Properties of New Two-Dimensional Nanomaterial Black Phosphorus

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Abstract. Two-dimensional (2D) materials have attracted broad interest because of their low-dimensional effect, and black phosphorus has become a member of them due to the successful preparation. Phosphorus has several allotropes, white phosphorus, red phosphorus and black phosphorus. Black phosphorus is most thermodynamic stable in them. Black phosphorus was obtained by a phase transition from white or red phosphorus at high pressure and high temperature. It is a natural p-type semiconductor in which each layer is vertically stacked by the van der Waals force. The thickness of black phosphorus can be scaled down to the atomic layer scale known as phosphorene by mechanical exfoliation or liquid exfoliation. Compared with black phosphorus, phosphorene’s physical properties have significant changes. The band gap in bulk black phosphorus is 0.3 eV and can be expanded to 1.0 to 1.5 eV depending on the layer numbers. Nevertheless, the poor chemical and structural stability of black phosphorus and phosphorene raises important concerns. In the past century, the synthesis, physical properties, and device applications have been extensively investigated in various studies. In this review article, a lot of references of black phosphorus are cited to introduce systematically the research progresses of structure and preparation, the study of material properties and device performance, the chemistry of the degradation process and the anti-degradation treatments. At last, the development trend of phosphorene is mentioned.

1. Introduction

Two-dimensional crystals are composed of monatomic layers stacked on top of each other, which is an important direction for researchers to find new materials [1]. For example, graphene and two-dimensional transition metal sulfide have attracted extensive attention due to their excellent physical and chemical properties. And in photoelectricity, catalysis, chemical and biological sensing, spintronics, lithium ion batteries, supercapacitors, solar cells have important applications.

Some properties of two-dimensional materials are not found in bulk materials, such as the massless Dirac fermion effect of graphene. In addition, graphene has many excellent properties, such as high electron mobility, high thermal conductivity, room temperature hall effect and so on. However, due to the zero-bandgap effect of graphene, the logic switch of semiconductor cannot be realized, which limits the application of graphene in semiconductor field and photoelectric field [1]. Therefore, it is particularly important to find two-dimensional materials with suitable band gaps and high carrier mobility. Black phosphorus is a new type of direct band gap two-dimensional material [2]. The carrier
mobility and on-off ratio of fet can be up to $286 \text{cm}^2 \cdot \text{v}^{-1} \cdot \text{s}^{-1}$ and up to $10^4$. Moreover, the carrier mobility is closely related to the thickness of black phosphorus [2]. When the thickness is 10 nm, the carrier mobility can be as high as $1000 \text{ cm}^2 \cdot \text{v}^{-1} \cdot \text{s}^{-1}$ [2]. Therefore, this material can overcome the shortcomings of graphene and transition group metal sulphides, and is expected to be a good two-dimensional semiconductor material, and play an important role in the future optoelectronic field.

2. The structure of black phosphorus

2.1. The crystal structures

Black phosphorus is the most stable allotrope of phosphorus. It has been studied since the 1950s. Four crystal structures of black phosphorus are known: orthogonal, diamond, simple cube and amorphous. Each cell has eight atoms. Like graphite, black phosphorus is laminated. The difference is that the atoms in the same layer are not on the same plane, showing a kind of honeycomb fold structure, as shown in figure 1. In the layer, P atoms are connected to the three surrounding atoms through 3p hybrid orbitals, and s-p hybrid orbital makes the folded layered structure very stable [3]. There are strong covalent bonds and a single pair of electrons left in the layers, so each atom is saturated, and the atoms between the layers are acted on by van der Waals forces [3].

2.2. Band structure

There are many potential two-dimensional semiconductor materials, but only a limited number of one-component materials can realize continuous band gap regulation. Black phosphorus is a two-dimensional semiconductor material with a band gap of 0.3 eV. The single-layer black phosphorus has a direct band gap, and the measured size of the single-layer black phosphorus band gap is 1.5ev [4]. It can absorb light from visible light to infrared wavelength for communication, which becomes the biggest advantage of black phosphorus.

![Figure 1. The crystal structures](image)

3. Preparation of black phosphorus

3.1. Preparation of massive black phosphorus

In 1914, Bridgman turn white phosphorus to black phosphorus for the first time under 1.2 GPa and 200 °C. Later, black phosphorus was obtained by using red phosphorus as raw material under the high pressure of 8.0 GPa [5]. In order to be simple, efficient, non-toxic and large-scale production of black phosphorus. In 2007, Park et al. synthesized black phosphorus by high-energy mechanical ball milling method, and the synthesized pure black phosphorus had low crystallinity [6].
3.2. Preparation of single layer black phosphorus

3.2.1. Mechanical stripping method. The black phosphorus layer is weak, connected by van der Waals force [1], and easy to peel off. At present, the mechanical stripping method has been successfully used to obtain single or multi-layer black phosphorus nano-sheets using a method similar to stripping graphene. Liu et al. also successfully obtained black phosphorus with atomic thickness, and found that two-dimensional black phosphorus is a direct bandgap semiconductor. Lu et al [7] obtained 2D black phosphorus with different thickness (1-5 layers) after stripping black phosphorus by mechanical stripping method and then thinning it with argon ion. It is proved that the plasma thinning method can control the number of black phosphorus layers well [7].

3.2.2. Liquid phase stripping method. Although mechanical stripping has successfully obtained large areas of low dimensional black phosphorus with few defects, its low yield limits its application in the preparation of two-dimensional materials [8]. The principle of liquid phase stripping is that when the surface energy of the chemical solvent matches that of the two-dimensional material, the interaction between the solvent and the two-dimensional material can balance the energy required to peel the material, so that the block material can be peeled into a sheet material by means of ultrasound. This method has been successfully used to prepare multilayer or even single layer of graphene and MoS2. Brent et al [9] obtained a small amount of two-dimensional black phosphorus by liquid-phase stripping method. The preparation method was simple and easy to obtain. The black phosphorus crystal was dispersed by high-power ultrasound with n-methylpyrrolidone (NMP) for 24 h. The maximum size of the black phosphorus film measured under atomic force microscope can reach 200 nm x 200 nm, and the thickness is between 3.5 and 5 nm [10].

In general, there are three main methods to prepare two-dimensional black phosphorus at present: mechanical stripping method, liquid phase stripping method, and pulse laser deposition method. Among them, mechanical stripping method is the most common, followed by liquid stripping method, PLD method is the least.

4. Characterization of black phosphorus

4.1. Raman characterization

In two-dimensional materials, Raman spectroscopy is used to measure the number of layers of two-dimensional materials which is a convenient, accurate and lossless manner [11]. Raman signals of graphene with different layers were obviously different [11]. Therefore, in order to accurately measure the number of two-dimensional black phosphorus layers by Raman spectroscopy, it is particularly important to study Raman signals of two-dimensional black phosphorus at different layers for the direct measurement of two-dimensional black phosphorus layers.

Lu et al [12] obtained black phosphorus with different layers by means of plasma thinning, and reported Raman characteristics of black phosphorus with different layers. Raman results show that there are three characteristic peaks of black phosphorus between 350 cm\(^{-1}\) and 500 cm\(^{-1}\) wave number, and their positions are 470 cm\(^{-1}\), 440 cm\(^{-1}\) and 365 cm\(^{-1}\) respectively [12]. The vibration modes of these three peaks are \(A_{2g}\), \(B_{2g}\) and \(A_{1g}\) respectively. At the same time, as the number of layers decreases, the phenomenon of blue shift appears. As shown in the figure3(c), bp-1 with the lowest number of layers showed blue shift of 1.9 cm\(^{-1}\) and 2.9 cm\(^{-1}\) respectively when compared with bp-2, \(A_{1g}\) and \(B_{2g}\) peaks, while bp-3 showed blue shift of 14.5 and 16.4 cm\(^{-1}\) respectively [12]. This phenomenon also occurs in black phosphorus nanometer quantum dots. The phenomenon of blue shift is caused by the decrease of interlayer van der Waals forces due to the decrease of the number of layers.
4.2. TEM and AFM
As shown in figure 2, the morphological characteristics of black phosphorus can be observed by transmission electron microscope (TEM) and atomic force microscope. Through TEM and AFM, we can observe that the layer number of black phosphorus changed significantly.

4.3. XPS
x-ray photoelectron spectroscopy (XPS) is used to analyze the chemical composition of multilayer black phosphorus[13]. In the XPS measurement, two characteristic peaks appeared at 127.7 and 126.9 eV, as shown in figure 3, respectively representing two binding energies, $2p_{1/2}$ and $2p_{3/2}$. These two peaks are characteristic peaks of black phosphorus, and an extremely weak peak at 130.7 eV represents POX, which may be a part of black phosphorus oxidized during the detection process.

![Figure 2. a,b,c TEM of BP  d,e,f AFM of BP](image)

![Figure 3. The XPS and Raman of BP](image)

5. The stability of black phosphorus
Although two-dimensional black phosphorus has many advantages such as high carrier mobility and high leakage current modulation ability, it is easy to be degraded in the natural environment, which seriously restricts its future application in the industrial field [14].

Favron et al. [15] studied the degradation of black phosphorus with in situ Raman spectrum and electron energy loss spectrum, focusing on the light induced oxidation reaction of black phosphorus adsorption of oxygen in water. When in contact with the natural environment and under the combined...
action of visible light, black phosphorus is oxidized into P_{xO_y}. The photoinduced oxidation reaction can be explained by the following formula, where $\theta$ is 2D black phosphorus in the ground state.

$$\theta + h\nu \overset{\text{\rightarrow}}{\text{\Rightarrow}} \theta^*$$  \hspace{1cm} (1)

$$\theta^* + O_{2(aq.)} \rightarrow \theta_{2(aq.)}^* + \theta \rightarrow \theta_{\text{ox}}$$  \hspace{1cm} (2)

In the degradation process of black phosphorus, they also studied the variation rule of A$^2g$ peak strength of two-dimensional black phosphorus Raman with time, and found that only when oxygen, water and light acted together, the peak strength of A$^2g$ was significantly reduced with time, which indirectly proved that the degradation of two-dimensional black phosphorus was the result of the combined action of oxygen, water and light [15].

Wood et al. [16] used atomic force microscope, electrostatic microscope, transmission electron microscope, X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy to analyze the structure and chemical degradation process of mechanically stripped two-dimensional black phosphorus in air. Studies have shown that the reaction of black phosphorus with O$_2$ and H$_2$O to form phosphorus oxides is irreversible. On the self-assembled layer of hydrophobic monomolecular octadecyl trichlorosilane (OTS) and H-Si-based hydrophilic SiO$_2$, the black phosphorus nano-sheet was degraded more rapidly, thus further proving the mechanism of black phosphorus degradation.

These studies provide a theoretical basis for the chemical stability of two-dimensional black phosphorus and are helpful for further experiments and research.

6. Conclusion
The fatal disadvantage of two-dimensional black phosphorus is that it is easy to be degraded, and the combination of oxygen, water and light is the fundamental reason. At present, AlO$_x$, PMMA and h-BN were coated to prevent degradation. Most of the research and practical application need to be carried out in the atmospheric environment, and the convenient and fast anti-degradation measures need to be further studied. Like other two-dimensional materials, two-dimensional black phosphorus can be obtained by mechanical and liquid stripping. At present, the technology is not mature enough to prepare two-dimensional black phosphorus with large area and few defects with high efficiency and quality, which greatly hinders the research and application of two-dimensional black phosphorus. This is a difficult problem for future development.

In this paper, the basic properties of 2D black phosphorus are reviewed and its future development trend is analyzed. We hope that this will contribute to the future research and development of two-dimensional black phosphorus, and help researchers to produce high-performance transistors, sensors, microprocessors, lasers, light-emitting diodes, solar cells and other devices, and even more new nanotechnology.

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