Covalent Functionalization of Black Phosphorus

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Abstract

Black Phosphorus shows promising properties but its ambient stability remains a key issue that hinders its use in applications. We have investigated the degradation of black phosphorus in ambient conditions and demonstrate oxidation occurs through the formation of P-O-P species which react further to form volatile phosphoric acids. Covalent functionalization using aryldiazonium salts has previously been used to increase its ambient stability[1]. We present a new functionalization strategy using aryliodonium salts that does not induce oxidation and provides a higher degree of covalent functionalization by attachment to both O- and P- sites[2]. The iodonium functionalization strategy results in increased oxidation resistance due to inhibition of P-O-P formation. Furthermore, the diazonium route leads to oxidation, multilayer formation and non-covalent solvent passivation. We provide a comparison between the two functionalization methods and show that functionalization using alkyl- and aryliodonium salts is a more compatible stabilization strategy which also allows potential tuning of optical and electronic properties.

References

[1] Ryder, C. R.; Wood, J. D.; Wells, S. A.; Yang, Y.; Jariwala, D.; Marks, T. J.; Schatz, G. C.; Hersam, M. C. Covalent Functionalization and Passivation of Exfoliated Black Phosphorus via Aryl Diazonium Chemistry. *Nat. Chem.* **2016**, *8* (May), 597–602.

[2] van Druenen, M.; Collins, G.; Davitt, F.; Glynn, C.; O'Dwyer, C.; Holmes, J.D. submitted (2018)

Figures

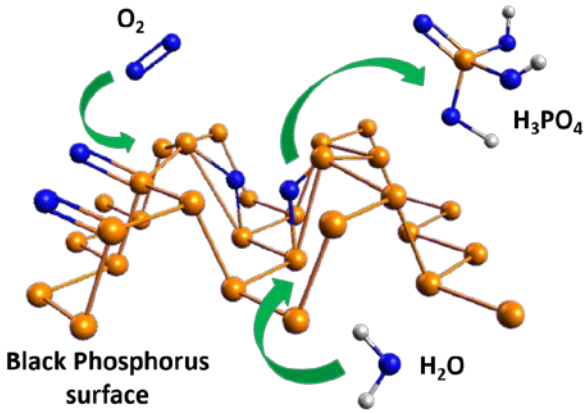

Figure 1: Oxidation of black phosphorus in ambient conditions

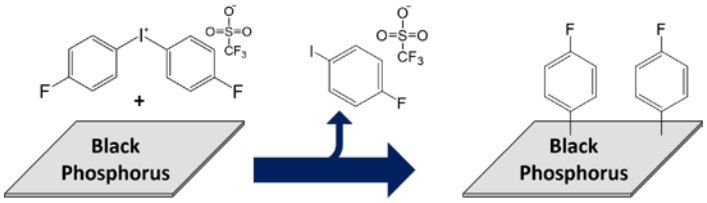

Figure 2: Functionalization of black phosphorus using aryliodonium salts