



Liquid-phase exfoliation of black phosphorus and its applications



Shenghuang Lin¹, Yingsan Chui¹, Yanyong Li, Shu Ping Lau*

Department of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

ARTICLE INFO

Article history:

Received 17 March 2017

Revised 28 March 2017

Accepted 28 March 2017

Keywords:

Black phosphorus

Two-dimensional materials

Solution exfoliation

Energy materials

ABSTRACT

Interest in two-dimensional (2D) materials is growing exponentially across various scientific and engineering disciplines owing to their fascinating electrical, optical, chemical, and thermal properties. As one of the newest members in the 2D nanomaterial family, black phosphorus (BP), has recently attracted much attention all over the world and shown great potential in novel nanoelectronics owing to its direct and narrow bandgap. Regarding to the scale production of BP and its related electronic devices, liquid-phase exfoliation reveals superior advances when compared with mechanical exfoliation. Remarkably, liquid-phase exfoliated BP flakes and quantum dots (QDs) exhibit exciting properties in electronic, energy storage, sensors, solar cells, photothermal effect, cancer theranostics and photonic devices. In this article, we discuss the exfoliation of BP in diverse solvents and extend the topic from BP flakes to QDs and summarize the significant advances recently made. We also outline future prospects of solution exfoliated BP nanomaterials, and comment on the challenges that need to be overcome for future applications.

© 2017 Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Contents

Introduction.....	16
Properties of black phosphorus.....	16
The allotropes of phosphorus and the electronic structure of BP.....	16
Exfoliation of BP via sonication.....	17
BP quantum dots.....	22
Applications.....	24
BP flakes.....	24
Transport layer.....	24
Field effect transistors.....	25
Optical devices.....	25
Photocatalyst.....	26
Energy storage devices.....	30
BPQDs.....	33
Humidity sensor and memory devices.....	34
Biomedical applications.....	34
Ultrafast photonics.....	34
Conclusions and outlooks.....	35
Acknowledgements.....	35
References.....	35

* Corresponding author.

E-mail address: apsplau@polyu.edu.hk (S.P. Lau).

¹ These authors are contributed equally to this work.

Introduction

The evolution of materials science plays an important role in the development of human society. The discovery of graphene [1–6], as a superstar in materials science, has obviously attracted great attention around the world and created tremendous impact in many fields. It is indeed enhanced the knowledge of layered two-dimensional (2D) materials in the past few years. It is no doubt that the research of layered 2D materials has been in the frontier of materials science [5,7]. To explore the unique properties of 2D materials, the first step is to isolate them from the bulk into few-layer or even single-layer form through mechanical or liquid-phase exfoliation process. The exfoliated 2D materials typically have weak van der Waals or electrostatic out-of-plane interactions and strong covalent or ionic in-plane bonds [8]. There are many kinds of 2D materials, which can be isolated from their bulk counterparts, e.g., graphene, GaSe, MoS₂, MnO₂ and black phosphorus (BP) [9–12]. Due to their interesting properties, 2D materials have been explored carefully when thinned down to atomic layer scale and reveal significant changes in the mechanical, physical and chemical properties. For example, the bandgap of MoS₂, a typical member belonging to the family of transition metal dichalcogenides (TMDs), varies from 1.29 eV to 1.8 eV when the thickness of bulk is thinned down to single-layer [13]. It has great potential applications in photovoltaics [14–16], photodetectors [17,18], and light emitters [19]. In addition to TMDs and graphene, scientists also pay much attention to explore new 2D semiconductors. Interestingly, the rediscovering of BP, a rare and stable allotrope of phosphorus, has excited materials scientists to make BP as a promising candidate for complementing graphene's deficiencies. Remarkably, both experimental and theoretical results revealed that BP possesses a direct bandgap ranging from 0.3 eV (bulk) to 2.0 eV (monolayer) [20], which can bridge the gap between zero-gap graphene and relatively large bandgap TMDs for infrared photonics and optoelectronics [21,22]. To make full use of the excellent physical and optical properties of BP, many efforts have been devoted to enlarging the size of BP flakes or films. For instance, BP film with lateral size of 4 mm can be prepared by converting a red phosphorus film at high-pressure [23]; and large-area amorphous BP film with a mobility of 14 cm² V⁻¹ s⁻¹ can be obtained through Pulsed Laser Deposition (PLD) technique [24]. In terms of the stability of few-layer BP in ambient air, advancements have been made to enhance the stability of BP. Typically, an encapsulation of BN (boron nitride) [25,26], Al₂O₃ [27,28] or PMMA [29] onto BP surface could effectively improve its stability. Although room temperature hole mobilities of ~1000 cm² V⁻¹ s⁻¹ with on/off ratios of ~10³–10⁵ can be achieved in mechanically exfoliated few-layer BP based field effect transistors (FETs) [30], such mechanical exfoliation technique suffers from low yield and a low production rate, which is not scalable for practical applications. As compared, solution-processed electronic devices are usually preferred due to its low cost, large area, flexibility and convenient materials integration [31]. Therefore, one possible solution is to exfoliate BP in liquid to give large scale dispersion of nanosheets to extend the application of BP. Herein, we critically review the recent advances in the preparation and applications of liquid-phase exfoliated BP. This review is an account of the current status of science in liquid-phase exfoliation of BP, with special attention paid to applications that have emerged in recent years.

Properties of black phosphorus

The allotropes of phosphorus and the electronic structure of BP

Phosphorus usually exists in various allotropes, such as gaseous, white, red, black and violet, which exhibit strikingly different properties as shown in Fig. 1 and Table 1 [32–34]. Diphosphorus (P₂) is one of the allotropes of phosphorus presenting its gaseous form through the thermolysis (cracking) of P₄ (white phosphorus) at 1100 K. Meanwhile, blue phosphorus, another unique and stable phase of phosphorus, has also been experimentally studied by *in situ* scanning tunneling microscopy (STM). Such blue phosphorus was grown by the MBE (molecular beam epitaxy) using BP as precursor [32]. It has been revealed that the rediscovered BP normally has an orthorhombic crystal structure with five valence electrons in its outer shell [35]. In addition to the orthorhombic phase, BP also exhibits rhombohedral or simple cubic phase [35]. Similar to graphite, adjacent BP atomic layers are stacked together through weak van der Waals interaction while the single layer is formed by sp³ phosphorus atoms through covalently bonding. Owing to the sp³ hybridization, each P atom is saturated and covalently bonded to three neighboring P atoms and has one lone-electron pair, leading to a quadrangular pyramid structure resembling a puckered honeycomb structure, as shown in Fig. 1, and hence results in a highly asymmetric band structure and unique in-plane anisotropic properties [36]. BP possesses different lattice constants for the armchair (4.37 Å) and zigzag edges (3.31 Å), from which the unique in-plane anisotropy can be observed, e.g., a high-degree anisotropy of effective masses [37]. But the blue phosphorus has only zigzag edges with the same lattice constant of 3.28 Å, revealing the different lattice constants by comparing with BP. White phosphorus (also called yellow phosphorus), the most toxic of the allotropes of phosphorus, consists of tetrahedral P₄ molecules, in which each atom is bound to the other three atoms by a single bond (as shown in Fig. 1D). Violet phosphorus (Fig. 1E) is a form of phosphorus that can be produced by day-long annealing of red phosphorus above 550 °C. Red phosphorus, possessing polymeric chain-like structure (Fig. 1F), can be formed through heating white phosphorus to 250 °C. But the most stable allotrope among the bulk forms of phosphorus is BP. The density of BP can be calculated through counting the BP atoms in the unit cell. Here we can extract the density of 2.69 g/cm³ for BP containing 8 atoms in the unit cell [30]. The crystal structure of BP can be clearly distinguished under high pressure [38] due to the anisotropic compressibility of BP induced by its asymmetric crystal structure. Generally, BP undergoes two reversible structural transitions at high pressures. The first transition occurs at around 5.5 GPa at room temperature, inducing the conversion of orthorhombic phase into rhombohedral phase and consequently resulting in the displacement of the puckered layers and a volume change. The second transition, from rhombohedral to simple cubic phase, appears when the pressure reaches 10 GPa. For ultrahigh pressure (even up to 60 GPa) [39], there is no further transition occurred, revealing the cubic phase remains stable when the pressure is higher than 10 GPa. It is worth noting that the temperature does not contribute to the phase transitions of BP [40,41]. Otherwise, the BP flakes could be decomposed at >400 °C by *in situ* TEM (transmission electron microscope) and the residual gaseous BP would be re-deposited to form amorphous phosphorus when the chamber was cooled down to room temperature [42], which provides an insight into the thermal stability of BP.

Download English Version:

<https://daneshyari.com/en/article/8917836>

Download Persian Version:

<https://daneshyari.com/article/8917836>

[Daneshyari.com](https://daneshyari.com)