

## Abstract

Liquid-Phase Pulsed Laser Ablation (LP-PLA) is a material processing and fabrication technique that offers distinct advantages over competing techniques. These include (1) it is a chemically ‘simple and clean’ synthesis, (2) it operates at ambient conditions (*i.e.* not extreme temperature and pressure), and (3) it can make novel materials that are unattainable by conventional, less energetic processes. These advantages allow us to combine selected solid targets and liquids to fabricate compound nanostructures with desired functions.

This thesis is mainly concerned with the fundamental aspects governing the self-assembly of nanomaterials made using LP-PLA. We have demonstrated that well-organized carbon nitride leaf-like nanostructures can be produced by LP-PLA using solid graphite and ammonia solution, without the assistance of any surfactants or pre-treatment. X-ray diffraction, Scanning electron microscopy, Transmission electron microscopy and X-ray photoelectron spectroscopy evidence shows that the nanostructured materials produced in this way are composed of crystalline  $\alpha$ - or  $\beta$ - $C_3N_4$ . The effect of various parameters including the reaction time, laser energy, and ammonia concentration has been studied systemically. A range of different carbon nitride structures with different length scales can be fabricated via a self-assembly ordering scheme. The size and morphology of these nanomaterials can be controlled by adjusting the growth conditions. A growth mechanism has been proposed based on our experimental observations, which is consistent with measured properties such as chemical bonding, and the optical bandgap.

We also combined the self-assembly concept with the LP-PLA technique. A two-step strategy was developed to control 2D or 3D carbon nitride well-defined hierarchical complex structures. In the first step, carbon nitride seed solutions were prepared by LP-PLA. In the second stage the chosen seed solution was deposited onto a silicon substrate. Via controlling the rate of evaporation, the starting seed

solution, and the size and the quantity of nanocrystals within the droplet, it was possible to create a range of nanoscale structures, including dense nanospheres, highly-symmetric flowers, hollow core-shell and uniform grass-like structures, respectively. The growth of such complex structures is governed by an evaporation-driven self-assembly process. The small building blocks, such as nanoparticles (NPs) or nanorods (NRs), nucleate on the existing crystals and share the same edges, to form a close-packed arrangement. By varying the design of the building blocks, materials combination, interfacial chemistry, and confining dimensions, we fabricated new structured materials with useful functional properties.

A similar growth by LP-PLA had been applied to a ZnO system. When ablating a zinc target in an aqueous solution of sodium dodecyl sulfate (SDS), ZnO nanostructures with a wide range of morphologies similar to those of carbon nitride were observed. The formation mechanism of highly ordered structures again appears to involve an increase of the structural complexity from zero-dimensional NPs to one-dimensional NRs, and then broadening of these into two-dimensional nanoleaves.

Our studies indicated that the self-assembly process can easily be incorporated into current LP-PLA process with standard facilities. We believe such a combination is an effective method to synthesize a series of nanomaterials with controlled size and morphology via suitable choice of solid target material and liquid media. A thorough understanding of this controllable self-assembled growth is the key step towards nanosystem applications. Further work in this regard would be very interesting.

## **Author Declaration**

I declare that the work in this dissertation was carried out in accordance with the Regulations of the University of Bristol. The work is original, except where indicated by special reference in the text, and no part of the dissertation has been submitted for any other academic award. Any views expressed in the dissertation are those of the author:

SIGNED: ..... DATE: .....

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## List of abbreviations

|         |  |
|---------|--|
| 0D      | Zero-dimensional                                 |
| 1D      | One-dimensional                                  |
| 2D      | Two-dimensional                                  |
| 3D      | Three-dimensional                                |
| AOT     | Bis(2-ethylhexyl)sulfosuccinate                  |
| BSE     | Backscattered electron                           |
| CCD     | Charge-coupled device                            |
| CNTs    | Carbon nanotubes                                 |
| CPD     | Critical point dryer                             |
| CRT     | Cathode ray tube                                 |
| CTAB    | Cetyltrimethylammonium bromide                   |
| CVD     | Chemical vapour deposition                       |
| CVTC    | Chemical vapour transport and condensation       |
| EDX     | Energy dispersive X-ray spectroscopy             |
| EELS    | Electron energy-loss spectroscopy                |
| FCC     | Face-centered-cubic                              |
| FESEM   | Field emission scanning electron microscopy      |
| FET     | Field effect transistor                          |
| FFT     | Fourier-filtered transform                       |
| FP-LAPW | Full-potential linearised augmented plane-wave   |
| FTIR    | Fourier transform infrared spectroscopy          |
| HFCVD   | Hot filament chemical vapour deposition          |
| HPHT    | High-pressure high-temperature                   |
| HRTEM   | High resolution transmission electron microscopy |
| IR      | Infrared   |
| LDA     | Lauryl dimethylaminoacetic acid                  |

|        |  |
|--------|--|
| LMTO   | Linear muffin-tin orbitals                 |
| LP-PLA | Liquid-Phase pulsed laser ablation         |
| LRM    | Laser Raman spectroscopy                   |
| MBE    | Molecular beam epitaxy                     |
| MDP    | Microdiffraction pattern                   |
| MOCVD  | Metal-organic chemical vapour deposition   |
| MOVPE  | Metal-organic vapor phase epitaxy          |
| NEXAFS | Near-edge X-ray absorbance                 |
| Nd:YAG | Neodymium-doped yttrium aluminium garnet   |
| NMR    | Nuclear magnetic resonance                 |
| NPs    | Nanoparticles                              |
| NRs    | Nanorods                                   |
| NTs    | Nanotubes                                  |
| NWs    | Nanowires                                  |
| OES    | Optical emission spectroscopy              |
| OGM    | Octaethylene glycol monododecyl            |
| PECVD  | Plasma-enhanced chemical-vapour deposition |
| PLA    | Pulsed laser ablation                      |
| PL     | Photoluminescence                          |
| PP     | Pseudopotential plane-wave                 |
| SAED   | Selective Area electron diffraction        |
| SAM    | Self-assembled monolayer                   |
| SEM    | Scanning electron microscopy               |
| SDS    | Sodium dodecyl sulfate                     |
| STM    | Scanning tunneling microscopy              |
| TEM    | Transmission electron microscopy           |
| UV     | Ultraviolet                                |
| UV-Vis | Ultraviolet-visible spectroscopy           |
| VLS    | Vapour-liquid-solid                        |
| XPS    | X-ray photoelectron spectroscopy           |
| XRD    | X-ray diffraction                          |