ADVANCED MATERIALS

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Large-Scale Synthesis of Nitrogen-Rich Carbon Nitride Microfibers by Using Graphitic Carbon Nitride as Precursor**

By *Yuanchun Zhao, Zheng Liu, Weiguo Chu, Li Song, Zengxing Zhang, Dongli Yu, Yongjun Tian, Sishen Xie,** and *Lianfeng Sun**

Carbon nitride materials have been of great interests to the scientific community due to their unique properties such as extreme hardness, low density, chemical inertness, biocompatibility, etc.[1,2] According to theoretical calculations published elsewhere,[3,4] some covalent carbon-nitrogen compounds (e.g., β-C_3N_4 and cubic-C_3N_4) are expected to possess a very high bulk modulus even exceeding that of diamond. However, due to the great thermodynamic stability of carbon and N_2 molecules, the experimental synthesis of crystalline carbon nitride with C_3N_4 stoichiometry remains a challenge to date. In recent years much attention has been paid to the graphitic form of carbon nitride (g-C_3N_4) which was successfully synthesized via the polycondensation of triazine-based compounds.[5–7] During the polycondensation reaction the nucleus of tri-*s*-triazine (tri-ring of C_6N_7) is energetically more stable than that of *s*-triazine (ring of C_3N_3). Therefore, it is widely accepted that the tri-*s*-triazine nucleus forms the basic unit for the formation of the graphene-like sheet of g-C_3N_4.[8,9] Graphitic carbon nitride is regarded as the most promising candidate to complement carbon materials in various potential applications. Apart from its application as the precursor for the synthesis of superhard carbon nitride phases, it has also been investigated as a mesoporous material,[10] a high-performance tribological coating,[11] a metal-free catalyst,[12] the nitrogen source for the synthesis of metal nitrides,[13] and as the precursor for the preparation of carbon nitride nano/microstructures.[14,15]

Vapor-grown carbon microfibers (VGCFs) are already widely used as efficient fillers in composites,[16] and supporting substrates for the growth of nanoscale materials.[17] However, the large-scale synthesis of nitrogen-rich carbon nitride 1D nano/microstructures, in particular the synthesis of microfibers with a large length-diameter ratio has not been reported yet. Although several experimental approaches for the synthesis of carbon nitride nano/microstructures have been published, these experiments are actually performed at the C and N atomic level (e.g., at high temperatures),[18,19] which commonly results in low nitrogen incorporation ($<$15 at %) due to the high thermodynamic stability of N_2. In this communication, we present graphitic carbon nitride, which exhibits high thermal stability, as a precursor for the synthesis of nitrogen-rich carbon nitride microfibers. The tri-*s*-triazine and/or *s*-triazine rings present in the precursor remain stable during the microfiber growth process,[20] thus ensuring a high nitrogen content in the final product. Additionally, we demonstrate that the large-scale synthesis of carbon nitride microfibers can be realized via a thermal evaporation process.

Graphitic carbon nitride ($C_3N_{4.4}$) was prepared via a "step-by-step" pyrolysis route from melamine (2,4,6-triamino-*s*-triazine, $C_3N_3(NH_2)_3$).[21] Elemental analysis indicated the presence of residual hydrogen ($\sim$1.58 wt%) in the as-prepared product. Residual hydrogen atoms bind to the edges of the graphene-like C–N sheet in the form of C–NH_2 and 2C–NH bonds. The hydrogen terminated C–N sheet is energetically more stable, and thus has a high thermal stability. Figure 1 shows the thermogravimetric analysis (TGA) result of the precursor carbon nitride. The product is relatively stable up to $\sim$715 °C, after which it starts to decompose and lose mass.

In order to synthesize carbon nitride microfibers, the precursor carbon nitride was placed in a quartz boat and heated to 680 °C under N_2 atmosphere (see Experimental). We found that after the precursor was held at 680 °C for one hour, there was still ca. 55% of the precursor left. However, when it was held at 720 °C for the same amount of time, there was no residual carbon left in the quartz boat. This means the nuclei of *s*-triazine and tri-*s*-triazine which are present in the precursor remain stable during the thermal evaporation. The precursor is evaporated as CN_x ($x > 1$) nucleus vapor phase, rather than in N_2 form (residual carbon should be left in this case). Due to the

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[*] Prof. L. Sun, Dr. Y. Zhao, Dr. Z. Liu, Prof. W. Chu
National Center for Nanoscience and Technology
No. 2, Zhongguancun 1st North Street, Beijing 100080 (P.R. China)
E-mail: slf@nanoctr.cn
Prof. S. Xie, Dr. L. Song, Dr. Z. Zhang
Institute of Physics, Chinese Academy of Sciences
P.O. Box 603, Beijing 100080 (P.R. China)
E-mail: ssxie@aphy.iphy.ac.cn
Prof. Y. Tian, Prof. D. Yu, Prof. L. Sun
State Key Laboratory of Metastable Materials Science and Technology, Yanshan University
Qinhuangdao 066004 (P.R. China)
Dr. Y. Zhao, Dr. Z. Liu
Graduate School of Chinese Academy of Sciences
Beijing 100049 (P.R. China)

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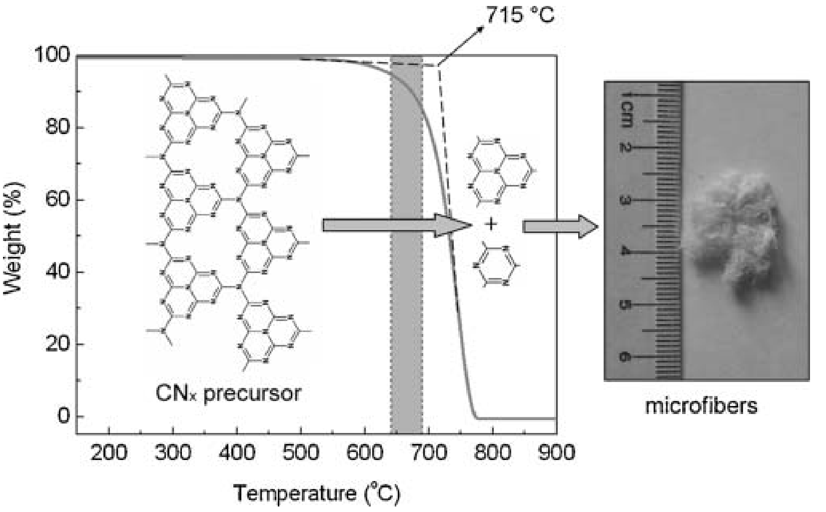

Figure 1. Thermogravimetric analysis (TGA) result for the carbon nitride precursor and schematic illustration of carbon nitride microfiber formation. Both, TG analysis and thermal evaporation were carried out under nitrogen flow at a heating rate of 10 K · min^{-1}.

high thermal stability of the precursor, the carbon nitride precursor is gradually sublimed and produces a constant CN$_x$ vapor pressure; which is not only important for the large-scale formation of one-dimensional structures, but also for achieving a large length-diameter ratio (Fig. 1).

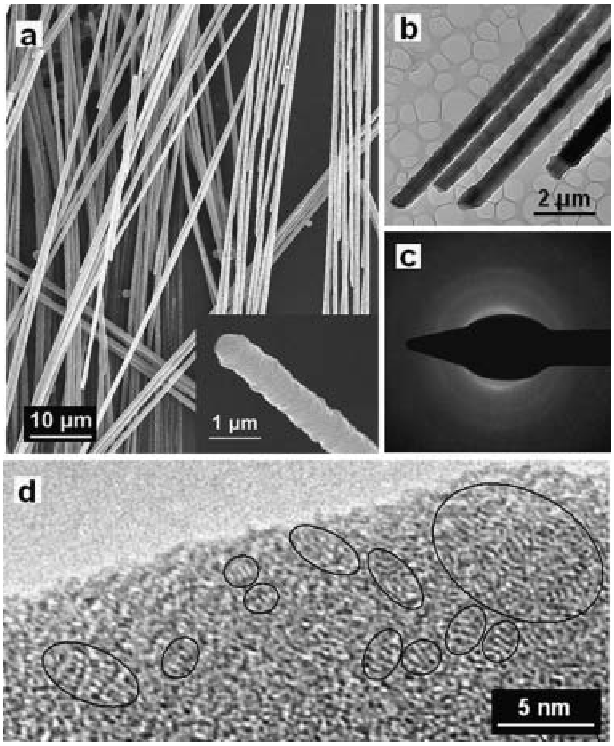

Figure 2. a) A typical scanning electron microscopy (SEM) image of as-obtained carbon nitride microfibers. The inset shows the tip of an isolated microfiber. b) Transmission electron microscopy (TEM) image of carbon nitride microfibers, and c) a corresponding selected area electron diffraction (SAED) pattern. d) High resolution (HR-) TEM image of a carbon nitride microfiber, revealing the product has graphitic structure.

Figure 2a shows a typical scanning electron microscopy (SEM) image of the obtained carbon nitride microfibers. It can be seen that as-prepared microfibers have a uniform size distribution with a mean diameter of approx. 0.8 μm. Most of them are several hundred micrometers long, a few microfibers are even up to 1 mm in length. The inset shows the tip of an isolated microfiber, which exhibits a hemispherical shape with a diameter of ~0.82 μm. Also, the microfiber has a rough surface. A bright-field transmission electron microscopy (TEM) image and the corresponding selected area electron diffraction (SAED) pattern are shown in Figure 2b and c, respectively. The SAED pattern presents three broad diffraction rings for the graphitic structure, which can be indexed as (002), (10*l*) and (004) planes, respectively.

The high resolution (HR) TEM result shown in Figure 2d also reveals that the prepared product has a graphitic structure, which is weakly ordered. Many small crystalline regions, formed by 3–8 parallel fringes, can be observed quite clearly in the HRTEM (encircled regions). The fringe-spacing of the ordered regions shows a broad distribution, which is consistent with a *d*-spacing of ~0.33 nm for the (002) plane given by the SAED pattern. The X-ray diffraction (XRD) pattern of the microfibers exhibits a sharp peak at 27.13 ° that can be assigned to the (002) plane (data not shown). The corresponding *d*-spacing is 0.328 nm, which is very similar to the XRD result for our carbon nitride precursor.[21]

Figure 3 shows an electron energy loss spectrum (EELS) collected from the edge region of a carbon nitride microfiber. It reveals the presence of ionization edges at ~285 and 400 eV,

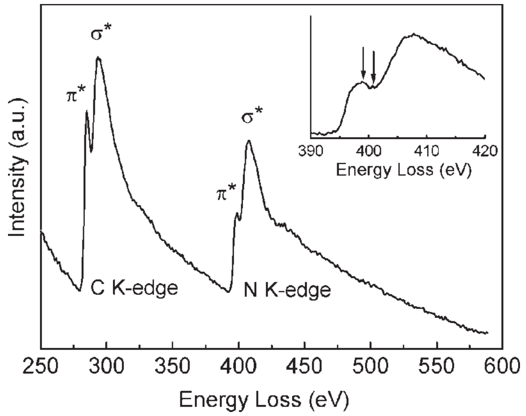

Figure 3. Electron energy loss spectrum (EELS) obtained from the edge region of a carbon nitride microfiber, showing the K-shell ionization edges for C (~285 eV) and N (~400 eV). Well-defined π^* and σ^* features of the C K-edge suggest a graphite-like sp^2 bonding situation. The inset shows the π^* peak splitting present in the fine structure of the N K-edge. Further quantitative analysis revealed a nitrogen-carbon ratio of ~1.21.

corresponding to the C and N K-shells, respectively. The well-defined π^* and σ^* features of the C K-edge confirm an sp^2 hybridization bonding state. For the N K-edge, both peaks related to π^* and σ^* states are very similar to that of the C K-edge of the sample, which indicates that the N atoms are also sp^2 hybridized.[14] Moreover, the inset shows the N K-edge fine structure, where it's revealed that the π^* peak is split into two fine peaks at ~398.8 and 400.7 eV,[18,19] respectively. The former can be attributed to nitrogen atoms in the *s*-triazine/tri-*s*-triazine nucleus, while the latter, which is very small, may relate to the nitrogen atoms bonded to the edges of the nucleus in the form of C–NH_2 and 2C–NH.[22] Moreover, it is to be noted that no peaks at ~532 eV are observed, indicating that the obtained carbon nitride microfibers are oxygen-free. Based on the EELS spectrum, further quantitative analysis was carried out. The N/C ratio of the sample is approx. 1.21 (45.28 ± 5.6 at% C and 54.72 ± 6.7 at% N), which is close to a C_3N_4 stoichiometry. The composition data is reasonably consistent with the result of the elemental analysis (39.49 wt% C, 58.34 wt% N and 2.17 wt% H; N/C=1.27), which confirms that our product is nitrogen-rich.

Fourier transformed infrared (FTIR) spectroscopy of the carbon nitride microfibers confirmed the existence of a graphite-like sp^2 bonding state (Fig. 4a). For direct comparison, the spectra of the carbon nitride precursor and melamine are given as well. The main absorption band in the range of 1100–1650 cm^{-1} corresponds to C–N and C=N stretching vibrations, which are generally associated with skeletal stretching vibrations of the *s*-triazine/tri-*s*-triazine rings. As can be seen the 1100–1650 cm^{-1} part of the carbon nitride precursor spectrum exhibits more unique absorption peaks, which means the chemical environment of the carbon-nitrogen bonding feature becomes more complicated after polycondensation. Stronger absorptions in the range of 1200–1380 cm^{-1} can be assigned to the secondary (2C–N) and tertiary (3C–N) amine fragments, which correspond to an increase in C–N single bond character,[5] while for the carbon nitride microfibers, which is more similar to melamine, the absorptions between 1200 and 1380 cm^{-1} decrease. This indicates that during thermal evaporation most of the tri-*s*-triazine nuclei in the precursor decompose into *s*-triazine-based units. Obviously, the decomposing reaction of the tri-*s*-triazine is not a simple inversion of the de-amination condensation (from *s*-triazine units to tri-*s*-triazine structures); moreover the tri-*s*-triazine units are possibly being partially destructed and rearranged. This leads to the conclusion that after evaporation a cyano group is formed; which would explain the observation of the CN stretching band at 2188 cm^{-1}.[1,23] Furthermore, the spectra show broad bands at 3339 and 3202 cm^{-1}, which can be assigned to the stretching vibration modes of NH_2 and NH groups, respectively. The 500–850 cm^{-1} band is linked to the ring breath or bending vibration modes, and the bending vibration modes of the C–NH_2 group.

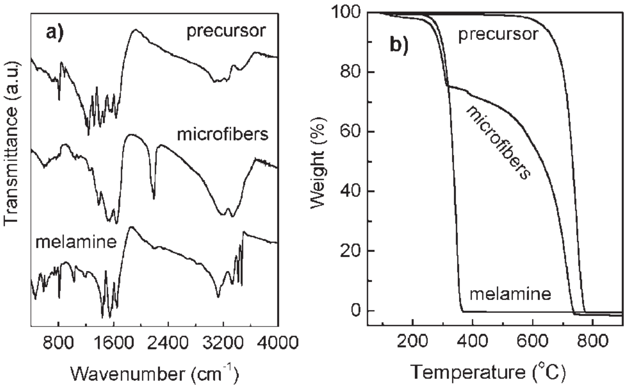

Figure 4. a) Fourier transformed infrared (FTIR) spectra and b) TGA curves of the obtained carbon nitride microfibers, the graphitic carbon nitride precursor, and melamine.

TGA curves of as-obtained microfibers as well as the precursor and melamine are shown in Figure 4b. They are in good agreement with the FTIR results. The carbon nitride precursor only exhibits one inflexion point at ~715 °C, related to the decomposition of the tri-*s*-triazine units. However, it is significantly different for the as-prepared carbon nitride microfibers. The TGA curve of the microfibers shows a sharp mass loss at ~310 °C, and then looses weight gradually until ~720 °C. The first mass loss is quite similar to that of melamine, thus it can be attributed to a loss in *s*-triazine-based units. The second step in the TGA curve of the microfibers differs from the behavior of pure melamine and is related to the loss of tri-*s*-triazine-based units or other advanced condensates.

We also studied the photoluminescence (PL) properties of the carbon nitride microfibers. PL spectra were recorded using a He-Cd laser as excitation source ($\lambda = 325.0$ nm). At room temperature the carbon nitride microfibers exhibit blue luminescence. The emission band is centered at 468 nm, and shows a broad feature with a full width at half maximum (FWHM) of approx. 130 nm. It is widely accepted that nitrogen incorporation plays a key role in PL emission;[24] and that the photoluminescence properties of carbon nitride may correlate with the $\pi \rightarrow \pi^*$ electronic transitions in the π-conjugated polymeric units.[25] EELS and FTIR results have confirmed the existence of a π-bonding state, which can be assigned to the π-conjugated *s*-triazine/tri-*s*-triazine units in the as-prepared sample. Moreover, the weakly ordered microstructure of the microfibers (as shown in Fig. 2d) is thought to be the main reason for the broadened PL spectrum. Photoluminescence properties of our product are similar to that of nitrogen-rich carbon nitride nanoparticles,[6] and thin films.[26]

The growth process of one-dimensional structures is unusual and interesting. Considering no catalysts were employed in our experiments, the common one-dimensional growth mechanism of vapor-liquid-solid (VLS) can be ruled out. Therefore, we propose that the growth mechanism is possibly governed by a vapor-solid (VS) process. In order to provide a good understanding of the growth process, we carried out more controlled experiments. About 2 g carbon nitride precursor were evaporated at 680 °C for 10 min and we were only able to find the coating deposited on the inner-wall of the quartz tube. As shown in Figure 5a both, small initial nuclei and short

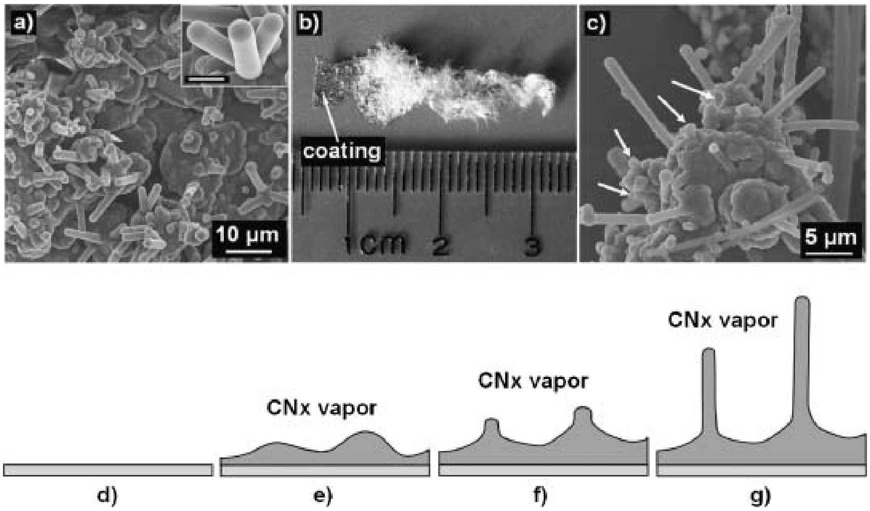

Figure 5. a) SEM image of the carbon nitride coating deposited on the inner-wall of a quartz tube (duration of deposition: 10 min). The inset shows three short rods, scale bar equals 3 μm. b) Optical image of as-grown carbon nitride microfibers demonstrating that they were grown from the coating (duration of evaporation: 30 min). c) SEM image of the coating indicated in (b), after the as-grown microfibers were peeled off. The arrows point towards the fractured roots of the microfibers. d) - g) Schematic process of the vapor-solid governed growth of carbon nitride microfibers.

microrods are present on the rough surface of the coating. We then extended the evaporation time to 30 min at identical experimental conditions and were able to produce a large quantity of carbon nitride microfibers at a temperature of approx. 300 °C (Fig. 5b). Figure 5c shows the SEM image of the coating after the microfibers were peeled off. As indicated by the arrows, fractured roots of the microfibers can be found, as well as some short microfibers which are still standing on the surface. Therefore, we suggest the following mechanism for the growth of microfibers: Firstly, the evaporated CN_x vapor phase is carried to the downstream region of quartz tube by the N_2 gas flow; then, the CN_x vapor phase deposits on the inner-wall of the quartz tube. Due to the surface free energy difference between CN_x vapor and quartz, the smooth surface of the quartz tube provides a uniform environment for 3D island growth with the islands growing larger later on and eventually overlapping and forming a film (Fig. 5d–e). However, because of the low temperature of the deposition area, the following deposition step (CN_x vapor depositing on the CN_x film) tends to become a stacking process. This does not only result in a rough surface of the obtained coating, but also has a higher probability of forming micrometer-scale nuclei which is important for the growth of microfibers (Fig. 5a and f). It is well known that the condensation of the CN_x units in the vapor N is closely related to the curvature radius of the surface 1/r as shown in equation (1).[27]

$$N \propto p = p_0 \exp\left(\frac{2\sigma\Omega}{rkT}\right) \tag{1}$$

Where p is the pressure, p_0 the equilibrium pressure on plane surface, σ the surface energy, Ω the volume of the CN_x nucleus, k the Boltzmann constant, and T the absolute temperature. Once stable micrometer-scale nuclei are formed, the high curvature radius will lead to a much larger growth rate owing to the higher condensation of vapor around the nuclei (or the tip of the microfibers). Therefore, one-dimensional growth will dominate subsequent processes and the formed nuclei grow into microfibers (Fig. 5c and g). Our successful synthesis is attributed to both, the high thermal stability of the precursor and the low experimental temperature, which allows the CN_x nuclei in the precursor to remain stable during vapor transfer. Additionally, they act as the basic units during microstructure assembly, which makes the produced microfibers nitrogen-rich. However, during the growth process the high nitrogen content and the low experimental temperature result in a weakly ordered graphitic structure, rather than a perfect crystalline form.

In conclusion, microfibers of nitrogen-rich carbon nitride (N/C atomic ratio ~1.27) were synthesized on a large scale via a thermal evaporation method. A precursor with a high thermal stability as well as a suitable synthesis temperature are significant in providing a constant CN_x ($x > 1$) vapor phase, which consequently ensures a high nitrogen content in the microfibers. The microfibers have graphitic structure and exhibit sp^2 hybridization features. A blue photoluminescence was observed with a broad FWHM, which is closely related to the high nitrogen content and weekly ordered microstructure of the microfibers. Our development of a vapor-phase synthesis may also pave the way to other specific structures based on a nitrogen-rich carbon nitride system, such as one-dimensional nanostructures and micro/nano-spheres.

Experimental

Graphitic carbon nitride powder, the precursor for the growth of microfibers, was prepared via "step-by-step" pyrolysis of melamine (2,4,6-triamino-*s*-triazine, $C_3N_3(NH_2)_3$) [21]. A quartz boat loaded with ~2 g of the as-prepared brown powder was placed into the centre of a tube furnace. Pure nitrogen was introduced into the quartz tube at a flow rate of 200 sccm (standard cubic metre per minute) for ~30 min before the flow rate was decreased to 50 sccm; the pressure inside the tube was held constant at ~1 atm. The furnace was gradually heated to 680 °C at a rate of $10\,\mathrm{K \cdot min^{-1}}$ and held at this temperature for one hour. After cooling the tube furnace to room temperature a faintly yellow-colored, fluffy product was found in the downstream region of the tube.

The morphology of the product was analyzed by scanning electron microscopy (SEM, Hitachi S-4800, 10 kV). High-resolution transmission electron microscopy (HRTEM, FEI Tecnai F20 G2, 200 kV) was performed to characterize the microstructure of the obtained microfibers. Chemical composition and bonding properties of the product were analyzed using electron energy loss spectroscopy (EELS) which were carried out on a JEOL JEM-2010 transmission electron microscope equipped with a Gatan-ENFINA-776 parallel collection electron energy loss spectrometer (accelerating voltage: 200 kV).

Elemental analyses were performed using a Flash EA1112 CNH analyzer (CE Elantech, Lakewood, NJ). Fourier transformed infrared (FTIR) spectra were recorded on a Perkin-Elmer Spectrum 100 instrument. Thermogravimetric analyses (TGA) were performed at a heating rate of $10\,\mathrm{K}\cdot\mathrm{min}^{-1}$ under nitrogen flow (Perkin–Elmer, Pyris Diamond TGA/DTA).

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