°C [12]. Based on CVD, the synthesis of MoS_2 was prepared from high purity MoO_3 powder and S powder in two separate Al_2O_3 crucibles and placed into quartz tube of CVD process. The SiO_2/Si substrates were faced down and placed on the crucible of MoO_3 powder together with annealing at 650°C for 15 min and N_2 flow (1 sccm) at ambient to obtain 2D- MoS_2 on Si substrates [13].

2.4 Silicon nitride (Si_3N_4)

Si_3N_4 has been widely synthesized by using carbothermal and nitriding reactions. For example, SiO_2/C mixture on alumina boat was placed in a high

temperature tubular furnace with a flow rate of nitrogen and hydrogen under optimal condition to promote the formation of Si_3N_4 [14]. Fe- Si_3N_4 composite was also prepared by FeSi_{75} powder as a precursor under reaction of high purity nitrogen flow via flash combustion at a high temperature of 1450°C [15].

3. Applications of 2D materials

3.1 Graphene

Graphene has been widely used for various applications including energy storage, solar cells, and gas sensor. Abdelkader et al. [16] reported the fabrication of flexible printed graphene supercapacitor device for wearable electronics by using graphene oxide ink and a screen-printing technique. The supercapacitor device can give a capacitance as high as 2.5 mF cm^{-2} and maintain 95.6% in cyclic stability over 10,000 cycles. Shin et al. [17] reported the fabrication of graphene/porous silicon Schottky-type solar cells by doping with silver nanowires (AgNWs) into graphene/porous silicon nanocomposite. Moreover, graphene has been widely applied in sensing application. For example, graphene was combined with carbon nanotubes to form as the 3D carbon nanostructures or the pillared graphene structures for toluene-sensing applications at room temperature [18]. We reported fabrication of various layer graphene gas sensors for NO_2 detection and investigated the layer effect of graphene to NO_2 detection. We found that bilayer graphene gas sensor exhibited the highest response and highest sensitivity to NO_2 at room temperature due to accessible active surface area and unique band structure of bilayer graphene [3]. Very recently, we demonstrated a new type of graphene gas sensor based on AC electroluminescent (EL) principle [4]. This device can monitor carbon dioxide (CO_2) at room temperature via changing EL emission upon CO_2 gas concentration. Advantage of our graphene-based electroluminescent gas sensor over typical current gas sensor is to directly integrate with a smart phone via light sensor without any modification of smart phone hardware.

3.2 Tungsten disulfide (WS_2)

WS_2 nanoflakes were used for lithium ion battery applications. They showed reversible capacity of 680 mA h/g and 86.2% of the initial capacity after 20 cycles [19]. Pawbake et al. reported that WS_2 nanoparticle was used for photodetector and humidity sensing applications [20]. It was found that the WS_2 nanoparticle-based humidity sensor exhibited sensitivity of 469%, response time of ~ 12 s, and recovery time of ~ 13 s. In case of based photodetection application, WS_2 showed a sensitivity of $\sim 137\%$ under white light illumination. The response and recovery times were ~ 51 and ~ 88 s, respectively [20].

3.3 Molybdenum disulfide (MoS_2)

MoS_2 have been extensively applied in sensor, optical, energy device, and electronics. For example, tactile sensor was fabricated from MoS_2 for electronic skin applications. MoS_2 owns its outstanding properties such as good optical transparency, mechanical flexibility, and high gauge factor compared with conventional strain gauges [21]. Wang et al. studied the conductivity and thermal stability of the MoS_2 /polyaniline (PANI) nanocomposites with increasing the amount of MoS_2 for supercapacitor application. The results showed that the MoS_2 /PANI of 38 wt% exhibited specific capacitance up to 390 F/g and retained capacitance of 86% over

1000 cycles [22]. MoS₂ was also synthesized to form hydrangea-like flowers or clusters comprising MoS₂ nanosheet for high-dielectric and electrical energy storage applications [23]. Moreover, Yin et al. synthesized the biocompatible nanoflowers between MoS₂ with polyethylene glycol (PEG) for antibacterial applications [24].

3.4 Silicon nitride (Si₃N₄)

Most applications of Si₃N₄ have been used in terms of the improvement of properties such as surface modulation for orthopedic applications [25] and biomedical applications [26]. Also, Si₃N₄ owns good optical properties. The Si₃N₄ was fabricated as photonic circuits to spectroscopic sensing [27]. The Si₃N₄ was used for nonlinear signal processing applications [28]. Furthermore, Si₃N₄ was microfabricated as the waveguides and grating couplers for new nanophotonic approach of light delivery for optogenetic applications [29].

4. Conclusion

In summary, the emerging 2D materials provide high impacts for science and advanced technologies. They own unique physical, optical, mechanical, and electrical properties. Therefore, 2D materials have become one of the hottest topics in this era due to their potential various applications such as gas/chemical sensors, healthcare monitoring, biomedicine, electronic skin, wearable sensing technology, flat panel displays, optoelectronics, photodetector, catalysis, electrochemical sensing, bio sensing, water/air purification, supercapacitor, batteries, fuel cells, and advanced electronics devices.

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