

*Brief Communication*

## Ultra fine carbon nitride nanocrystals synthesized by laser ablation in liquid solution

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### Abstract

Crystalline carbon nitride nanopowders and nanorods have been successfully synthesized at room temperature and pressure using the novel technique of pulsed laser ablation of a graphite target in liquid ammonia solution. High-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), and Fourier transform infrared spectroscopy (FTIR) were used to systematically study the morphology, nanostructure and chemical bonding. The experimental composition and structure of the nanoparticles are consistent with the theoretical calculations for  $\alpha$ -C<sub>3</sub>N<sub>4</sub>. After 2 h ablation the particles had a size distribution ~8–12 nm, whereas after 5 h ablation the particles had grown into nanorod-like structures with a crystalline C<sub>3</sub>N<sub>4</sub> tip. A formation mechanism for these nanorods is proposed whereby nanoparticles are first synthesized via rapid formation of an embryonic particle, followed by a slow growth, eventually leading to a one-dimensional nanorod structure.

### Introduction

The prediction in 1989 by Liu and Cohen (1989) of a super-hard carbon nitride solid has motivated extensive world-wide experimental and theoretical research to synthesize such a compound. From minimum energy calculations it is generally accepted that CN compounds are metastable under atmospheric conditions (Liu & Wentzcovitch, 1994). Therefore, non-equilibrium processes might be required to promote the formation of the super-hard phase. It has been claimed that the carbon nitride compound could be formed in thin amorphous films by several methods, such as radio frequency plasma deposition (Kumar et al., 1996; Teter & Hemley, 1996), pulsed laser ablation

(Zocco et al., 1999), ion-beam-assisted deposition (Hammer et al., 2000), ion implantation (Niu et al., 1993) and magnetron sputtering (Lopez et al., 1998). However, to date, so-called CN compounds have been far below the ideal composition for C<sub>3</sub>N<sub>4</sub> and most reported compounds are non-crystalline (Muhl & Mendez, 1999). More recently, Yang and Wang (2000) demonstrated that carbon nitride nanocrystals with cubic structure can be prepared by using a pulsed laser induced liquid–solid interfacial reaction. Another step forward was reported by Yin et al. (2003), who have synthesized highly crystalline  $\beta$ -carbon nitride nanorods using a combination of mechanically ground graphite nanoparticles and high temperature chemical reactions.

In this paper, we report a successful synthesis of ultrafine crystalline  $\alpha$ -carbon nitride powder that was created by the novel method of pulsed laser ablation in liquid solution. This technique is effective due to the relative simplicity and low cost of the experimental setup. Moreover, nanoparticles produced by laser ablation of solid targets in a liquid environment are free of any counter-ions or surface-active substances (Wang et al., 2002). Therefore, this method could be applied to the fabrication of nanorods or nanowires of related one-dimensional (1D) materials.

### Experimental procedures

Carbon nitride nanoparticles were produced by laser ablation of a graphite target submerged in an ammonia solution. The experimental setup was similar to our previous report (Pearce et al. 2004). The solid graphite target (Testbourne Ltd., 99.99%) was placed inside a sealed stainless steel container, which was then filled with a 5 ml solution of 35% ammonia (Fisher Scientific) in water. The ammonia solution covered the target to a depth of 5 mm. The second harmonic of an Nd:YAG laser (Spectron Laser Systems, 532 nm, and repetition rate of 10 Hz) was focused onto the target using a 25-mm focal length quartz lens. The laser had a pulse length of 15 ns and a maximum output of 120 mJ/pulse, which is sufficient to easily obtain breakdown in the liquid. The fluence of 532 nm radiation at the target surface was measured to be  $15 \text{ J cm}^{-2}$ . The spot size of the laser

beam on the surface of graphite was about 0.5 mm in diameter. The ablation was typically carried out for 2–5 h. The suspension obtained was then repeatedly centrifuged at 13000 rpm, and the settled powder was washed several times with deionised water and dried overnight at  $60^\circ\text{C}$  in an oven.

Transmission electron microscopy (TEM), selected area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM) were used to identify the structure and morphology of the prepared powders. TEM was performed in bright field mode using a JEOL 1200 EX electron microscope operating at 120 kV. HRTEM was carried on a JEOL 2010 electron microscope at 200 kV. In general, a droplet of suspension was pipetted onto a wholly carbon-coated TEM grid, washed several times (using deionised water) in order to remove ammonia traces, and allowed to dry. The potential existence of C–N, C=C and C  $\equiv$  N bonds was supported by Fourier-transform infrared spectroscopy (FTIR), using a KBr disk for analysis to obtain a spectrum.

### Results

#### *Nanostructures in solid-liquid growth*

TEM images (Figure 1A) showed that highly uniform spheroid-shaped nanoparticles were produced after 2 h laser ablation. The size distribution was obtained by measuring the diameters of more than 800 particles in sight on the given micrograph

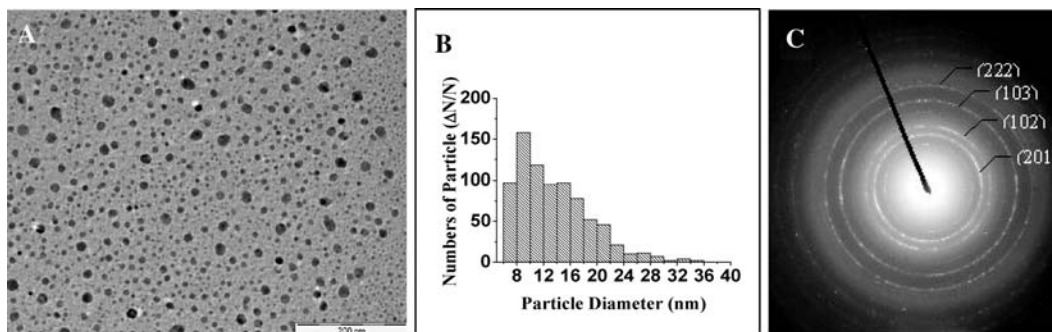


Figure 1. (A) A TEM image of the nanoparticles produced after 2 h ablation of a graphite target in ammonia solution, scale bar 200 nm; (B) Size distribution of the nanoparticles by measuring the diameters of more than 800 particles. The average particle size is  $\sim 8$ –12 nm; (C) SAED pattern of the nanoparticles, which corresponds closely to the calculated interlayer  $d$ -spacing of  $\alpha$ -C<sub>3</sub>N<sub>4</sub>.

(Figure 1A), and this gave an average diameter for the nanoparticles of  $\sim 8$ – $12$  nm (see Figure 1B). An SAED pattern (Figure 1C) recorded from particles without any tilt indicated that the nanoparticles were polycrystalline. The first four peaks from the centre, with interlayer  $d$ -spacings of 2.45, 2.15, 1.52 and 1.31 Å, respectively, were indexed as (201), (102), (103) and (222) with reference to the calculated structure for  $\alpha$ -C<sub>3</sub>N<sub>4</sub> (Teter & Hemley, 1996; Wang et al., 1998).

Carbon nitride has several forms. The  $\alpha$ -C<sub>3</sub>N<sub>4</sub> form is predicted to have a lower energy and is more stable than all the other forms at all volumes (Liu & Cohen, 1989; Teter & Hemely, 1996). In fact, the existence of a metastable  $\alpha$ -C<sub>3</sub>N<sub>4</sub> with a hexagonal structure ( $a = 6.4665$  Å,  $c = 4.7097$  Å, space group: P31c (159)) has been confirmed by many researchers C<sub>3</sub>N<sub>4</sub> (Teter & Hemely, 1996; Wang et al., 1998).

The lattice indices of  $a_0$  and  $c_0$  in our experiment were calculated to be 6.6145 Å and 4.7297 Å from the spacing of (201) and (103) planes, which are slightly larger than the values reported previously (Teter & Hemely, 1996; Wang et al., 1998).

It was also found that the structural order of the carbon nitride increased for longer ablation time, leading to nanorod-like structures with a crystalline C<sub>3</sub>N<sub>4</sub> tip. Figure 2A contains a representative TEM image of nanorods from samples after 5 h laser ablation. Those nanorods were very straight and smooth along the whole length, in a highly aligned arrangement. It revealed that the nanorods have sharp tip-like ends. Figure 2B shows a SAED pattern from the [110] zone-axis indicating a single

crystal of C<sub>3</sub>N<sub>4</sub>. Diffraction patterns taken from different parts of the nanorods show exactly the same pattern, which indicates the single crystallinity of the whole nanorod. Figure 2C shows a HRTEM micrograph of the (102) planes corresponding to  $\alpha$ -C<sub>3</sub>N<sub>4</sub> crystalline with an interplanar distance of 0.218 nm (Wang et al., 1998), which was recorded from the region at the top of the nanorod indicated by the open box in Figure 2A.

#### Chemical bonding in nanorods

Further information regarding the chemical bonding structure was obtained from FTIR spectroscopy. Figure 3 is an FTIR spectrum from the nanorods prepared by 5 h of laser ablation that clearly shows several peaks related to the chemical bonding between carbon and nitrogen (Lu et al., 1999): the region 1000–1500 cm<sup>-1</sup> corresponds to C–N single bonding, while the regions 1500–1750 cm<sup>-1</sup> and 2150–2300 cm<sup>-1</sup> are related to C=N and C≡N bonding, respectively. In our case, the two peaks at 1034 cm<sup>-1</sup> and 1384 cm<sup>-1</sup> correspond to the C–N stretching mode. The absorption bands at 1637 cm<sup>-1</sup> is assigned to the stretching vibrational modes of the C=N. Moreover, a small but clear peak at 2264 cm<sup>-1</sup> can probably be attributed to C≡N bonds, although it is much weaker compared with the other stretching modes. A broad band centred at 3434 cm<sup>-1</sup> is due to NH group vibrations (Likhaicheva et al., 2002).

The result is in accordance with those obtained by TEM, HRTEM and SAED, which suggests the formation of crystalline  $\alpha$ -C<sub>3</sub>N<sub>4</sub>.

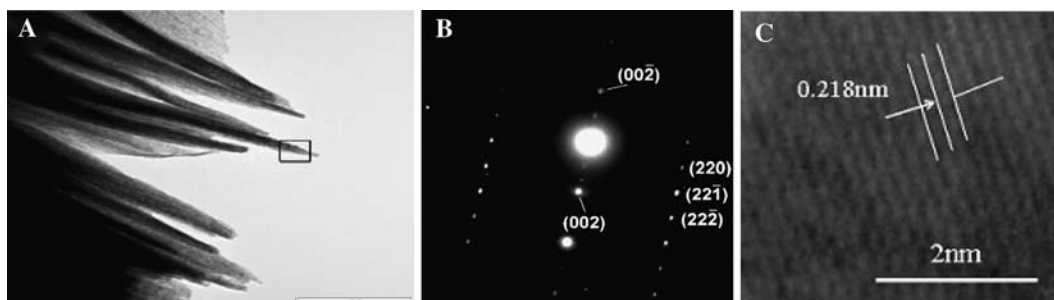


Figure 2. (A) TEM image of carbon nitride nanorods synthesized using a solid-liquid laser ablation system for 5 h, scale bar 200 nm. (B) SAED pattern of the tip of a nanorod from the [110] zone-axis indicating the area is single crystal C<sub>3</sub>N<sub>4</sub>. (C) High-resolution TEM image of the region at the top of the nanorod indicated by the open box in (A).

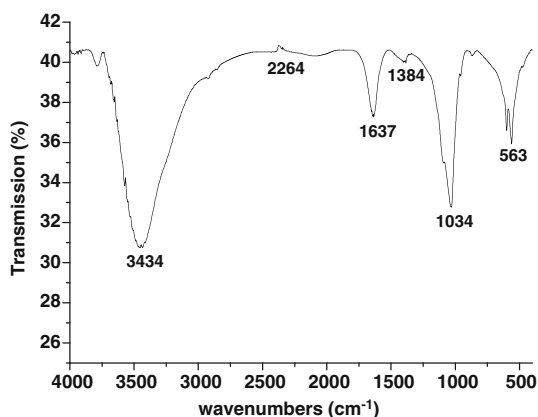


Figure 3. FTIR spectrum of the nanorods showing two peaks at 1034 and 1384  $\text{cm}^{-1}$  corresponding to C–N stretching modes. The absorption bands around 1637 and 2264  $\text{cm}^{-1}$  are assigned to the vibrational modes of C=N and C $\equiv$ N bonds, respectively, which suggests the formation of crystalline  $\alpha$ -C<sub>3</sub>N<sub>4</sub>.

## Discussion

Our studies indicate that the nanorods were formed either by the aggregation of nanoparticles or by slow growth (Yang et al., 2006). Figure 4A showed some evidence to support this finding; the wall of the nanorod exhibited a few small particles which were not transferred completely. In some regions, it was also seen that some nanoparticles comprise the frame of nanorods. In the darker area around the upper right corner of Figure 4B

sufficient nm-sized particles exist to provide a growth source for nanorods. It is possible that these C<sub>3</sub>N<sub>4</sub> clusters connected together to form a rod-like structure which then extended to form nanorods. Once carbon nitride nanoparticles had nucleated, they may have diffused along the surface to growth sites, then assembled into nanorods and grew in the axial direction.

The formation and growth of single crystal  $\alpha$ -C<sub>3</sub>N<sub>4</sub> provides an alternate mechanism compared to other reported techniques (Kumar et al., 1996; Hammer et al., 2000; Niu et al., 1993). This complex reaction process could generally be expressed in terms of following overall equation:



This is consistent with the reports by Yin et al. (2003). However, the corresponding formation of carbon nitride nanorods during pulsed laser ablation in liquid solution, requiring much lower thermal activation, has not been reported previously. Thus, the laser ablation solid-liquid system employed here presents a new synthesis route to new binary materials. During the reaction process, as the high power laser beam reaches the surface of the graphite target, it ejects material predominantly as atomic or ionic species (Wang et al., 2002). These highly energetic ions and electrons will be contained within the thin layer of liquid, in this case ammonia, resulting in the formation of a high temperature, high pressure, and high density

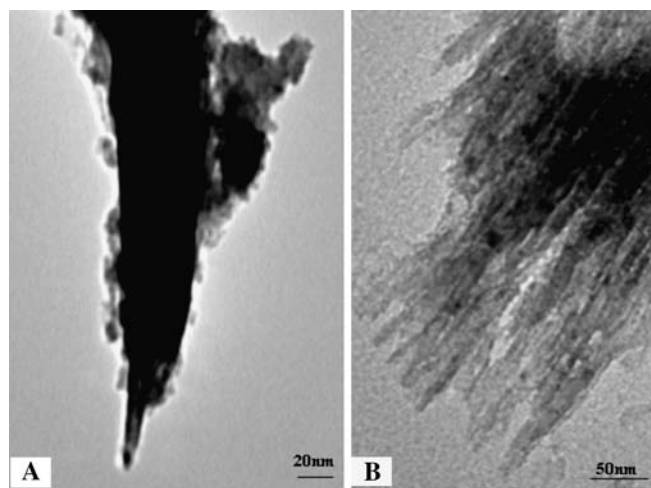


Figure 4. (A) TEM image of single nanorod with a very sharp tip, showing some nanoparticles on its wall. (B) TEM image of a typical bundle of carbon nitride nanorods with large quantities of particles on the rod-frame.

(HTHPHD) plasma of evaporated materials (Yang et al., 2000). Many of the species from the solid target and the liquid solution may react together to form embryonic particles (see Figure 1A), as seen by TEM observation. Due to the very short laser pulse length (15 ns), the growth times of the nuclei are very short and the plasma is rapidly quenched by the liquid phase. This may aid the preferential formation of small metastable-phase nuclei with a uniform particle distribution. In subsequent steps, large quantities of the carbon nitride particles slowly grow along the favorable direction, eventually leading to nano-crystalline metastable structures (as seen in Figure 2A), i.e. the production of non-aggregate, mono-disperse and uniform  $\alpha$ -C<sub>3</sub>N<sub>4</sub> nanorods in the nm scale range.

## Conclusions

Nanocrystalline  $\alpha$ -carbon nitride structures were obtained by liquid-phase PLD from a solid graphite target in an ammonia solution. Ultrafine particles were found with diameters of 8–12 nm. It is believed that the reaction time is very important in determining the nature of the structures. Shorter times lead to nanoparticles, whereas longer ablation times give single crystalline nanorod structures. The liquid phase PLD technique is easily controllable, convenient, low-cost, and effective, and thus could be applied to the fabrication of nanorods or nanowires of a range of related materials.

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