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Review

Phosphorene – The two-dimensional black phosphorous: Properties, synthesis and applications

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ABSTRACT

Black phosphorus (BP) is known to human beings for almost a century. It started receiving more attention of scientists and researchers worldwide in last three years, with its ability to exist in two-dimensional (2D) form, popularly known as phosphorene. In the post-graphene-discovery period, phosphorene is probably receiving most attention, owing to its excellent properties and hence, high potential for practical applications in the field of electronics, energy and infrastructure. In this article, attractive properties of phosphorene, which makes it unique and comparable with graphene or transition metal dichalcogenides (TMDs), are highlighted. As the question of its environmental instability remains critical, a comprehensive overview of synthesis methods of phosphorene and black phosphorus are presented, to inspire in-situ methods of phosphorene synthesis and fabrication towards improving further investigation into this wonder material. In addition, the article also focuses on opportunities in nano-electronics, optoelectronics, energy conversion/storage, sensors etc arising from phosphorene's remarkable properties.

Contents

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1. Introduction

Black phosphorus was first synthesized in 1914 by Bridgeman through a process involving application of high hydrostatic pressure and temperature (up to 200 °C and 1.2 GPa) to white phosphorus [1]. Commercially, black phosphorus is not as popularly used as its other two most common allotropes – white phosphorus and red phosphorus. Similar to graphite, BP consists of layers of puckered structure held together by Van der Waals forces [2]. This was probably the motivation behind the use of mechanical exfoliation method for extraction of black phosphorus. Very few layer black phosphorus was successfully exfoliated from bulk black phosphorus using a blue tape (PVC film coated with a pressure sensitive acrylic-based adhesive) in 2014 [3]. In similitude with the name of 'graphene', this isolated single layer of black phosphorus is called phosphorene.

Until 2013, various 2D materials were known to be fabricated by mechanical exfoliation method, but graphene was the only one in its elemental form. The other 2D materials were composed of more than one element. It might be argued that silicene is also a stable material at room temperature [4]. However, silicene cannot be obtained through mechanical exfoliation. So, without any surprise, the discovery of black phosphorus took the scientific community by storm. Its properties are so unique that it managed to fill the gap provided by graphene and TMDs. To compare, contrast and summarize the structure, methods of synthesis and promising

Table 1
A compendium of structure type, year of synthesis, methods of synthesis and promising applications for graphene, other 2D materials and some major TMDs.

2D materials	Year of first report	Composition and structure	Major Methods of preparation	Major Applications
Graphene	2004	Carbon; hexagonal honeycomb structure	Exfoliation (Chemical, Liquid & Mechanical) [5], Chemical Vapor Deposition (CVD) [5], Substrate-assisted epitaxial growth [5], Unwrapping CNTs [6], Surface Segregation [7], Molecular Beam Epitaxy (MBE) [8]	Gas and bio-sensors; Graphene Field Emission Transparent Electrodes; Electronics, Thermal and Mechanical applications; Energy storage applications [5]
Hexagonal Boron Nitride Nano-Sheets (h-BNNS)	2004	Boron Nitride; hexagonal honeycomb structure	Exfoliation (Chemical [9], mechanical [10] and liquid [11]), electron beam irradiation and CVD [7], Surface Segregation [7]	Nanoelectronics-ultrathin insulating films [12], catalysis [8]
MoO_3	2009	Molybdenum, Oxygen double layer structure [13]	Modified hot plate method; plasma assisted paste sublimation process; organic solvent assisted grinding and sonication method [14]	Biosensing, organic light emitting diodes; hydrogen gas sensing; photoluminescence; field emission [13]
Silicene	2010	Silicon; partially flat hexagonal honeycomb structure [15]	Substrate (Au/Ag/Al) assisted epitaxial growth [16], surface segregation on zirconium diboride thin films [17], chemical exfoliation [18]	FET [19], Topological electronics; Thermoelectric Systems; Nano Electro Mechanical Systems (NEMS) [20]
MoS_2	2010	Molybdenum-Sulphur TMD; hexagonal structure with Mo and S_2 atoms located at alternating corners	Exfoliation (chemical, mechanical and liquid); CVD synthesis via thermal vapor sulfurization (TVS) and thermal vapor deposition (TVD); Vapour-solid growth [21]	FET; memory device; Photodetector; Photovoltaic device [21]
WS_2	2012	Tungsten, Sulphur TMD; hexagonal structure with W and S_2 atoms located at alternating corners	Exfoliation (Chemical and Mechanical) [22], Ambient pressure CVD on gold foils [23]	Photo detecting; Chemical sensing [23]
WSe_2	2012	Tungsten, Selenium TMD; hexagonal structure with W and Se_2 atoms located at alternating corners	Mechanical exfoliation [24], CVD [25]	Photovoltaic; Photoelectrochemical (PEC) devices [26], FET [27]
Germanene	2014	Germanium; nearly flat honeycomb structure	Epitaxial growth on Au surface [28]	Topological electronics, Thermoelectric Systems, Nano Electro Mechanical Systems (NEMS) [20]
$MoSe_2$	2014	Molybdenum, Selenium TMD; hexagonal structure with Mo and Se_2 atoms located at alternating corners	CVD via thermal vapor Selenization of MoO_3 [29]	Optoelectronics; Photo detecting and other nanoelectronic applications [29]
Blue Phosphorene	2014	Phosphorus; Out-of-plane buckled honeycomb structure with two atom unit cell in zig-zag orientation [30]	Not yet synthesized; Theoretical predictions based on ab initio calculations [30]	Solar cells; Photodetection devices [30]
Borophene	2015	Boron; corrugated cardboard structure with out-of-plane buckling [31]	Electron beam evaporation (using Ag as substrate) [31]	Electronic sensors; semiconductor devices; tribological applications [31]
Stanene	2015	Tin; hexagonal honeycomb structure [32]	MBE on Bismuth Telluride substrates [33], Chemical Exfoliation [34]	Topological electronics; Thermoelectric Systems; Nano Electro Mechanical Systems (NEMS) [20], Photonics [34]