

## **Appendix B**

# **Attempt to fabricate carbon phosphide by liquid-phase pulsed laser ablation**

### **§ B.1 Introduction to carbon phosphide**

Given the intense research surrounding  $C_3N_4$ , other materials with low mass covalent atoms were postulated, such as carbon phosphide [1],  $C_3P_4$ . This material can be considered with respect to  $C_3N_4$ , but with P atoms substituted for N atoms. The prototype structures for  $C_3P_4$  assume that C atoms are 4-fold coordinated with P atoms and P atoms are 3-fold coordinated to C atoms.

However in contrast to  $C_3N_4$ , the most stable  $C_3P_4$  crystalline structure was predicted, using first-principles density-functional theory, to be the pseudocubic form [2,3,4] (Figure B.1). The reason for this is due to the differences between P and N, as P shows greater preference for tetrahedral coordination found in the pseudocubic phase [2]. It is also noted that, compared to all  $C_3N_4$  phases, a much lower bulk modulus value (156 GPa) for pseudocubic  $C_3P_4$  is predicted [2].

$C_3P_4$  is further calculated to be metallic (no band gap) [2]. This may be due to the fact that although N and P have similar valency they have different electronegativity. In particular, the electronegativity of  $N > C > P$  and hence, this leads to different bonding properties. Subsequently, as the electronegativity of P is less than C, it may donate electrons to C to allow metallic behaviour. This will be in contrast to the tightly-bound electrons in N due to its higher electronegativity [5].

PC (Figure B.1) has also been studied as a possible product during carbon phosphide synthesis. It has the same atom co-ordination as  $C_3P_4$  but with a two-dimensional  $sp^3$ -bonded network, rather than the three-dimensional network present

in  $C_3P_4$ . It is most stable in the GeSe structure (has a bond angle close to tetrahedral), is an insulator and has a bulk modulus of only 64 GPa [2].

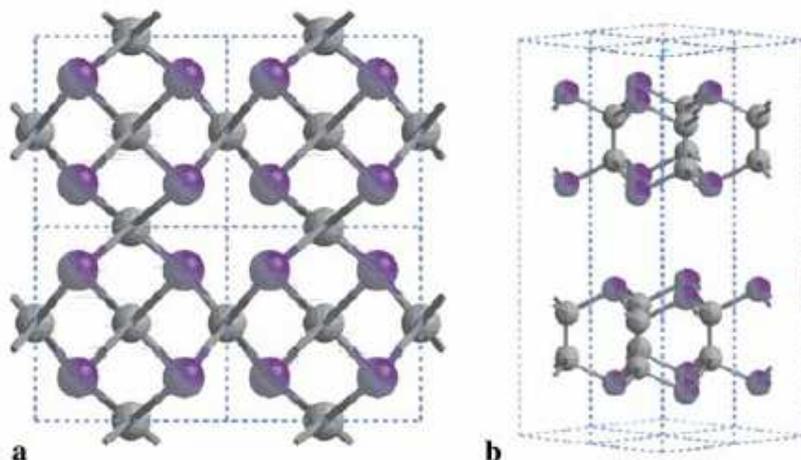


Figure B.1 Theoretical structures [2] for (a)  $C_3P_4$ , (b) PC stoichiometries. The lighter and darker grey spheres represent the carbon/phosphorus atoms, respectively, while the dashed lines depict the unit cell boundaries.

Few reports of any carbon phosphide synthesis are found in literature. Pearce *et al* [6] have show production of amorphous carbon phosphide films, with a P/C ratio as high as 3:1 (and ~10% hydrogen), using radio frequency plasma deposition. The P/C content was further shown to be controllable via the ratio of  $PH_3/CH_4$  in the gas mixtures that are plasma activated. This led to further research in the area, such as the production of diamond-like carbon films containing 0~26 at.% P deposited on substrates using vacuum PLA of graphite/phosphorus targets [2]. However, it is clear that presence of crystalline  $C_3P_4$  by any source has not been reported in literature to date, and hence its synthesis may be challenging.

## § B 2 Experimental details

The typical ablation process was used a target consisting of approximately 2 g of solid phosphorus (Aldrich, 99.999%) with a 5 ml liquid phase of each of the

following: toluene; cyclohexane; benzene and hexane. These were ablated at various laser fluences (75-125 mJ/ pulse) and ablation times of 1-5 h. Red phosphorus powder (Aldrich, 99%) and graphite powder (1:4) target disks were also produced using a high pressure press. The disks were tried with a variety of liquid phases, laser fluences and ablation times. Then the obtained products or powders were rinsed with ethanol and dried at room temperature, followed by characterization using TEM, SAED and FTIR.

### **§ B 3 Results and discussion**

Initially, red phosphorous and graphite powder target disks were produced and subjected to ablation. However, it was found that under ablation they disintegrated very quickly into powder so that any ablated product would be hard to extract for TEM images or characterization. Characterization was attempted but did not produce any positive results. This may also be due to the very low relative yield of product in the reactants, or because no bulk solid target was present in the synthesis. The lack of a bulk target surface may prevent the unique conditions that LP-PLA can provide, for example cavitation and hence high pressure.

Synthesis of nanocrystalline carbon phosphide using a phosphorus lump target in a carbon-containing liquid phase seems more promising after numerous experimental trials. Nanorod structures can be found under the TEM observation (shown in Figure B.2(a)), which are highly ordered and uniform with a width of around 250 nm, indicating that they formed via growth along a preferential axis. Figure B.2(b) shows a single 100 nm-wide nanorod tapered to a point identically either side, indicating a single crystal. It indicated that the structures may be altered in shape during formation due to the liquid environment which allows the small nanoparticles to self-adjust their orientation.

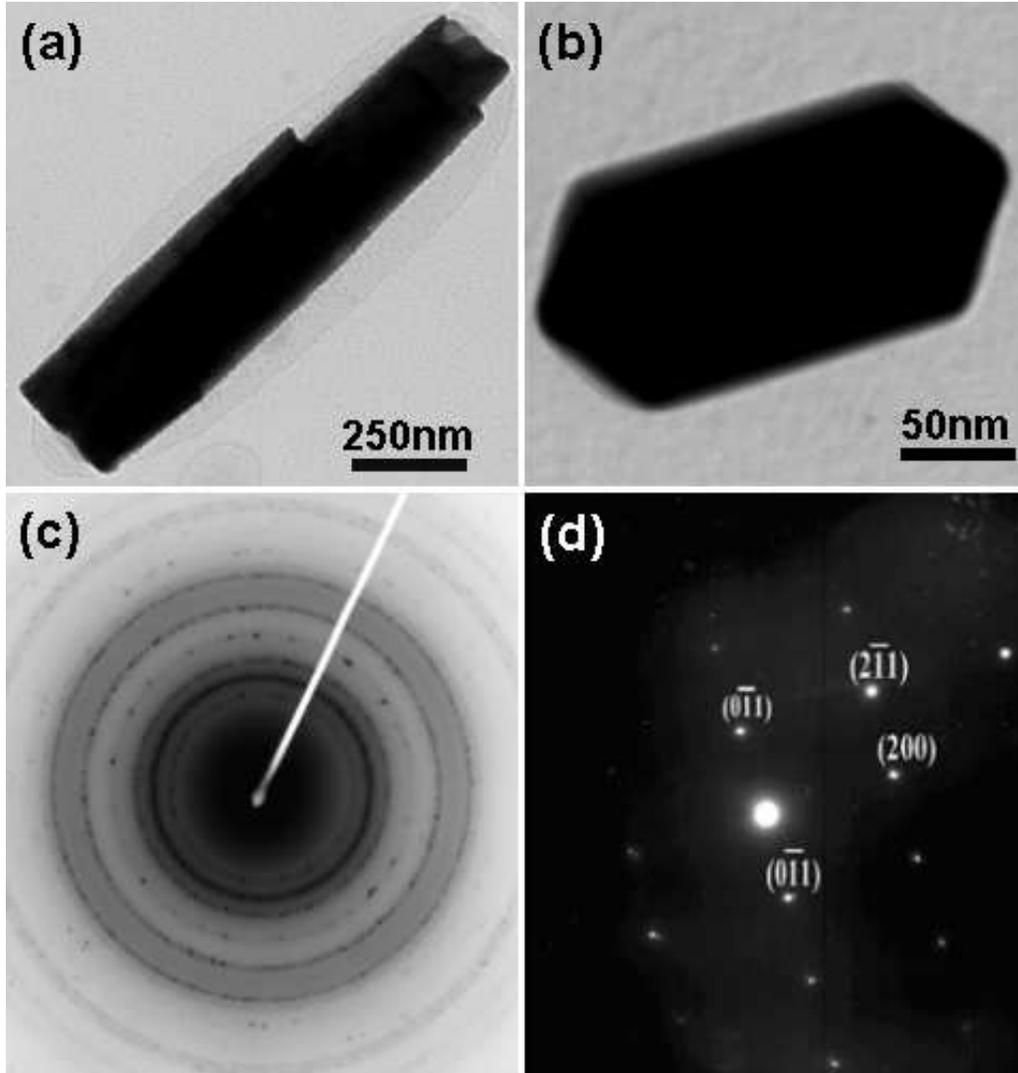


Figure B.2 TEM images for the samples produced by LP-PLA 3 h of solid phosphorus in toluene liquid. (a) 75 mJ/ pulse, (b) 100 mJ/ pulse. (c) Representative SAED ring pattern taken from the aggregate structures. (d) SAED dot pattern taken from the nanorod shown in (a), which was indexed to pseudocubic- $C_3P_4$ .

Figure B.2(c) shows a typical SAED ring pattern that could be indexed to  $C_3P_4$ . This pattern was found from the aggregate structures and had a good comparison with the theoretical  $d$ -spacings for pseudocubic- $C_3P_4$  (Table B.1) [5]. The percentage error is low and within the error margins of the analysis, whilst intensities are not perfect but show no major errors. The pseudocubic phase of  $C_3P_4$  is also to

be expected, as it has been predicted to be the most energetically favourable phase [2]. The SAED dot pattern (Figure B.2(d)) was further found for the nanorods in Figure B.2(a). These were indexed to the pseudocubic-C<sub>3</sub>P<sub>4</sub> <011> zone-axis. Therefore, the nanorod is crystalline throughout, as expected from its uniform topography. Although carrying out XRD analysis was impossible, as the abundance of nanostructures was low for ablations under all conditions, the SAED evidence presented here suggests that a pseudocubic-C<sub>3</sub>P<sub>4</sub> nanorod may have been synthesised under a 3 h ablation at 100 mJ/ pulse using phosphorus and a toluene liquid phase.

Table B.1 Calculated *d*-spacings (from Figure B.2(c) SAED pattern) with comparison to theoretical pseudocubic-C<sub>3</sub>P<sub>4</sub>

| Experimental |           | Pseudocubic-C <sub>3</sub> P <sub>4</sub> (Theoretical)* |                |             | % Error |
|--------------|-----------|--|----------------|-------------|---------|
| <i>d</i> (Å) | Intensity | <i>d</i> (Å)   | ( <i>hkl</i> ) | Intensity   |         |
| 2.396        | Medium    | 2.384  | 101            | Very Strong | -0.503  |
| 2.064        | Strong    | 2.065  | 200            | Medium      | 0.048   |
| 1.83         | Medium    | 1.847  | 201            | Weak        | 0.920   |
| 1.497        | Medium    | 1.460  | 102            | Medium      | -2.534  |
| 1.275        | Medium    | 1.245  | 300            | Medium      | -2.410  |
| 1.076        | Medium    | 1.104  | 202            | Weak        | 2.536   |
| 1.032        | Weak      | 1.002  | 212            | Weak        | -2.994  |
| 0.973        | Very weak | 0.973  | 310            | Very weak   | 0.000   |
| 0.892        | Very weak | 0.881  | 103            | Very weak   | -1.249  |

Further analysis was performed to confirm the synthesis of C<sub>3</sub>P<sub>4</sub> by using FTIR spectroscopy. A typical FTIR spectrum, shown in Figure B.3, had peaks that could be assigned to appropriate vibrations [7]: 757 cm<sup>-1</sup> P-C; 1039 cm<sup>-1</sup> C-C skeletal; 1141 cm<sup>-1</sup> C-H vibrations; 1411 cm<sup>-1</sup> and 1627 cm<sup>-1</sup> C-H deformation vibrations; 1627 cm<sup>-1</sup> and 1695 cm<sup>-1</sup> C=O stretching vibrations; 2321 cm<sup>-1</sup> P-H; 2844 cm<sup>-1</sup> and

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\* Calculated using CaRIne Crystallography v3.1 and theoretical measurements from Lim *et al* [5].

2916  $\text{cm}^{-1}$  C-H stretching vibrations; 3178  $\text{cm}^{-1}$  and 3375  $\text{cm}^{-1}$  O-H stretching vibrations.

Crucially, the peak at 757  $\text{cm}^{-1}$  could be assigned to C-P and hence indicate the formation of  $\text{C}_3\text{P}_4$ . However, to validate the production of  $\text{C}_3\text{P}_4$  further analysis techniques would be required. XPS and Raman spectroscopy were both tried but did not produce positive results. This was probably because higher volumes of ablated material are needed for these techniques.

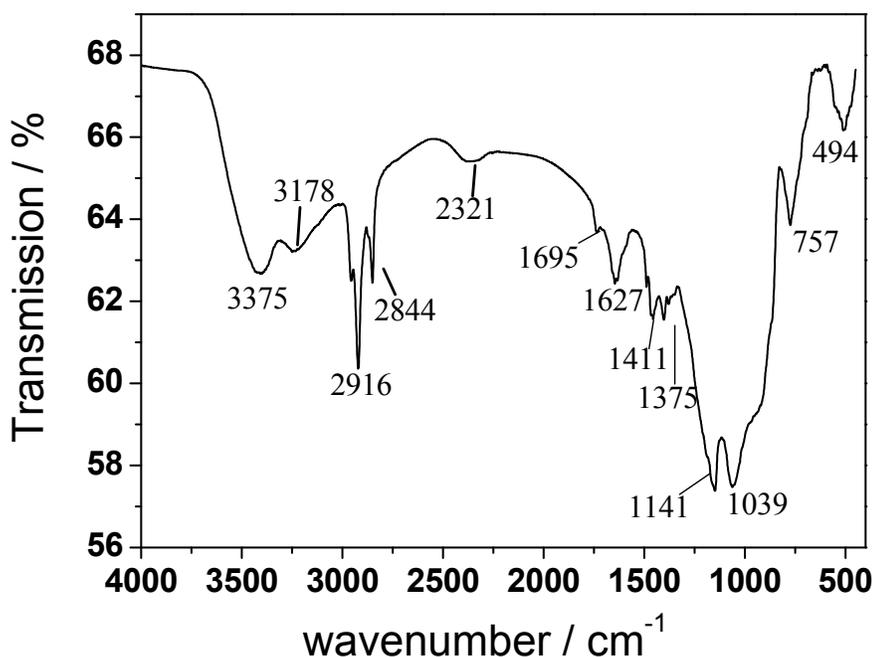


Figure B.3 Typical FTIR spectrum for the ablated product.

#### § B 4. Conclusion

LP-PLA of a phosphorous lump target with a liquid phase of toluene produced nanostructures with a rod-like shape but with low abundance. A SAED ring pattern from the aggregate structures and crystalline patterns from nanorod structures were further indexed to pseudocubic- $\text{C}_3\text{P}_4$ . FTIR spectroscopy also showed the presence

of C-P single bonds indicating the presence of  $C_3P_4$ . However, as only SAED pattern and no further evidence were found, the successful synthesis of  $C_3P_4$  cannot yet be confirmed. Furthermore, as only one pattern was found and only a small number of nanostructures, it indicates that the synthesis of crystalline carbon phosphide is very difficult.

## **Bibliography**

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