Effect Of Ultrasonic Irradiation On The Allotropes Of Phosphorus

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Abstract

Two-Dimensional (2D) materials have recently been under investigation due to their unique structure. Since the advent of graphene many materials have been discovered to have a similar structure of layered sheets with in-plane covalent bonds and out-of-plane Van der Waals forces. This lattice structure allows the materials to be exfoliated into single or few layered sheets which are only few atoms thick. This is very promising for applications in nanotehcnoloy and nanoelectronics because they represent the fundamental limit of how thin devices can be made. Elemental phosphorus exists in four allotropes each having different structural, electrical and chemical properties. These allotropes are identified by their color including white, red, violet, and black phosphorus. Of the four allotropes, black phosphorus (black P) has a crystalline lattice of phosphorus atoms with layered sheet structure similar to graphene. Black P is a semiconductor with a layer dependent band gap between 0.3eV for bulk samples and 2.0eV for monolayer phosphorene which makes it a candidate for field effect transistor applications as opposed to graphene which is a conductor. Currently, a stable form of black P has been challenging and expensive to synthesize through chemical vapor deposition processes. In this investigation, red P was successfully transformed into black P as a result of ultrasonic irradiation. The process of ultrasonication involves resonating high frequency sound waves in a solution to create cavitation bubbles. These bubbles are vacuums which from between waves of pressure and implode to create temperatures near 5000K and pressures of up to 8GPa on a 2 to 5 micron scale within the solution. This high frequency ultrasonic exposure to phosphorus results in change in color from red to black and a prominent A_{2g} Raman peak which is observed in black P.

Keywords: Black Phosphorus, Ultrasonication, Liquid Synthesis, High Pressure, High Temperature

1. Introduction

Due to the two-dimensional (2D) character of the graphene[1], interest in both the electronic and structural aspects of other 2D materials have recently been heavily researched. This class of materials possess a variety of different electronic ground states, such as superconductivity[2], lattice deformation, and Mott transition[3]. Of these 2D materials phosphorene has gathered significant interest due to its unique structural[4, 5], optical[5, 6] and electronic[6, 7, 8] properties. Phosphorene is the second elemental 2D material to be discovered after graphene which is 2D elemental carbon[1]. There have been a number of other compounds discovered to have 2D structures including the transition metal dichalcogenides[9] and 2D elemental silicon (silicene)[10].

   Elemental phosphorus (P) occurs in four distinct allotropes which exhibit different properties due to the structure of the material. These allotropes are white, red, violet and black. White phosphor has a structure of loosely bound P_4 molecules[10], while red is an amorphous network[11] and violet is an organized lattice of P_8 and P_9 groups[12]. Much like graphite, black P has a structure of stacked 2D sheets held together by weak van der Waals forces and can be exfoliated to produce monolayer black phosphorus (called phosphorene)[13]. 2D materials have been under investigation because they currently represent the fundamental limit of how thin devices can be made. Making devices smaller has been the main thrust of the semiconductor industry since its inception and building devices by atomic layer is one of the avenues

being studied to increase device density[14]. There has been a significant amount of interest and research done on phosphorene in the field of nano-electronics[13] recently because it may be well suited for this layer by layer device fabrication. As a semiconductor with a bandgap ranging between 0.3eV (bulk) and 2.0eV (monolayer), black phosphorus is a promising candidate for optoelectronic and flexible transistor applications[13]. However, black phosphorus does not occur naturally and is synthesized through high temperature and high pressure processes that does not lend to low-cost thin-film synthesis[15, 16, 17].

In this investigation, high frequency ultrasonic radiation was used in order to augment a transition from red phosphorus to black phosphorus. Ultrasonication is a tool that is used frequently in cleaning processes[18, 19, 20], however, due to the rapid implosions occurring at a localized point, it can also be used to drive some chemical reactions[21]. During the ultrasonication process, high frequency acoustic waves interact with the material and create ~5µm cavitation bubbles in aqueous solution[21]. Cavitation bubbles form vacuums in liquids around fast moving solid bodies such as a propeller or by high-intensity sound waves. In acoustic cavitation the bubbles are formed due to the acoustic pressure waves between regions of compression and decompression. Due to the high hydrostatic pressure outside these bubbles they implode and in doing so, create a significant amount of heat (~5000K)[21] and high pressure (~8GPa)[22]. In the presence of these conditions, highly reactive radicals are generated (H^- and OH^+ in water) which can be used to drive chemical reactions[21]. To exert these high pressures and temperatures, a diamond anvil cell (DAC) can be used[23]. The use of a DAC however severely limits bulk manufacturing since sample sizes range from 5-300um. With the use of ultrasoncation however, production is not restricted to size and quantity of the sample. The high pressure and high temperature effect of ultrasonication can be used to transition between the different phosphorus allotropes.

2. Methodology

In this investigation a VCX 650 20kHz horn ultrasonicator by Sonics & Materials and an Elmasonic P 37 - 80kHz ultrasonic bath were used in the synthesis of the phosphorus allotropes. Several tools were used in the characterization of the products including a Cary 5000 UV-VIS NIR Spectrometer system for the absorbance measurements, a Kratos Axis Ultra SEM-EDX system for the Energy Dispersive X-ray spectroscopy, a WeiTek micro-Raman system with 432nm laser for all Raman spectra, and an electrical probing system, HP 4156c, was used for the current-voltage measurements.

3.   Results and Discussion

Ultrasonication on a dispersion of red phosphorus in water significantly changes the color of the material. The change was observed in both dispersions treated by a 20kHz horn ultrasonicator and a 40 to 80kHz ultrasonic bath with the samples in vials submerged in the aqueous bath. While the bulk of the sample was still red in color after 60 minutes of ultrasonication at an average energy of 60watts a black substance had deposited at the bottom of the beakers and vials and a violet film was synthesized on the inside walls of the beaker. **Figure 1a** shows the three resulting products - red P, violet P and black P. Violet phosphorus (aka Hittorf's phosphorus) can be synthesized by annealing amorphous red phosphorus at a temperature of 550ᵒC[16] while black phosphorus has been reported to form from white phosphorus at pressures of 1.2GPa and a temperature of 1100K[15] or from red phosphorus at pressures of 7.5GPa at ambient temperatures[23]. With ultrasonication, both of these were formed at ambient temperature and pressure after as little as 30 minutes of treatment with greater yield with a 1-2 hour treatment.

The UV Vis spectra shows the light absorbance of the three distinct products. **Figure 1b** shows the difference in their light absorbance as quantitative confirmation of the color difference. Additionally, since none of these products show a peak in the visible range (300nm – 800nm) their band gap must be either in the ultraviolet or infrared region. This eliminates bandgaps between 1.55eV and 4.13eV for these materials. Black Phosphorus has a tunable band gap of 2eV for monolayer to 0.3eV for bulk[24] which is consistent with our result since the sample was a bulk material its peak would appear in the ultraviolet range above the tested absorbance.
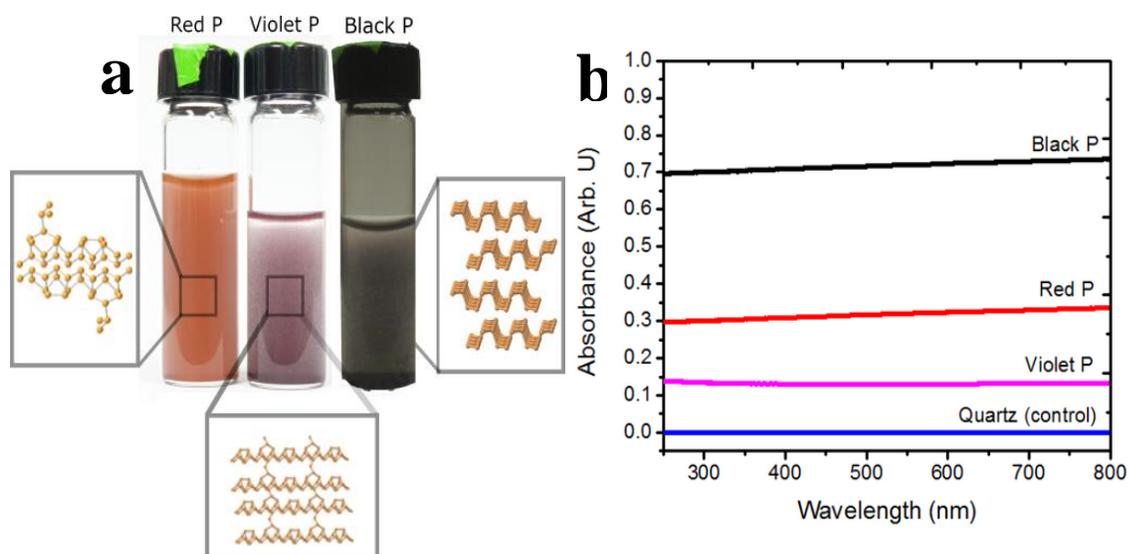
Figure 1. a) Three vials containing the products of ultrasonic treatment of a dispersion of red phosphorus in water with insets depicting the bond structure of amorphous red P, violet P and black P. **b)** The absorbance and transmission of visible light for the three synthesized polytypes with black P absorbing the most light followed by red P and violet P.

To further analyze these products energy dispersive x-ray (EDX) spectroscopy was used to find the elemental components of the products the results are shown in **Figure 2**. The EDX showed that all three products have a prominent peak at 2.0KeV which corresponds to elemental P. The only other peaks found were for Si (1.7KeV) which is the substrate our sample is deposited on and C (0.3KeV) which is a common contaminant in the chamber. This suggests that all products were allotropes of elemental phosphorus and not any other compound.
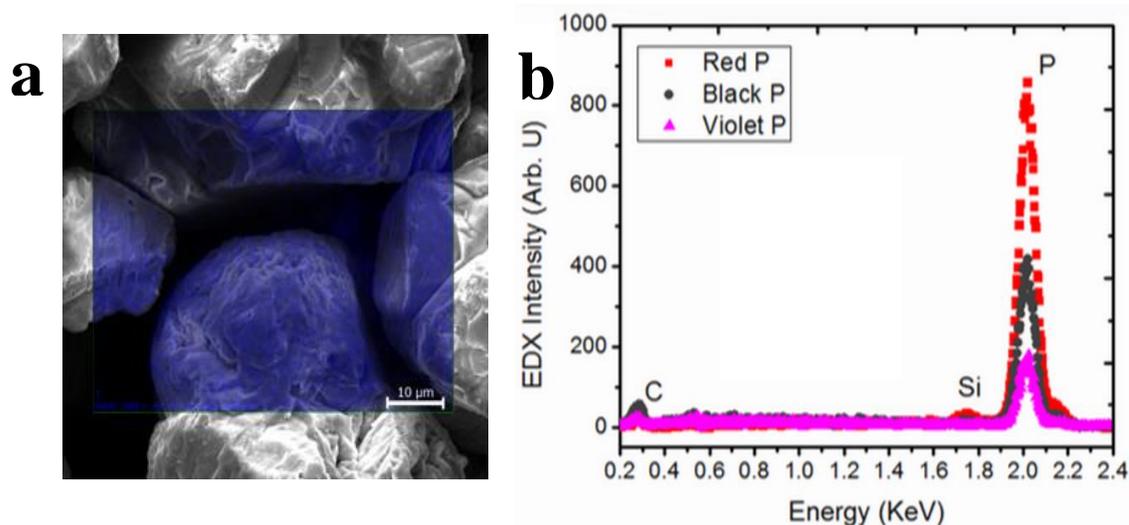
Figure 2. a) The SEM-EDX mapped region shows black phosphorus. The blue regions represent where the P peak was detected. **b)** Energy dispersive X-ray spectroscopy of the three products (red, violet, black) all show a strong phosphorus peak with no other elements present in significant amounts.

Raman Spectroscopy was used to determine differences in the vibrational and optical modes. Black P is known to have three modes[25] A_{1g}, B_{2g}, and A_{2g}. These modes correspond to atomic vibrations of the crystal lattice in the out of plane direction (A_{1g}) and two different directions in plane with the sheet (B_{2g}, and A_{2g})[25] shown in the insets of **Figure 3b**. Raman spectra from the red and violet P have bands from 300cm^{-1} to 500cm^{-1} which contain a convolution of several modes. D.J. Olego *et al* have shown the relationship between amorphous red P and violet P to be continuous with intermediate forms being more organized than amorphous red P but less organized than violet P[26]. Some consider violet P to be another form of red P rather than a distinct allotrope[11]. The red and violet phosphorus also showed very similar spectra which is consistent with literature[26] while black P had an A_{2g} mode typical of black phosphorus due to the out of plane lattice vibration[25] (**Figure 3a**). The synthesized sample was not pristine, but it was clear that black phosphorus was present in the product (**Figure 3b**). The synthesized black P A_{2g} peak is shifted to higher frequency, and could be due to defects caused by the ultrasonication process. Mechanical exfoliation was attempted on the synthesized black P to examine if layers were held together by Van Der Waals forces. The exfoliation resulted in clusters of black P and did not produce monolayer or few layered samples. This suggests that the synthesized black P is polycrystalline in form and a mixed state (i.e. amorphous and crystalline domains) was synthesized.
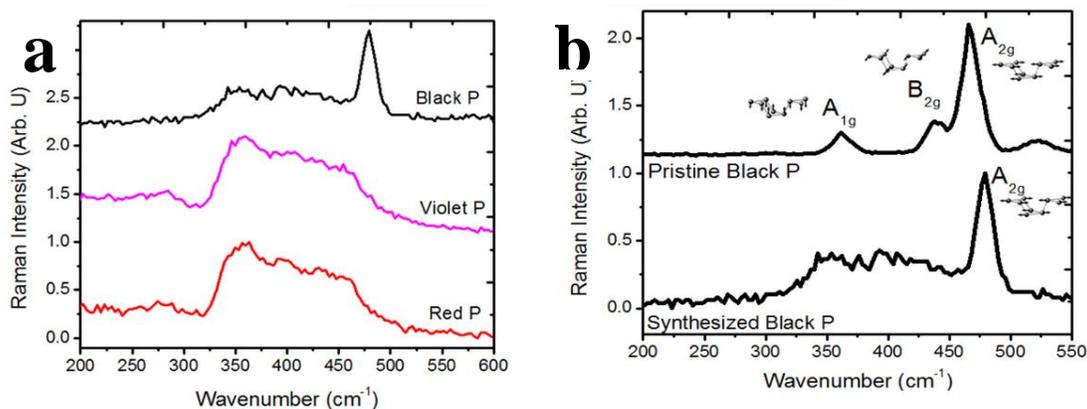
Figure 3. a) The Raman spectra for the three synthesized samples is shown **b)** The Raman spectra of the ultrasonically synthesized black phosphorus compared to a pristine exfoliated sample.

Studying the electrical characteristics help understand how these products might be useful in microelectronic applications. Therefore, to study the electrical characteristics of the synthesized material, two-point probe measurements were taken to determine the current-voltage profile of the three different synthesized polytypes. In addition, our electrical measurements showed the product to have extremely high resistance, red having a resistance of 7.8GΩ while violet phosphorus has 30TΩ and black has 3TΩ. The sample size was not well controlled for this measurement. The results are for qualitative comparison. **(Figure 4)** This high resistance is not expected since bulk black phosphorus has a band gap of 0.3eV. This further suggest that a polycrystalline form of black phosphorus was produced with only small localized areas having the 2D buckled sheet structure. Further research to eradicate the defects in black P will need to be conducted such that applications in microelectronics can benefit from few layer or monolayer flakes of black P[13].
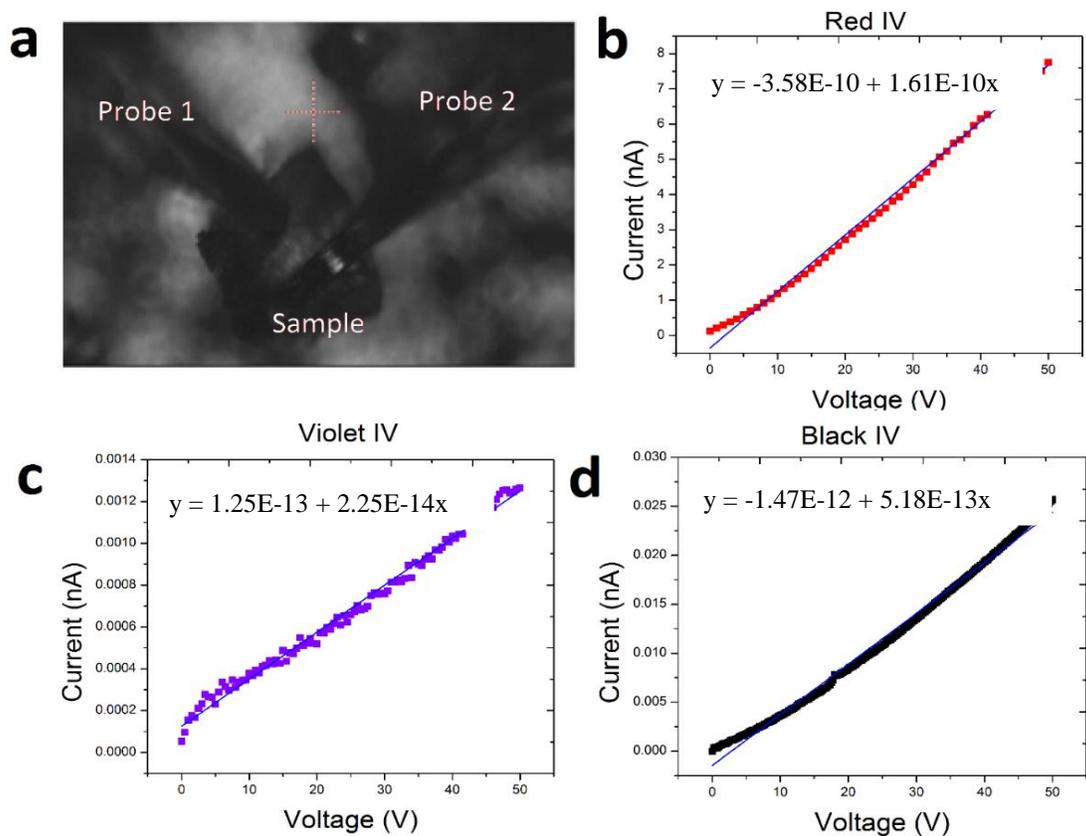
Figure 4. a) The inset picture shows the method used to take these measurements a two point probing system with the voltage applied across the two needles set directly onto a flake of the product. **b)** Red P electrical profile curve. **c)** Violet P electrical profile curve. **d)** Black P electrical profile curve. These graphs show the current-voltage relationship of red, black and violet phosphorus.

4. Conclusion

This research shows that black phosphorus can be synthesized through ultrasonic radiation of red phosphorus dispersed in water. However, further research needs to be conducted to eradicate defects in black P such that applications can benefit from few layer or monolayer films. The samples that were synthesized were in a polycrystalline form rather than large single crystal sheets. Therefore, efforts should be made to increase the size of the continuous crystal domains of the product. In addition, methods to mechanically exfoliate monolayer or few layered flakes from this product should be another focus of future research. Due to the expenses associated with the current techniques used to synthesize black phosphorus, ultrasonication warrants further exploration to offer a new route to produce high quality, few layered phosphorene.

5. Acknowledgements

6. References

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