Ph.D. thesis

Experimental studies on the exfoliation and oxidation behavior of few-layers black phosphorus

Juan Fernando Gómez Pérez

Supervisors:
Dr. Ákos Kukovecz
Dr. Zoltán Kónya

Doctoral School of Environmental Sciences

University of Szeged, Faculty of Science and Informatics,
Department of Applied and Environmental Chemistry

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1. Introduction

Black phosphorous (BP) is the thermodynamically stable allotrope of phosphorous under ambient conditions. It is a layered material that can be exfoliated into a monolayer two-dimensional (2D) material similar to graphene: phosphorene.

The rediscovery of graphene[1] in 2004 opened a new chapter in condensed matter material science. Although interest in layered materials can be traced back to at least three decades[2,3], two-dimensional (2D) materials have commanded the attention of researchers from all over the world most intensively during the last decade. Even so, various difficulties have limited the exploitation of graphene in industrial applications: lack of standardization, defect control, and production scalability were among the main issues, because the properties of any 2D material depend strongly on the quality (i.e. the number of layers and defects) of the structure. 2D materials offer new opportunities due to their physical and electronic properties: the possibility to tune their bandgap and their large area to volume ratio are the main examples.

Nowadays, more than 500 types of 2D materials can be found in literature[4], but only three mono-element 2D materials have been demonstrated until now: graphene, silicene, and phosphorene. Other monoelements have been predicted (i.e. stanene or tinene from Sn; borophene from B; and antimonene from Sb) but they have not been fully demonstrated at experimental level[5]. The list of 2D materials keeps growing constantly. For example, a new allotrope (blue) of phosphorus was synthesized[6,7] very recently, only two years after it was predicted by computational studies[8].

Black phosphorus is a p-type semiconductor with a bandgap of 0.3 eV in bulk state and approx. 2.2 eV for the isolated monolayer. Therefore, unlike other 2D materials, black phosphorus offers opportunities in the infrared part of the spectra (infrared optical sensors[9]) for samples thicker than approx. 5 nm and opportunities in the visible range (e.g. thin-film solar cells[10]) for few-layers systems. This versatility and operational range have no parallel in other 2D materials.

Since 2014, an increasing interest has been observed for black phosphorus[11–13]. This has been boosted by approaching the performance limits of Si-based semiconductor technology and the realizing the technological limitations of graphene (i.e. absence of a well-defined bandgap)[14,15]. Different phosphorene applications have been evaluated at the experimental level, for instance:

broadband photoresponse FET transistors[16], hydrogen evolution catalyst[17] and sensors for different analytes: NO_2[18–20], NH_3[21], humidity[22–24], Hg^{2+}[25] and biosensors[26]. In some cases the results have surpassed the figures of merit of graphene or MoS_2[27], reinforcing the status of phosphorene as a promising material.

Up to date, information on the environmental applications of black phosphorus is still very limited, as 80% of the papers published until 2015 was still at the theoretical level[4], and issues on stability are yet to be addressed in detail. Nevertheless, semiconductors in general have a long tradition for successful environmental applications. For instance, TiO_2 has proven useful for the photocatalytic degradation of persistent pollutants and disinfection during the last two decades. Currently, in the field of 2D materials, van der Waals heterostructures are among the most exciting materials with promising applications in photocatalysis and energy harvesting as they can be tuned for light absorption and enhance the electron-hole stability[28].

Black phosphorus suffers from prompt oxidation in comparison with other 2D materials and its stabilization is yet unsolved[29]. Several theoretical papers[30–33] have addressed the oxidation of black phosphorus recently, and the available experimental works encourage the bandgap engineering possibilities. While black phosphorus passivation with native oxides is theoretically possible, control over the types of oxides being formed has not been achieved yet, and a better understanding on the oxidation process is required to overcome the hurdles for future applications.

The instability of exfoliated black phosphorus has promoted its functionalization. The functionalized materials exploit the advantages of dissimilar components to create novel nanostructures[34] and modulate their electronic properties. Additionally, functionalization through different approaches (i.e. covalent, noncovalent, van der Waals heterostructures) has been under research in recent years for the passivation of few-layers BP, but a better understanding of the oxidation processes is required. The signatures of oxidation have been presented in different studies and its effects are not only topographical, but electronic as well. The electronic structure modulation caused by oxidation is much larger than the quantum confinement effect, and some groups have theorized on the few-layers black phosphorus oxides as a better possibility for the future applications[32].

Computational studies have demonstrated the formation of different types of oxides with interesting properties (e.g. transparent passivation and electronically neutral oxides). Nevertheless, contradictory results on the stability and identification of metastable oxides limit the possibilities of bandgap engineering by native oxides.

In this work, a discussion on the oxidation of black phosphorus is presented and novel methodologies are proposed for the identification of black phosphorus oxides transitions. The results contribute to solving some of the controversies on the stability of the metastable oxides, on the identification of the primary outcome of oxidation and on mechanistic oxidative processes.

2. Experimental

Bulk BP crystals were purchased from HQ Graphene (Groningen, the Netherlands) and stored in argon atmosphere. In a typical experiment, the exfoliation was made by ultrasonication (Liquid Phase Exfoliation, 120 W, 35 kHz). Approximately 5 mg of bulk BP was added to 10 mL of solvent (either N-methyl-pyrrolidone, NMP or acetone) in a glass vial tightly closed with a septum cap and purged with argon to reduce the dissolved oxygen content. The temperature of the bath was kept constant at 298 K to avoid variations in the surface tension components of the solvent caused by the temperature increase during the ultra-sonication.

The exfoliated materials were investigated with a battery of characterization techniques: TEM, AFM, FTIR, XPS, XRD and Raman spectroscopy. The Raman microscope (Senterra II, Bruker) was coupled with a temperature-controlled stage and *in situ* Raman measurements were interpreted in correlation with thermogravimetric results.

3. New scientific results

3.1. Results related to the liquid phase exfoliation and characterization of black phosphorous

3.1.1 Despite previous negative literature reports I have demonstrated that the liquid phase exfoliation of black phosphorus in acetone is possible, even though it does require longer sonication periods in comparison with other high boiling point solvents. Acetone exfoliated black phosphorus exhibits optical bandgaps between 1.4 eV and 2.2 eV in agreement with the flame thicknesses in the range of 0.5 nm to 2 nm as determined by our AFM measurements.

3.1.2 I have devised a protocol for evaluating the topographical effect of transferring NMP-exfoliated black phosphorus to acetone through several vacuum steps. The acetone-stabilized materials show a size disaggregation towards the few-layers black phosphorus. The suspensions were found to be composed of monolayers, bilayers and up to 4-layers flakes. This composition is the most relevant for the evaluation of the quantum confinement effects on the chemistry of black phosphorus.

3.1.3 I have demonstrated that there exists a linear correlation between AFM and DLS results concerning the topographical characteristics of liquid phase exfoliated material in both acetone and NMP. This correlation can be exploited as a fast measure for the characterization of few-layers black phosphorus suspensions, because hydrodynamic size assessment is less time consuming than AFM characterization and more representative than TEM. DLS results are based on the size distribution of thousands of flakes, therefore, they are less prone to operator bias than TEM image analysis.

3.1.4 I have performed the first detailed experimental characterization of the thermal stability of acetone-exfoliated black phosphorus. These results evidenced that the obtained material can be thermally treated for the removal of remnant solvent without any significant lattice transformations.

3.1.5 I have confirmed the presence of a blueshift in the Raman spectra of BP related to the confinement of few-layer flakes. This finding contributes to an interesting ongoing literature debate on whether or not there is a correlation between Raman blueshift and the presence monolayers.

3.1.6 I have demonstrated that the exfoliation degree of BP is correlated with modulations in the thermal expansion coefficients and the harmonic phonon frequency, as calculated from the in situ Raman spectra of liquid phase exfoliated materials.

3.2. A novel approach for tracking the oxidation of exfoliated black phosphorus

3.2.1 I have demonstrated the correlation between the thermoanalytical properties (TGA and DSC), the electrical resistance and the *in situ* Raman spectra of acetone-exfoliated black phosphorus for the first time in literature. Based on these results it was possible to associate the oxidation processes with the thermal expansion of the lattice.

3.2.2 I was the first to describe a practically perfect agreement between the computationally predicted thermal expansion of the black phosphorus lattice and the temperature-induced red shift of all Raman vibrational modes at low temperatures. This finding could serve as a basis for a novel analytical method to evaluate sorption on exfoliated black phosphorus.

3.2.3 In practical terms, I have highlighted an operational limit for the use of black phosphorus in real world applications. At temperatures above 220 °C phase transitions are expected, and –according to computational works– this may modify the electronic structure of the material drastically. This is especially relevant for optoelectronic devices that depend on light absorption.

3.2.4 I have verified the presence of a blueshift in the vibrational modes of black phosphorus at the early stages of oxidation. These results are in excellent agreement with recent reports on the appearance of partially oxidized Np and on the diminishing of photoluminescence in samples exposed to air.

3.3 Relative thermal stability of phosphorene oxides

3.3.1 I have proposed a mechanistic model that includes a phase transition between phosphorene oxides to explain the experimentally observed thermal behavior of the material above 373 K. This is a new approach in black phosphorus literature and is a contribution to the field of defects engineering. Additionally, the proposed model gives support to the widely used empirical oxidation indicator (the Raman A_g^1/A_g^2 peak ratio) that lacked a mechanistic explanation until now. Surface oxides with a low concentration of chemically-bonded oxygen are dominant below 373 K. A higher concentration of chemically bonded oxygen is incorporated with dominance of surface oxide between 373 K and 493 K. At approx. 493 K, the surface to planar oxide transition takes plac, which is characterized by lattice deformation in the stacking direction perpendicular to the plane. Planar oxides are present between 493 K and 673 K, then sublimation starts at approx. 673 K. Note that defects and impurities can affect the precise temperature values because they lower the activation energy of oxidation reactions.

4. Practical applicability of the results

Exfoliating black phosphorus in acetone instead of high boiling point solvents offers advantages for the cleansing of the remnant solvent that may be relevant in precise BP characterization works affected adversely by adsorbed contaminants. Acetone exfoliated materials have been characterized by a battery of characterization techniques and the results evidenced the narrow distribution of the topographical characteristics.

Other results presented in this work provide a fundamental description of phosphorene oxides with respect to the transitions between the two types of dominant oxides that exhibit very different electronic structures. An endothermic phase transformation of exfoliated black phosphorus was detected and the process was located in the stacking direction of the lattice structure. Additionally, the electrical measurements demonstrated an anomalous increment in the electrical resistance is associated to the thermogravimetric (TGA and DSC) processes at the same temperature range of the lattice distortion as indicated by *in situ* Raman measurements.

The possibility of bandgap engineering of exfoliated black phosphorus by oxidation has been proposed, but as demonstrated in the dissertation, the identification of the different types of oxides was not sufficiently unambiguous until now. My work has uncovered a transition that contributes to the understanding of the oxidation process and defects engineering. Moreover, these results offer an explanation for the applicability of an empirical oxidation indicator that lacked mechanistic support in the current literature of exfoliated black phosphorus.

The most practical result of my work is the identification of the practical high temperature threshold that black phosphorous can withstand without phase transition. This is relevant because it underlines that exposure to higher temperatures induces significant electronic structure changes that affect the performance of such devices.

5. Papers related to the thesis

1. **J. Gómez-Pérez**, Z. Kónya, and Á. Kukovecz, "Acetone improves the topographical homogeneity of liquid phase exfoliated few-layer black phosphorus flakes," Nanotechnology, vol. 29, no. 365303, 2018.
   IF$_{2018}$: 3.404 **Independent citations:** 1

2. **J. Gómez-Pérez**, B. Barna, I. Y. Tóth, Z. Kónya, and Á. Kukovecz, "Quantitative tracking of the oxidation of black phosphorus in the few-layers regime," ACS Omega, vol. 3, pp. 12482–12488, 2018.
   IF$_{2018}$: N.A. (new journal) **Independent citations:** 1

3. **J. Gómez-Pérez**, D. G. Dobó, K. L. Juhász, A. Sápi, H. Haspel, Á. Kukovecz, and Z. Kónya. "Photoelectrical response of mesoporous nickel oxide decorated with size controlled platinum nanoparticles under argon and oxygen gas," Catal. Today, vol. 284, pp. 37–43, 2016.
   IF$_{2016}$: 4.636 **Independent citations:** 0

6. Presentations, posters, attending conferences

1. **Abstract and poster: "Tracking the oxidation of black phosphorus in the few-layers regime"**
   J. Gómez-Pérez, B. Barna, I. Y. Tóth, Z. Kónya, and Á. Kukovecz.
   8th Szeged International Workshop on Advances in Nanoscience, Szeged, Hungary, 2018.

2. **Abstract: "Black phosphorus oxidation: problem or opportunity"**
   J. Gómez-Pérez, Z. Kónya, and Á. Kukovecz.
   Junior EUROMAT, Budapest, Hungary, 2018.

3. **Abstract: "Solvent exchange assessment for liquid phase exfoliated Black Phosphorus"**
   J. Gómez-Pérez and Á. Kukovecz.
   12th Conference for Young Scientists in Ceramics. Novi Sad, Serbia, 2017.

4. **Abstract and poster: “Understanding the photoelectrical response of mesoporous nickel oxide decorated with controlled size platinum nanoparticles in different atmospheres.”**
   J. Gómez-Pérez, D. G. Dobó, K. L. Juhász, A. Sápi, H. Haspel, and Á. Kukovecz.
   7th Szeged International Workshop on Advances in Nanoscience, Szeged, Hungary, 2016.

7. Other publications

1. Sápi, U. Kashaboina, A. Baán Ábrahámné, **J. Gómez-Pérez**, I. Szenti, Gy.Halasi, J. Kiss, B. Nagy, T. Varga, Á. Kukovecz and Z. Kónya “Synergetic of Pt nanoparticles and H-ZSM-5 zeolites for efficient CO2 activation: Role of interfacial sites in high activity”. Submitted. 2019

2. E. Lantos, L. Mérai, A. Deák, D. Sebők, **J. Gómez-Pérez**, I. Dékány, Z. Kónya and L. Janovák. “Preparation of sulfur hydrophobized plasmonic photocatalyst towards durable superhydrophobic coating material” J Mater Sci Technol. Submitted. 2019.

Peer-reviewed papers total: 3	out of this, related to the topic of the thesis: 3
Cumulative impact factor: 8.040	out of this, related to the topic of the thesis: 8.040
Independent cites total: 2	out of this, related to the topic of the thesis: 2

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