

# Hierarchical architecture of self-assembled carbon nitride nanocrystals†

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A range of complex nanostructures have been observed by the self-assembly of carbon nitride nanocrystals, which involved an increase of the structural complexity from 0D → 1D → 2D → 3D evolution.

Over the past decade, self-assembly and alignment of nanostructured materials have been widely investigated.<sup>1</sup> It is believed that the ability of nanostructures to self-assemble in this manner provides potential building blocks for microscale or nanoscale devices. Many types of inorganic nanoparticles have been investigated, including metals, metal oxides, and other semiconductors. These inorganic nanocrystals self-assemble into a range of structures, such as compact hexagonal networks, rings, strips, tubes, columns and labyrinths.<sup>2</sup> For example, ZnO forms micron- and submicron-scale “dandelion”-like structures, which are comprised of single-crystalline building units (either nanorods (NRs) or nanoparticles (NPs)),<sup>3</sup> and which can be constructed *via* a modified Kirkendall process in solution, where the pre-formed oxide layer serves as a shell template for the initial nucleation and growth. Also, uniform Sb<sub>2</sub>S<sub>3</sub> nanorod bundles have been synthesized on a large scale using a hydrothermal technique, at a temperature of 180 °C for 20 h.<sup>4</sup>

However, to date, there has been little effort devoted toward the understanding of the self-assembly processes of Group IV–V compounds, such as carbon nitride. Carbon nitride has been the subject of numerous publications since the prediction by Liu and Cohen<sup>5</sup> in 1989 that crystalline C<sub>3</sub>N<sub>4</sub> should have superhard properties. However, successful synthesis of bulk amounts of this material still remains a challenge. The synthesis difficulties are due to its low thermodynamic stability and complex bonding environment. Recently Li and co-workers<sup>6</sup> demonstrated a range of self-assembled carbon nitride morphologies (including nanotube bundles, aligned nanoribbons and microspheres) can be prepared by a solvothermal technique. Also, our recent findings<sup>7</sup> indicated that the instantaneous high temperature, high pressure and high density conditions that arise when a high-intensity focused laser beam impinges upon a graphite target confined by a thin layer of liquid ammonia can promote growth of crystalline carbon nitride nanoparticles. In this communication, we will demonstrate a

successful synthesis of carbon nitride hierarchical nanostructures *via* liquid phase pulsed laser ablation (LP-PLA), whereby the nanocrystals self-assemble into complex three-dimensional (3D) superstructures. Fabrication of these 3D carbon nitride structures from small building blocks *via* self-organization suggests that LP-PLA may be a “brute force” method of synthesizing novel materials that have hitherto been inaccessible using milder, more conventional techniques.

The nanostructures were prepared *via* a LP-PLA system detailed elsewhere.<sup>7a</sup> Briefly, a solid graphite target was placed in a sealed stainless steel cell at room temperature containing 3–5 ml of 25–35% ammonia solution (about 5–10 mm liquid layer). The laser beam (Nd : YAG, 532 nm, pulse duration 15 ns, operating at 10 Hz, fluence 50–125 mJ pulse<sup>-1</sup>) was directed by a prism and then focused using a 25 mm focal-length lens through a quartz window in the top wall of the cell, then through ammonia to form a ~0.5 mm diameter spot on the surface of the graphite target. Optical emission spectroscopy (OES) was used to monitor the composition of the plasma accompanying the LP-PLA process (see ref. 7(d) for further details). Following ablation for 0.5–10 h, a suspension containing a mixture of unreacted graphite and ablation product, both in the form of NPs, remained in the cell. This suspension changed from colourless, to pale brown (2 h), and then dark brown (5 h), dependent on the ablation time, indicating an increase in solid product and/or a change in composition of the solid due to prolonged interaction with the laser. The suspension was stable, with no precipitate being observed for months or even longer. The graphite sediments were filtered and removed as much as possible by boiling with 70% perchloric acid before further characterization.

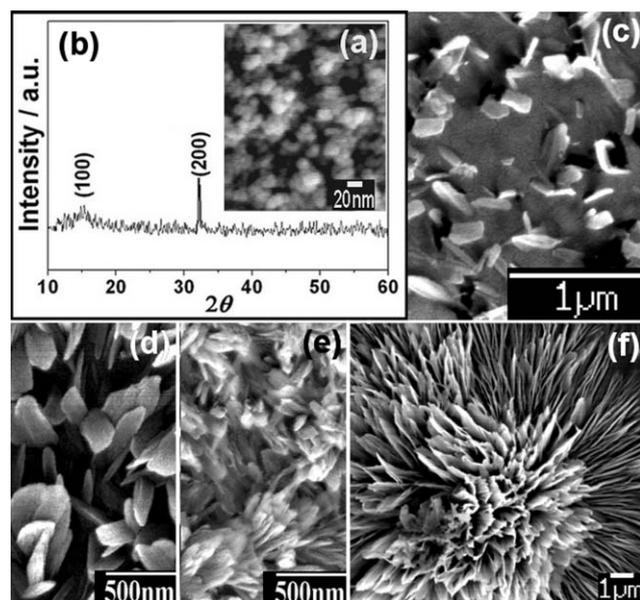
For materials analysis, the suspension was pipetted onto a silicon wafer or TEM grid, and then allowed to dry in air or in a sealed tube. This procedure allowed the time taken to evaporate the liquid to be controlled. The product was characterized using X-ray diffraction (XRD, Bruker-AXS D8 Powder Diffractometer, Cu K $\alpha$  radiation), field emission scanning electron microscopy (FE-SEM, JEOL 6300 F), transmission electron microscopy (TEM, JEOL 1200 EX, 120 kV), high-resolution (HR) TEM (JEOL 3000 F, 300 kV), energy-dispersive X-ray analysis (EDX) and micro-diffraction analysis (MDA).

It was found that the size and morphology of the ablation products were a complicated function of laser power, ablation time, ammonia concentration and drying time. Four main classes of structure are identified in the ablation product, categorised based upon their shape and size. The first of these were irregular, but roughly spherical NPs which were found in large quantities after every experiment (Fig. 1a). They have been identified as crystalline carbon nitride<sup>7</sup> and are about 10 nm in diameter. The

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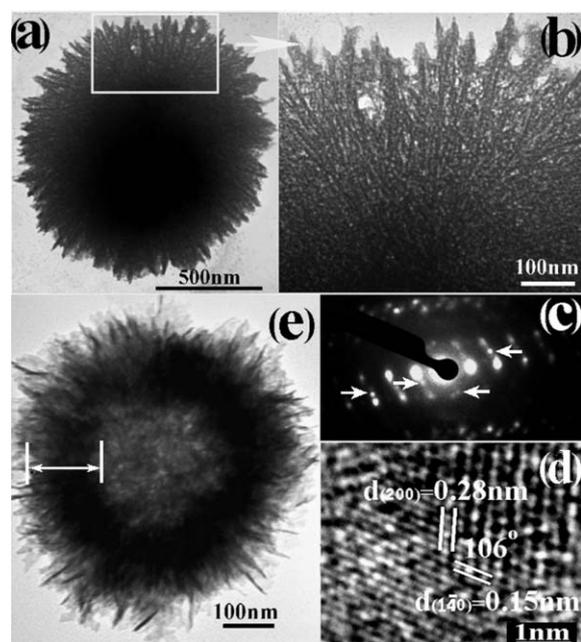


**Fig. 1** (a) Dense clumps of NPs deposited on the Si substrate. (b) Representative XRD pattern. (c)–(e) SEM images of carbon nitride ‘nano-petals’ for ablation times of: (c) 0.5 h, (d) 2 h, and (e) 3 h. (f) Overall ‘flower-like’ structure following 5 h laser irradiation (synthesis conditions: 35% ammonia solution, laser power 125 mJ).

quantity of these NPs and their location with respect to the larger structures (see later) were dependent upon the deposition and drying conditions.

The second class of structure had the shape of thin plates with rounded edges. Since they were the components of the larger ‘flower-like’ structures (described later), they have been termed ‘nano-petals’. XRD analysis of these nano-petals showed that they were crystalline, and all the diffraction peaks were consistent with (*h*00) preferential orientation, as shown in Fig. 1b. The crystallographic information was indexed to hexagonal  $\beta$ - $\text{C}_3\text{N}_4$  ( $P6_3/m$  (176)) with lattice constants  $a_0 = 6.4017 \text{ \AA}$  and  $c_0 = 2.4041 \text{ \AA}$ .<sup>8</sup> This indicated that these nano-petals were two-dimensional (2D) aligned crystallites of  $\beta$ - $\text{C}_3\text{N}_4$  which preferentially aligned themselves perpendicularly to the surface of the Si substrate, as shown in Fig. 1c and 1d. The number and length of these nano-petals increased with increasing laser ablation time from 0.5–2 h for the same laser fluence. With even longer ablation times (3 h), the concentration of these nano-petals in the suspension increased, and upon subsequent drying of the liquid, they began to aggregate and self-assemble (Fig. 1e). By carefully controlling the drying process, ‘flower-like’ spiked, crystalline superstructures were formed (Fig. 1f). This third class of structure, now fully three-dimensional, with sizes 1–20  $\mu\text{m}$ , is created when many nano-petal structures coalesce at a common centre with multi-fold symmetry.

Fig. 2a shows a symmetric carbon nitride ‘flower’ together with its nano-petal building blocks (which look like flattened rods in the TEM). Fig. 2b shows that these nano-petals appear fused together and ‘interwoven’ to form a lattice-like framework of the flower-like superstructure. The figure also shows the NPs that surround each nano-petal, and which fill in the holes within the framework to produce a dense, solid structure. EDX analysis confirms that carbon and nitrogen are present in all these structures, and MDA (Fig. 2c) was also consistent with crystalline hexagonal  $\beta$ -phase

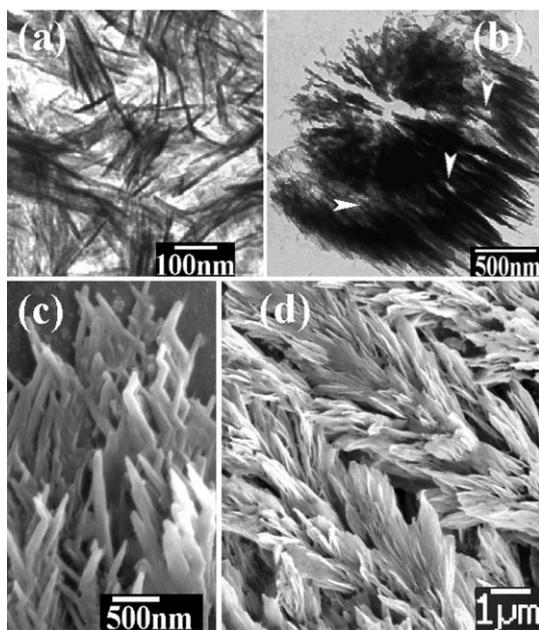


**Fig. 2** (a) TEM image of samples produced by LP-PLA of a graphite target in 35% ammonia solution (laser fluence  $125 \text{ mJ pulse}^{-1}$ ) for 5 h. (b) A higher magnification image of the framed region in (a), showing high density of NPs surrounding the nano-petal framework. (c) [001] Zone axis MDA pattern from the tips of nano-petals in (b). Arrows point to different sets of [001] reflections (see text). (d) HR-TEM image recorded from the edge of the flower nanostructure that is oriented along [001]. (e) TEM image of a hollow flower formed after 8 h LP-PLA and prolonged drying.

carbon nitride oriented along the [001] zone axis.<sup>8</sup> Several [001] patterns in Fig. 2c can be identified at the same time, indicating that the nano-petals consist of several domains, with different rotational orientations contributing to the diffraction pattern. The HR-TEM image in Fig. 2d shows that the nano-petals at the very edge of the flower contain very few defects and are single crystalline, as was anticipated from the MDA pattern. The lattice fringes ( $d_{200} = 0.28 \text{ nm}$ ,  $d_{140} = 0.15 \text{ nm}$ ) and their angles ( $106^\circ$ ) are in good agreement with the calculated values for hexagonal  $\beta$ - $\text{C}_3\text{N}_4$ .<sup>8</sup>

The smaller NPs, which lie in and around the nano-petal framework comprising the flowers, appeared to be mobile with respect to this framework, and diffused outward from the centre of the flower with longer drying times. The results of this diffusion can be seen in Fig. 2e, where the solid carbon nitride flower (similar to that in Fig. 2a) has become hollow. The nanoparticles have diffused from the centre but remain loosely attached to the outside, making the outer shell of the flower appear fuzzy. The thickness of the fuzzy shell was  $\sim 140 \text{ nm}$  and that of the hollow core was  $\sim 200 \text{ nm}$  (shown as a lighter colour in the image). When the suspension was placed onto a hot-plate at  $200^\circ \text{C}$ , the hollowing process was accelerated, but there was no obvious morphology change of the overall flower.

For lower ammonia concentration (25%), a fourth class of structure was observed. Instead of nano-petals, the carbon nitride formed one-dimensional (1D) elongated nanoneedles or nanorods (NRs). For low laser power (50 mJ) and short ablation time (2 h), the product contained mostly a sparse collection of these isolated NRs (Fig. 3a). However, with increasing laser power (125 mJ) and



**Fig. 3** (a) TEM image of isolated carbon nitride NRs obtained by LP-PLA in 25% ammonia solution (laser fluence at  $50 \text{ mJ pulse}^{-1}$ , 2 h ablation time). (b) TEM image of an incomplete carbon nitride flower (25% ammonia solution, laser fluence at  $125 \text{ mJ pulse}^{-1}$ , 10 h ablation time) formed by the coalesced NRs. The arrows highlight the channels between the shell and the core. (c) After drying for 12 h, numerous aligned 'interwoven' NRs form the framework of the flower. (d) After 24 h drying, the NRs have restructured to form 3D shapes.

ablation time (10 h), the concentration of NRs increased, and in some regions they began to coalesce into incomplete flowers (Fig. 3b). Just as for the nano-petals mentioned earlier in Fig. 2(b), these NRs also appeared to be "fused" together into a similar lattice-like framework (Fig. 3c), and the radial distribution of the NRs formed channels leading from the centre of the flower to the edge. These channels may form the conduits along which the NPs diffuse outwards. When the evaporation time of the liquid was increased to from 12 h to 24 h, the 'interwoven' NRs developed a more complicated 3D structure, as shown in Fig. 3d. A possible explanation is that the longer time for evaporation of liquid allows sufficient time for the diffusion of all the NPs out of the flowers, leaving some liquid trapped in the gaps between the NR framework. With prolonged time, the wet NR framework has the opportunity to recrystallise or restructure into the shapes shown in Fig. 3d.

In order to investigate the source of the energetic species present during the laser ablation, the constituents of the plasma were measured using OES. ESI† Fig. S1 shows a wavelength-resolved emission spectrum of the ablation plume induced by 532 nm laser excitation. Emission from atomic C and  $\text{C}^+$  is observed as a direct result of the ablation process. But the presence of very sharp atomic H,  $\text{N}^+$  and N peaks shows that the ammonia is also being dissociated in the PLA process, either directly by interaction with the high energy laser, or indirectly as a result of reactions with the

high-kinetic-energy ejected atoms and particles in the plume. Such intense plume reactions have been seen previously during PLA of graphite in vacuum or in gaseous nitrogen or argon backgrounds.<sup>9</sup> In the spectral range 350–425 nm, intense emission from the CN Violet band was observed, and this confirms that a reaction has occurred between carbon atoms from the ablated solid and N from the liquid ammonia. The spectrum also displays strong  $\text{C}_2$  Swan band emission. The highly energetic CN and  $\text{C}_2$  species in the ablation plume may serve as potential sources for carbon and nitrogen combination.<sup>10</sup> When CN species reached the supersaturation level, heterogeneous nucleation in such a short time might result in the self-assembly of the hierarchical superstructures described here. Further investigation of this proposed mechanism is required.

In summary, this work has shown that it is possible to form self-assembled nanostructures and microstructures of crystalline carbon nitride. Through pulsed laser ablation of graphite in ammonia solutions, 3D well-arranged architectures could be generated. The mechanism appears to involve an increase of the structural complexity from 0D NPs to 1D NRs, and then broadening of these into 2D nano-petals, which finally coalesce to 3D flowers. Factors such as the ammonia concentration, the reaction time and the rate of evaporation of the liquid are important in defining the structures observed. It is proposed that CN radicals in the ablation plasma play a key role in the growth mechanism. This unique process provides more insight into laser-induced chemical reactions in general, and of crystalline carbon nitride phases in particular, and may provide an alternative synthesis method for other composite nanostructures.

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## Notes and references

- (a) Z. Y. Tang, N. A. Kotov and M. Giersig, *Science*, 2002, **297**, 237; (b) B. Liu and H. C. Zeng, *J. Am. Chem. Soc.*, 2005, **127**, 18262.
- (a) V. Germain and M. P. Pileni, *Adv. Mater.*, 2005, **17**, 1424; (b) C. Petit, J. Legrand, V. Russier and M. P. Pileni, *J. Appl. Phys.*, 2002, **91**, 1502.
- B. Liu and H. C. Zeng, *J. Am. Chem. Soc.*, 2004, **126**, 16744.
- Q. F. Lu, H. B. Zeng, Z. Y. Wang, X. L. Cao and L. D. Zhang, *Nanotechnology*, 2006, **17**, 2098.
- A. Y. Liu and M. Cohen, *Science*, 1989, **245**, 841.
- J. Li, C. B. Cao, J. W. Hao, H. L. Qiu, Y. J. Xu and H. S. Zhu, *Diamond Relat. Mater.*, 2006, **15**, 1593.
- (a) L. Yang, P. W. May, L. Yin, R. Brown and T. B. Scott, *Chem. Mater.*, 2006, **18**, 5058; (b) L. Yang, P. W. May, L. Yin, T. B. Scott, J. A. Smith and K. N. Rosser, *Nanotechnology*, 2006, **17**, 5798; (c) L. Yang, P. W. May, L. Yin, J. A. Smith and K. N. Rosser, *J. Nanopart. Res.*, 2007, DOI: 10.1007/s11051-006-9192-4; (d) L. Yang, P. W. May, L. Yin, J. A. Smith and K. N. Rosser, *Diamond Relat. Mater.*, 2007, DOI: 10.1016/j.diamond.2006.11.010.
- J. Wang, J. Lei and R. Wang, *Phys. Rev. B*, 1998, **58**, 11890.
- (a) G. M. Fuge, M. N. R. Ashfold and S. J. Henley, *J. Appl. Phys.*, 2006, **99**, 014309; (b) F. Claeysens, M. N. R. Ashfold, E. Sofoulakis, C. G. Ristoscu, D. Anglos and C. Fotakis, *J. Appl. Phys.*, 2002, **91**, 6162.
- (a) J. B. Wang, G. W. Yang, C. Y. Zhang, X. L. Zhong and Z. H. A. Ren, *Chem. Phys. Lett.*, 2003, **367**, 10; (b) D. M. Teter and R. J. Hemley, *Science*, 1996, **271**, 53.