Black Phosphorus Synthesis and Exfoliation via Ball Milling

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I. Background

Motivation

- Black Phosphorous (BP) exhibits desirable optoelectronic properties in few-layer form
- BP has a direct band gap as a function of the number of layers (1-5)
- Current BP production is expensive and yields low volumes (chemical vapor transport and hot press)
- BP can be produced from inexpensive red phosphorous (RP) via high energy planetary ball-milling (PBM)
- BP mono/few-layers (phosphorene) can be exfoliated for potential use in electronic devices
- There is a need to optimize PBM and explore the efficiency of exfoliation via PBM

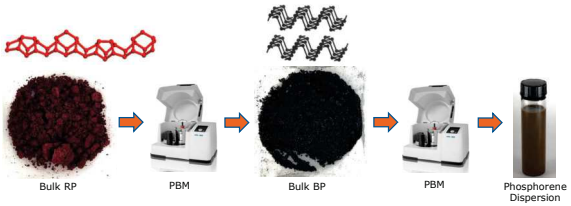
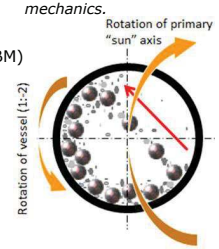


Figure 1: *Steps from RP to exfoliated BP solution. RP crystal structure (chain of cage) and BP crystal structure (2D hexagonal armchair) are shown.*

Figure 2: *Schematic of planetary ball milling mechanics.*



Solution

- Use in-situ pressure monitoring to identify when the allotrope conversion takes place during PBM
- Observe various milling intensities (rpm) to minimize milling duration and wear on vessel and media
- Observe BP suspension stability and exfoliation efficiency in isopropyl alcohol (IPA)

II. Experimental

Methods

- PBM runs were conducted for 1 hour at various milling intensities to identify intensity needed for conversion
- PBM at 300 rpm was analyzed at three 30 min intervals to observe the RP to BP conversion kinetics
- BP product was dispersed in IPA and milled at 150 rpm for 24 hours via PBM for exfoliation

Sample Preparation

Conversion

- In an argon glovebox, 1 g of RP powder was added to the PBM vessel with ~105 g SS 440C media. The vessel was loaded into the Retsch PM 100 PBM for processing (Figure 3)

Exfoliation

- In the argon glove box, bulk BP (0.25 g) was dispersed in 50 mL of IPA with 50 g of 5 mm ZrO_2 media

UV-Vis/ICP-MS

- A series of diluted solutions was made using 12 mL of IPA and quantities of drops from the exfoliated dispersion
- Aliquots of 3 mL were used for UV-Vis. The remaining 9 mL was used for ICP-MS dissolutions in nitric acid

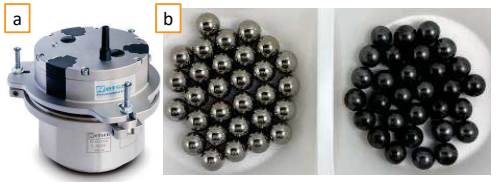


Figure 3: *(a) Retsch stainless steel PBM vessel with a GrindControl lid used for in-situ pressure monitoring. (b) New vs used SS 440C media after 200 hours total run time.*

Characterization

- X-ray diffraction (XRD) for bulk BP phase identification
- Raman spectroscopy for chemical identification
- UV-Vis spectroscopy for concentration identification
- ICP-MS for phosphorene content
- TEM for exfoliation effects

III. Results

Conversion

- The progress of the conversion was successfully observed via images and XRD (Figure 4)
- Extent of conversion after 1 hour was observed for various intensities via sampling with XRD (Figure 5)
- The conversion was identified by pressure changes preceding a steady state plateau via in-situ pressure monitoring (Figure 6)

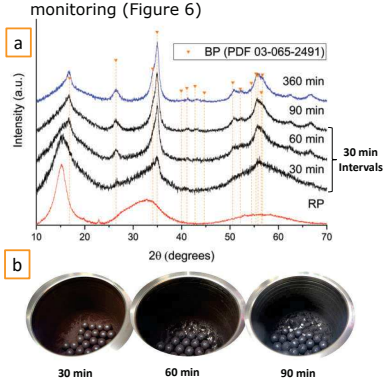


Figure 4. *(a) XRD patterns of BP milled for 6 hours at 300 rpm, a series of samples taken at three 30 min intervals, and pure RP. (b) Optical images show PBM vessel and powder at each interval.*

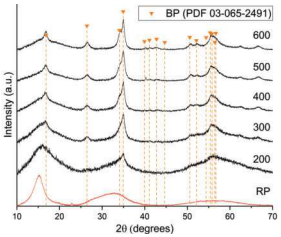


Figure 5: *XRD of BP after 1 hour at various intensities.*

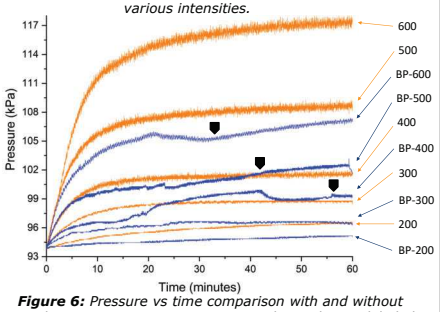


Figure 6: *Pressure vs time comparison with and without media at various intensities. Runs with powder are labeled as BP. Black markers indicate conversion completion.*

Exfoliation

- Preservation of BP was confirmed via Raman spectroscopy (Figure 7)
- UV-Vis absorbance and ICP-MS concentrations were used in Beer's Law to determine an extinction coefficient (***ε***) (Figure 8)
- The BP remaining in IPA was 0.5 mg/mL, indicating an exfoliation efficiency of 10%
- Presence of few layer BP flakes was confirmed via TEM imaging, though most flakes appear thicker (Figure 9)

Beer's Law: $A=\varepsilon bc$
UV-Vis
Absorbance: ***A***
Pathlength (cm): ***b***
ICP-MS
Conc. (g/L): ***c***

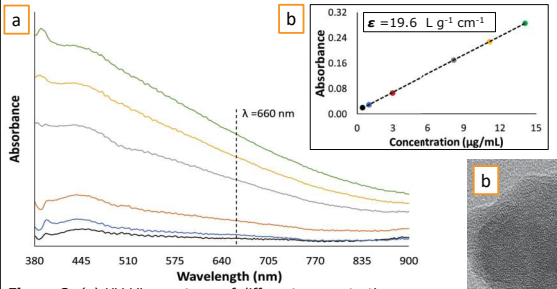


Figure 8: *(a) UV-Vis spectrum of different concentrations of BP dispersions; absorbance at λ=660 nm[1] was used in (b) Beer's Law curve to obtain extinction coefficient[2].*

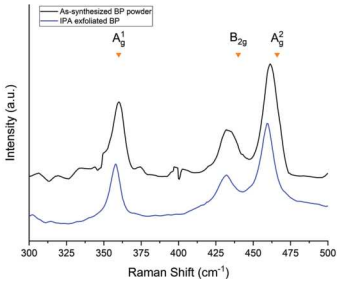


Figure 7: *Raman spectroscopy on bulk BP and the exfoliated dispersion. BP reference peaks are labeled for reference[1].*

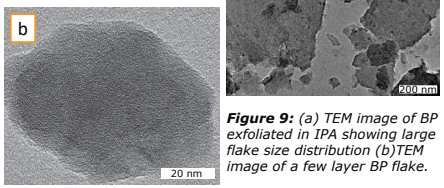


Figure 9: *(a) TEM image of BP exfoliated in IPA showing large flake size distribution (b)TEM image of a few layer BP flake.*

IV. Discussion

Conversion Summary

- Conversion of RP to BP via PBM was successful and occurs more rapidly as milling intensity increases
- In-situ pressure data for media only runs shows an increase in pressure as milling intensity increases. When powder is added to the PBM, the collisions become more inelastic resulting in lower pressures.
- By combining XRD and in-situ pressure monitoring, it is evident that the conversion takes place with an accumulation of impacts over time.
- The shortest conversion time (30 minutes) occurred at 600 rpm.

Exfoliation Summary

- Planetary ball milling successfully exfoliated BP into few-layer phosphorene.
- IPA was observed to exhibit resistance to sedimentation for phosphorene dispersions.
- The calculated extinction coefficient is comparable to what others have found with possible discrepancies due to concentration measurements, solvent choice, and wavelength used for absorbance[1],[2].

References

[1] Kang et al. (2016). Stable aqueous dispersions of optically and electronically active phosphorene. *Proceedings of the National Academy of Sciences*, *113*(42), 11688–1169
[2] Fu et al. 2017. 'Different-sized black phosphorus nanosheets with good cytocompatibility and high photothermal performance', *RSC Advances*, 7: 14618-24.

Acknowledgements

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