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Phosphorene: Overcoming the Oxidation Barrier

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Phosphorene, a single layer of black phosphorus, has recently emerged as a promising two-dimensional (2D) material for bridging the gap between graphene—a high mobility semimetal—and the transition metal dichalcogenides MoS_2 and WS_2, which are semiconductors but have lower carrier mobilities. One of the most acclaimed properties of phosphorene is thus the hole mobility, which typically reaches 10^2–10^3 $cm^2\ V^{-1}\ s^{-1}$ (at room temperature) for an optimal thickness of about 10 nm.[1−3] Combined with the variable bandgap between 0.3 and 2 eV (depending on the layer number and substrate),[4] relative immunity to most intrinsic defects,[5] and the possibility of operation in the ambipolar regime,[1] this makes phosphorene adequate for transistor and phototransistor applications.

As other 2D crystals, phosphorene can be obtained from exfoliation of the parent bulk material black phosphorus. Though still technically difficult, exfoliation and transfer techniques have seen great development ever since the discovery of graphene, and now it is even possible to build “van der Waals” devices by combining monolayers of different 2D materials.[6,7]

However, phosphorene is much less stable than graphene, due to its tendency to oxidize. This has been the object of a recent article by Utt and co-workers.[15] Upon oxidation, phosphorene’s properties change dramatically, even within 30 min of preparation.[8] Oxidation is to be expected, since the 3-fold coordinated phosphorus atoms in phosphorene have electron lone pairs at the surface, forming a preferred site for an oxygen atom to bond.[9] However, controlled oxidation of a pristine phosphorene layer should lead to a passivating oxide layer while preserving the properties of the phosphorene underneath.[10−12] Instead, what often happens with a few layer samples manipulated in air is a structural and/or electronic breakdown ultimately leading to complete disappearance of phosphorene. The rate of oxidation seems to depend on a number of factors including thickness and the presence of water and light.[13,14] It is thus understandable that two years into the investigation of phosphorene as a 2D semiconductor much effort has been dedicated to understand the oxidation mechanisms and ultimately how to control or prevent them.

Can phosphorene deliver on its promise of graphene-level utility? Understanding how and why it oxidizes, as Utt et al. demonstrate, is a key part of the equation.

Utt and co-workers highlighted the role played by intrinsic defects and curvature on the oxidation process.[15] It is found that dislocation lines, which would be virtually undetectable by electrical means in phosphorene due to the lack of gap levels,[5] are preferred sites for oxidation, leading to great lattice relaxation and breakage of the P−P bonds. This may contribute to the breaking of the material and loss of conductive behavior observed during the last stages of degradation.

Utt and coworkers were able to show how a curved phosphorene structure starts to amorphize as oxygen atoms are added.

Further, by using atomistic models with a large number of atoms (up to 600 atoms), Utt and co-workers were able to show how a curved phosphorene structure starts to amorphize as oxygen atoms are added. If phosphorene is curved, the oxygen process tends to increase the curvature. This can be noticed in the conical phosphorene model represented in Figure 1 (where Tr(g) and Det(g) are respectively the trace and determinant of the metric tensor, H and K are the mean and Gaussian curvatures, respectively, and τ is the local thickness). A corollary of this finding is that phosphorene nanotubes, if realized, would be prone to oxidation, which would change their structure. The increase of curvature with oxidation may also be related to the increase of roughness observed experimentally (in a larger, micrometer scale).[10]

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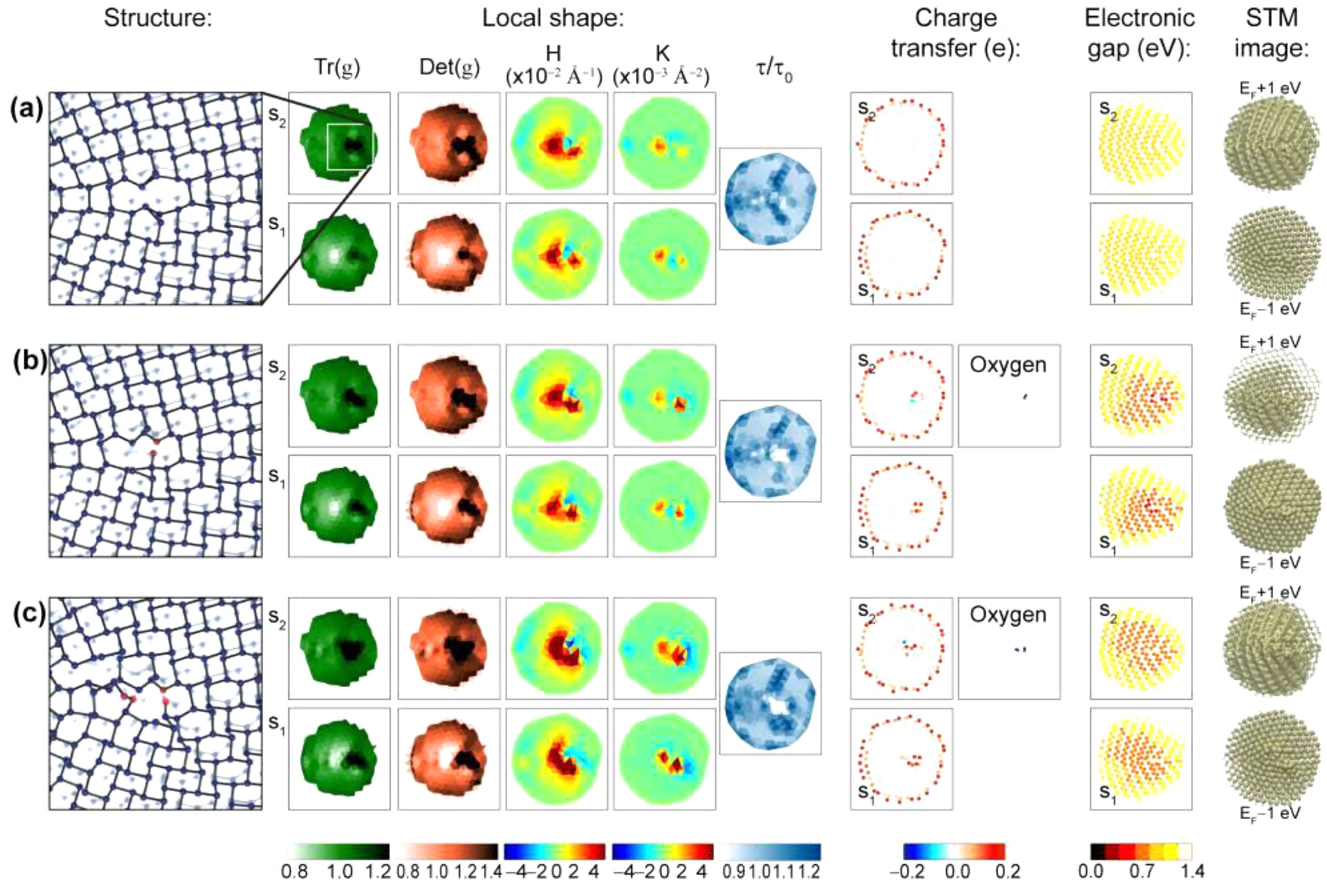

Figure 1. The figure shows conical phosphorene structure (a) without oxygen dimers; (b) with one dimer; and (c) with two dimers. The shape information now indicates a clear tendency toward amorphization as BP oxidizes: BP sees fluctuations on its metric and curvature, and it bulges too as seen in the/0 subplots. Oxygen atoms gain electrons from BP, and the electronic gap is reduced as these two dimers are absorbed. Simulated STM images are also shown. Reprinted with permission from ref 15. Copyright 2015 American Chemical Society.

For phosphorene-based technology to thrive, it is therefore crucial to develop techniques to control or suppress oxidation. Because of the intensified effort in this area, some effective encapsulation methods have been proposed. One consists of encapsulating or "sandwiching" phosphorene between BN layers. In this manner, graphene contacts can also be incorporated to make fully 2D heterostructure transistors.[7] Encapsulated devices are preserved for at least two months after fabrication.[7]

An alternative is AlO_x encapsulation using atomic layer deposition.[16,17] This technique has been used to create flexible phosphorus-based transistor device structures that are stable for more than 2 weeks and resist more than 5000 bending cycles.[17]

The existing progress in this area has shown that the phosphorene's propensity to oxidate should not be viewed as an impediment for phosphorene devices to become visible. We hope additional theoretical and experimental study of this oxidation process will facilitate the advance of phosphorus-based technologies.

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