Phosphorene: An Emerging 2D Material with Unique Applications

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The pioneering study of graphene in 2004 revealed that 2D materials exhibit unique properties because of the quantum confinement and size reduction effects.[1] Graphene has a high carrier mobility, thermal conductivity and mechanical strength, all of which have paved its way for advanced technological applications.[2] Over the past decade, new 2D materials are being extensively explored to unveil characteristics that can broaden their utilities. One such 2D material is phosphorene (Figure 1), which is a single- or few-layer form of black phosphorus (BP).[3] Phosphorene distinguishes itself from other 2D materials due to its thickness dependent direct bandgap that spans over a wide range of electromagnetic spectrum (mid-IR to visible).[3] It also has extremely high carrier mobility for a 2D semiconductor (~1000 $cm^2 V^{-1} s^{-1}$) and displays unique in-plane anisotropy.[3,4]

Phosphorene has a corrugated structure with each phosphorus (P) atom covalently bonded to other three P-atoms (Figure 1).[5] Despite the suffix 'ene', the P-atoms are sp^3 hybridized and yield the puckered configuration to maximize the distance between single electron pair positioned at each atom.[6] Its structure is also responsible for the anisotropy in the material where the preferred electron transport direction (armchair) is perpendicular to the preferred thermal conduction direction (zigzag) (Figure 1).[7] In addition, phosphorene may exhibit preferential binding to certain molecules due to their interaction with the lone pairs in P-atoms.[8] Such molecular specificity combined with the high surface area of phosphorene makes it suitable for gas sensors.[8] Phospherene also has a direct bandgap that can be tuned by changing the number of layers (1.45 eV in monolayer to 0.33 eV in bulk).[9,10] Due to such broadband absorption, phospherene can serve as an excellent candidate for optoelectronic and photocatalysis applications.[11] The utility towards these applications are further enhanced by phosphorene's high carrier mobility compared to other 2D semiconductors.[3,11]

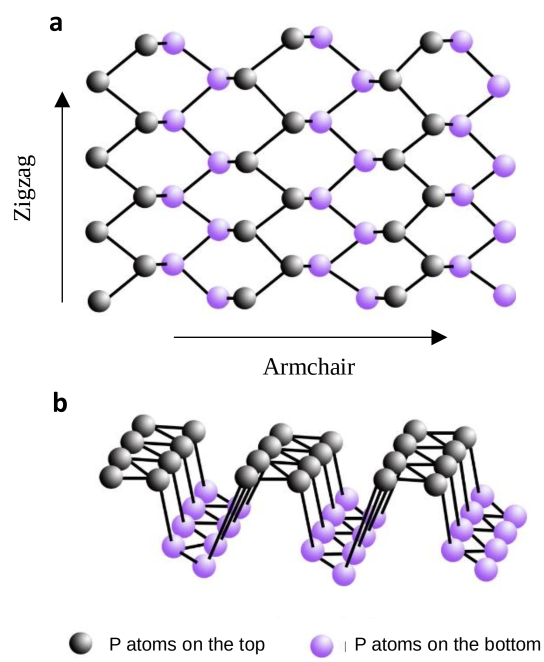

Figure 1. Structure of phosphorene: (a) top view, and (b) 3D view [5]

Since phosphorene is a relatively new 2D material, most of its applications are predicted on theoretical grounds. Yet, experimental studies validating its applicability have started emerging. For example, a theoretical study had demonstrated that the extent of molecular doping in phosphorene is greatly enhanced by adsorption of paramagnetic molecules such as nitrogen dioxide (NO_2).[12] As a result, NO_2 adsorption is expected to induce greater change in phosphorene's conductivity, making it a good NO_2 sensor.[12] To validate the theoretical predictions, Cho et al. tested phosphorene's role as a NO_2 sensor, and compared its performance with that of molybdenum disulfide (MoS_2) and graphene.[13] The group fabricated 2D sensors with comparable surface morphologies and flake sizes.[13] Their study revealed that phosphorene outperformed MoS_2 and graphene in NO_2 sensing by detecting upto 0.1 ppm concentration of NO_2, which MoS_2 and graphene were not able to achieve (Figure 2).[13] Phosphorene's response time was also superior compared to other 2D materials at all concentrations of gas flow and was 40 times faster at its maximum.[13] When these sensors were exposed to volatile organic compounds, phosphorene's response remained minimal, further validating its specific sensing characteristics towards NO_2. Almost identical Raman spectra of the sensors after an hour of exposure to NO_2 suggested its chemical intactness upon exposure [13]. However, phosphorene oxidized over the span of 30 days that reduced the maximum resistance change to 78 % under the flow of 100 ppm of NO_2 gas.[13] This study was a good experimental demonstration that validated phosphorene's application as a gas sensor. However, the study did not report the performance of phosphorene in presence of gaseous mixtures or in ambient conditions, where phosphorene has been shown to degrade rapidly.[14] The conclusion about stability over repeated cycles is vague given that the time period for each cycle was not revealed. In addition, the study does not provide any information on the change in limit of detection resulting from the oxidization.

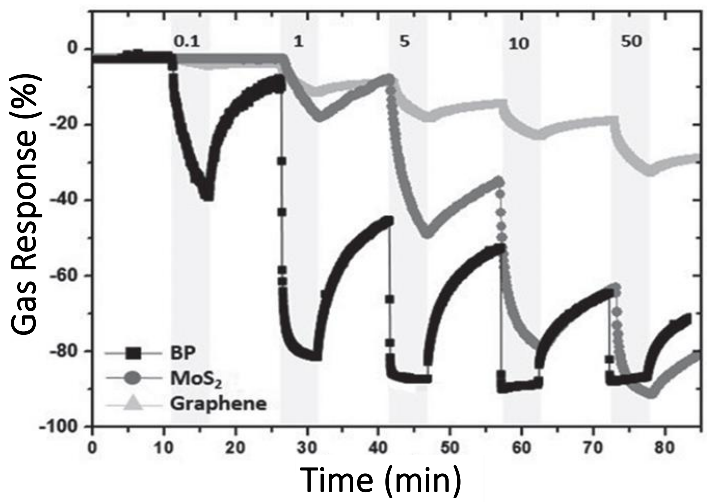

Figure 2. Resistance response of BP nanosheets, MoS_2 and graphene when exposed to NO_2 at different concentrations (0.1–50 ppm)[13]

Cho et al.'s study hinted at one of major limitations of phosphorene: its instability.[13] However, this instability of phosphorene can be a boon for biomedical application, where its degradation makes it very biocompatible. Phosphorene demonstrates absorption in mid-IR region to visible region, has negligible cytotoxicity and excellent aqueous dispersibility, and is permeable to cell membrane, making it suitable for photocatalytic biological applications. Capitalizing on these benefits, Wang et al. demonstrated the use of phosphorene for photodynamic therapy.[15] Upon illumination, phosphorene was shown to be an effective photosensitizer to produce singlet oxygen with a quantum yield of 0.91.[15] The singlet oxygen was then used for inhibiting the growth of tumor cells both *in vivo* and *in vitro*.[15] *In vitro* studies showed that 71.5% cancer cells suffered apoptosis when the cells with phosphorene were irradiated with 660 nm of light for 10 min[15]. Meanwhile, *in vivo* studies in mice injected with phosphorene and subjected to irradiation for 30 mins had smaller tumors than that of the control groups (Figure 3).[15] This study is an excellent demonstration that phosphorene's properties makes it highly suitable for biological applications. However, the study did not explore any side effects on the animal and its long-run effectiveness for tumor treatment.

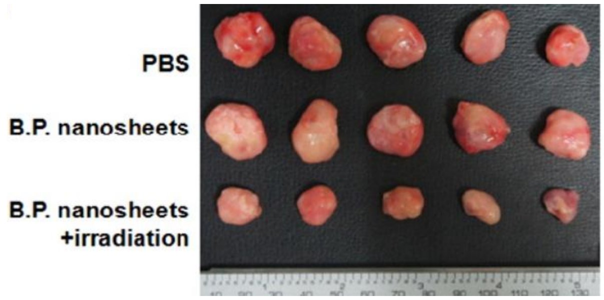

Figure 3. Images of tumor after treatment with phosphate-buffered saline (PBS) solution (control), B.P. nanosheets, and B.P nanosheets with irradiation[15]

The early studies on phosphorene have demonstrated that this material indeed broadens the scope and application of 2D materials. Its instability is a major bottleneck for exploring its full potential in the area of electronics, gas sensing and photocatalysis.[14] On the other hand, this inherent instability along with other intrinsic properties have made phosphorene an omnipotent 2D material for biomedicine.[16] Whether phosphorene is the next generation 2D material will be largely determined by the efforts to stabilize it.

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