Stability Characterisation of Liquid-Exfoliated Black Phosphorus nanosheets

Damien Hanlon, Claudia Backes, Andrew Harvey, Jonathan Coleman

Trinity College Dublin, Dublin 2, Ireland
hanlonda@tcd.ie

Abstract

Over the last number of years there has been significant interest in two-dimensional materials in the area of nanoscience. Initially research has been focused on the study of graphene, however; more recently focus has expanded to other 2D nanomaterials such as; BN, transition metal dichalcogenides (TMDs) and transition metal oxides (TMOs). Black phosphorus (BP) is a new layered material which has generated significant interest over the last year. It is only the second elemental 2D material to be studied after graphene. BP is a layered crystal in its bulk form, consisting of atomically thin layers of phosphorus atoms stacked on top of each other via van der Waals interactions, similar to the way graphene stacks to form graphite.[1, 2] However; in contrast to other layered 2D nanomaterials which display direct bandgaps in the monolayer form, BP displays a direct bandgap in the mono-, few-layer and bulk forms. This makes BP highly attractive for electronics and optoelectronics.[3]

Accordingly there have been numerous reports producing BP nanosheets via mechanical cleavage. However; to produce large quantities of material a scalable method is required. Therefore, BP crystal has been subjected to liquid phase exfoliation in cyclohexyl pyrrolidone (CHP), a common organic solvent. This process produces high quality nanosheets with lateral dimensions up to 3µm. These nanosheets unlike graphene and some other layered materials are unstable under ambient conditions.[4] This poses a significant problem for processing and fabrication of devices using BP. Herein a spectroscopic method is presented to track the degradation of the nanosheets in solution produced using liquid phase exfoliation. A stability metric is also presented, which can be used to determine the amount of reacted nanosheets in a given sample. It was found that the instability of the nanosheets predominantly occurs via a disproportionation reaction at the edges. Interestingly the stability of the nanosheets varies across different solvents where amide solvents show the greatest stability. Samples prepared using appropriate solvents can slow down the reaction which reduces the degradation to ~8% after 3 days.

References

1. Coleman JN. Liquid Exfoliation of Defect-Free Graphene. *Accounts of Chemical Research* 46, 14-22 (2013).

2. Hernandez Y, *et al.* High-yield production of graphene by liquid-phase exfoliation of graphite. *Nature Nanotechnology* 3, 563-568 (2008).

3. Xia F, Wang H, Jia Y. Rediscovering black phosphorus as an anisotropic layered material for optoelectronics and electronics. *Nature Communications* 5, 4458 (2014).

4. Favron A, *et al.* Photooxidation and quantum confinement effects in exfoliated black phosphorus. *Nature materials* 14, 826-832 (2015).

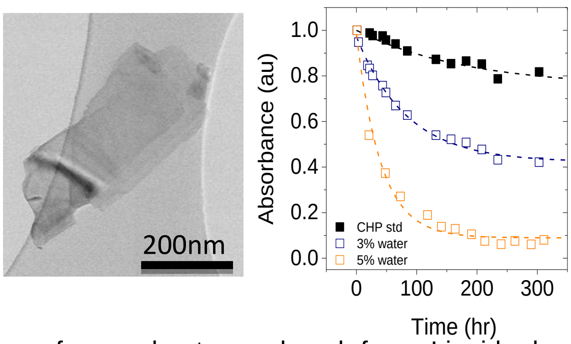

Figure 1: A) TEM image of nanosheets produced from Liquid phase exfoliation, B) Decreasing nanosheet concentration with varying water contents as a function of time.