Oxygen-functionalized graphene: computational modelling of structures, properties and application in phosphate sensing

Natalia Martsinovich
Negar Mansouriboroujeni, Xue Yong
Department of Chemistry, University of Sheffield, Sheffield S3 7HF, United Kingdom
n.martsinovich@sheffield.ac.uk

Graphene's excellent electronic and optical properties enable its use in a variety of applications. In particular, graphene is widely used as a sensor material to detect volatile gas molecules and as an electrode material in electrochemical sensors. While graphene's high electrical conductivity enables high-sensitivity measurements, selectivity is a challenge, which may be addressed by functionalizing graphene with various functional groups. In this project we collaborated with experimental partners to characterise oxygen-functionalized graphene materials and to design graphene-based sensors to detect phosphate, an essential plant nutrient [1]. We used theoretical modelling to investigate how the nature of oxygen functionalization affects electronic properties of graphene and its interaction with adsorbed phosphate. Density-functional theory (DFT) calculations were used to model flat and curved graphene sheets containing epoxide and hydroxyl groups and substitutional oxygen at different concentrations (1-12% oxygen). Curvature was found to have little effect on the electronic properties of graphene: curved graphenes remained semimetallic, with optical absorption spectra similar to graphene. However, oxygenation had significant effect on graphene's optical and electronic properties, with new states at the Fermi level for graphenes containing substitutional oxygen, and gap opening in functionalised graphenes with oxygen content above 6%. This tuning of graphene's properties by chemical functionalization can lead to new applications in electronics and sensors. As the next step, we investigated adsorption of several phosphate species (PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^{-}$, H_3PO_4) on pristine and oxygenated graphene (Figure 1). Adsorption of phosphate species was found to affect graphene's band structure and resulted in significant and distinct changes in pristine and oxygen-functionalized graphene sheets' electrical conductivities. In particular, our calculations predicted an increase in resistivity upon adsorption of phosphate on pristine graphene, which was experimentally verified by our collaborators [1]. These results suggest pristine and oxygen-functionalized graphene as promising materials for electrical sensors.

References

[1] Yong, X. et al. ACS Applied Nano Mater. (2023) 10.1021/acsanm.3c04147.

Figures

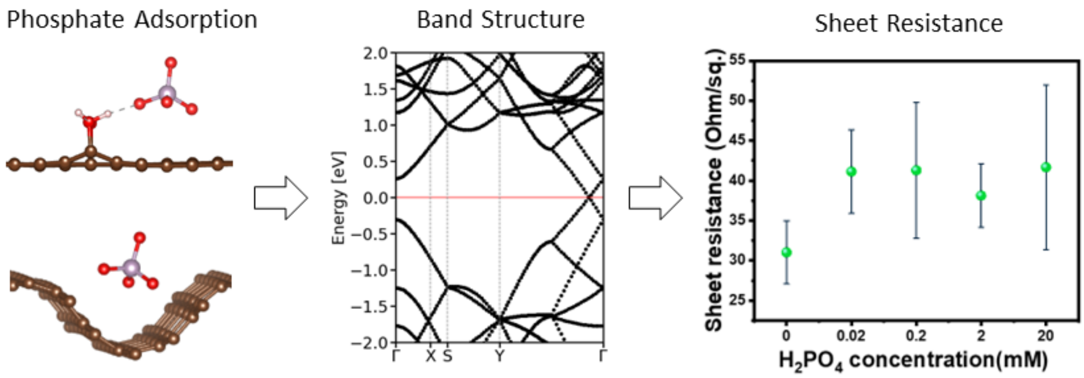

Figure 1: (a) Adsorption of phosphate on graphene, (b) representative band structure of graphene with adsorbed phosphate, (c) measured electrical resistance of graphene with adsorbed $H_2PO_4^{-}$ [1].