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Two-dimensional black phosphorus: Synthesis, modification, properties, and applications

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ABSTRACT

Black phosphorus (BP) discovered a century ago constitutes a new class of two-dimensional (2D) materials and is intensively studied as a 2D semiconductor. The high carrier mobility and tunable and moderate direct bandgap of BP deliver great promise in electronic and optoelectronic applications and the unique intrinsic anisotropy arising from the puckered structure produces extraordinary electronic, optical, transport, thermal, and mechanical properties that can be exploited in the design of new devices. Furthermore, the biodegradability and biocompatibility of BP bode well for biomedical applications. In this review, we discuss recent advances pertaining to the synthesis, modification, properties, and applications of BP and address some of the challenges and opportunities of BP research.

Contents

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1. Introduction

In the past decade, two-dimensional (2D) crystals have burgeoned to be one of the most extensively studied class of nanomaterials [1,2]. The atomically thin nature leads to strong quantum confinement effects and large surface-to-volume ratio, which are exceptional and fascinating properties that their bulk counterparts do not possess. These remarkable properties can be exploited in the electronic, optical, thermal, chemical and mechanical fields and the materials have thus attracted tremendous interest from both the scientific and practical standpoints [3–5]. Graphene, the first genuine 2D crystal, continues to be most widely studied materials since its emergence in 2004 [6–8]. However, although graphene possesses unique electrical, optical, and physical properties, the absence of a bandgap severely limits its application to the semiconductor industry. Hence, much effort has been devoted to the search of alternative 2D semiconductors which include graphene-analogous layered materials such as transition metal dichalcogenides (TMDs) [9–12] and black phosphorus (BP) [13–18].

BP, the most stable allotrope of phosphorus, was first synthesized in 1914 by Bridgman [19]. After a century, it was reintroduced to the scientific community as a member of 2D materials. Since it possesses several advantages over graphene and TMDs, it is attractive to future 2D devices [20,21]. For example, in contrast to TMD compounds, BP is an elementary crystal which can be prepared with high purity and unlike few-layer TMDs with indirect bandgaps, BP has a direct bandgap that varies from about 0.3 eV of the bulk to almost 2.0 eV of the monolayered structure [16]. Moreover, the direct bandgap can be tuned by adjusting the layer number, strain engineering, and chemical modification [22–24], thereby allowing broadband absorption from the visible to mid-infrared range rendering it suitable for many optoelectronic applications [25]. Another significant advantage of BP is its relatively high charge carrier mobility of up to 1000 $cm^2/V s$ observed from few-layer BP field-effect transistors (FETs) at room temperature and this value surpasses the mobility of TMDs-based FETs significantly [21]. Although the current on-off ratio of BP FETs ($\sim 10^3$–10^5) [13] is smaller than that of TMDs ($\sim 10^8$–10^{10}) [11], it is generally regarded to be a satisfactory trade-off between carrier mobility and current on-off ratio. As a matter of fact, BP bridges the gap in the mobility/on-off ratio between graphene and TMDs [13]. From the perspective of device applications, BP is preferred over TMDs due to its intrinsic ambipolar behavior, which is essential to the construction of logic devices consisting of both *n*- and *p*-type semiconductors [26–28]. The unique in-plane anisotropy of BP stemming from the puckered orthorhombic structure [29,30] produces unique electrical, optical, thermal, and mechanical properties [31–35] and provides more degrees of freedom to the design of novel devices. Another unusual feature that distinguishes BP from graphene and TMDs is its biocompatibility and biodegradability rendering the materials suitable for biomedical applications [36,37].

Despite these favorable properties, there are challenges and obstacles that must be overcome in order to bring the materials and technology to fruition. One of them is the environmental instability of BP thin films [38,39]. When exposed to an ambient environment with moisture and oxygen, phosphorus oxide is formed and degradation of BP adversely affects device performance and hinders research of its fundamental properties [40,41].

In this review, we describe recent research progress on nanoscale BP crystals focusing on the preparation of BP materials in the forms of bulk crystals, thin films, and quantum dots, passivation schemes for high stability, properties, and applications. A prospective on future research directions of the fascinating 2D materials is also presented.

2. Synthesis

2.1. Bulk crystal growth

Synthesis of black phosphorus (BP) crystals dated back to 1914 when Bridgman converted white phosphorus to BP at 200 °C and 1.2 GPa [19] and this high-pressure synthesis method was a common technique to obtain BP in the following 40 years.