

## **Chapter 7**

### **Conclusions and future work**

Fabrication of well-organized carbon nitride leaf-like nanostructures can be achieved by LP-PLA using solid graphite and ammonia solution, without the assistance of any surfactants or pre-treatment. Evidence has been provided to illustrate that the nanostructured materials produced in this way are composed of crystalline  $\alpha$ - or  $\beta$ - $C_3N_4$ . The morphology of the crystalline material changes at different length scales depending on the synthesis conditions, such as ammonia concentration, laser energy, and the reaction time. The geometrically complex  $C_3N_4$  nanostructures, such as interconnected networks, large mesoscale clusters, and multifold-symmetry flower-like structures, can be fabricated via a self-assembly ordered scheme using zero-dimensional (0D) nanoparticles or one-dimensional (1D) nanorods as basic building blocks. The formation mechanism of highly ordered architectures appears to involve an increase of the structural complexity from 0D NPs to 1D NRs, and then broadening of these into two-dimensional (2D) nanoleaves, which finally coalesce to three-dimensional (3D) flowers.

A two-step strategy was developed to control the 2D or 3D carbon nitride 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, the size and the quantity of nanocrystals within the droplet, it was possible to create dense nanospheres, highly-symmetric flowers, hollow core-shell and uniform grass-like structures, respectively. Such complex structures might have great potential in new technological applications.

From studies of the dynamics of self-assembly formation, it was found that the initial stage of the complex architectures (grass-like or flower-like) was composed of small aggregates of compacted 15-20 nm-sized dense, spherical particles. A slow drying process favoured an increase in the structural complexity. During drying, nanocrystals nucleate on the existing crystals and share the same edges, giving a close-packed arrangement. Although the mechanism is still not yet fully understood, our experiments indicated that formation of 2D or 3D functional structures in this work seems to be an evaporation-driven self-assembly process. By varying the design of the building blocks, materials combination, interfacial chemistry, and confining dimensions, in future we should expect to discover new materials properties.

LP-PLA of a zinc target in an aqueous solution of sodium dodecyl sulfate (SDS) produced ZnO nanostructures with similar morphologies to those seen with carbon nitride. These included nanoparticles, nanorods, and nanoleaves. The growth mechanism was also similar to that seen with carbon nitride formation. The room temperature photoluminescence (PL) spectra from different ZnO samples showed narrow bandwidth UV emission at  $\sim 380$  nm and strong visible emission, dependent on the conditions. PL also confirmed annealing as a good route to improving the intensity of UV emission from the sample, suggesting the material was excellent quality and that these zinc oxide nanocrystals have potential as an optoelectronic material.

This work has shown that LP-PLA 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 controllable self-assembled growth (their size, size distribution, shape, crystal structure, and even surface structure) is the key step towards nanosystem applications. With this improved physical and chemical control, solid-solution growth methods should provide versatile and powerful industrial-scale processes for assembling nanomaterials, and may ultimately allow nanoscience to move out of the laboratory and into wider use technology.

Further work would include gaining more experimental evidence for the self-assembly process in this system. Different crystalline or amorphous substrates might

affect the final structures. Achieving more controllable parameters for fabricating desired architectures is also important for future applications in the nanotechnology field.

Other experimental parameters could be changed and investigated, such as the laser pulse duration, laser wavelength and laser repetition rate, to see if these have an effect on the ablated product. The LP-PLA target and liquid phase could be further changed. Different liquids will be used for production of different materials, including aqueous liquids (water), polar liquids (methanol) and non-polar liquids (hexane, benzene). Some surfactants can be also used to modify the morphology of the structures. The chosen target (such as copper, tin, titanium, aluminium, *etc.*) can be varied by the design of the materials system. Novel materials systems, including binary composites or other combinations, might be very interesting to further demonstrate the reliability of the LP-PLA technique. A few more specific examples of target/liquid combinations could be tried. One example is carbon phosphide, which might be produced from ablation of a phosphorus target in a hydrocarbon liquid such as hexane. Both crystalline ( $C_xP_y$ ) and amorphous carbon phosphides would have important uses as wide band-gap optoelectronic materials [1, 2]. Similarly, solid carbon sulfides would be interesting. Liquid carbon disulfide ( $CS_2$ ) is well known, but there are few reports of solid phase materials containing high levels of C and S [3]. Indeed, for C:S mixtures around 50%, these would be considered alloys, and preliminary results from PLA in vacuum [3] show that the resulting amorphous  $CS_x$  films develop interesting electronic properties as the S content increases. Extending this to LP-PLA would require ablating a graphite target (or even a suspension of graphite nanoparticles) in  $CS_2$  liquid. Similar work could be attempted with carbon arsenides, by ablating arsenic in hydrocarbon liquids. Ternary compounds may also be possible, for example LP-PLA of phosphorus in a liquid amine may produce nanoparticles of composition  $C_xP_yN_z$ . With the improved fundamental understanding of laser ablation of solid targets in liquids, we believe LP-PLA will be easy to implement and offers great flexibility with regard to the number and variety of systems amenable to investigation.

## **Bibliography**

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