

Synthesis and field emission of carbon nanotubular fibers doped with high nitrogen content

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Nitrogen-doped carbon nanotubular fibers with a very high nitrogen concentration (~20 at.%) were synthesized through the aerosol-assisted decomposition of dimethylformamide in the presence of catalyst. The synthesized fibers process a novel “pearl necklace-like” morphology and exhibit an excellent field emission performance.

There has been enormous interest in doping carbon nanotubes with nitrogen atoms because the incorporated N can enhance the mechanical and conducting properties of the nanotubes.¹ The stimulus for this study also stems from the theoretical predictions of the hypothetical metallic CN nanotubes² and the covalently bonded β -C₃N₄,³ both possessing an unmatched hardness. In recent years significant work has been carried out on synthetic methods and the potential applications relating to field emission, energy storage and electron transport of carbon nitride (CN_x) nanotubes.

Several research groups have reported on CN_x nanotube growth using chemical vapour deposition (CVD) methods.^{4–12} Most of the syntheses have relied on catalytic pyrolysis of C or CN gas-phase precursors under N-rich atmosphere. The reported precursors included cyanuric chloride, pyridine, melamine, triazine, acetonitrile, C₆₀, methane, acetylene, camphor, and metal phthalocyanine. Extensive investigations indicated that N incorporation into C nanotubes strongly depends on the synthesis conditions such as precursor, catalyst, reaction temperature, and even gas flow.⁹ The pyrolysis of some N-free organic precursors (methane, for example) in the presence of NH₃ or N₂ could form CN_x nanotubes only with a low N content. The highest N doping level reported to date is <10%, implying difficulty in the formation of a C–N bond. The N incorporation is not effectively improved when N-rich solid precursors are utilized, the N content increasing only to <13%. Considering the fact that pyrolysis of a solid precursor (melamine, for example) at high temperature has been characterized by thermodynamic stability of NH₃, HCN and CH₄, the increased N content should be attributed to the existence of CN species in the vicinity of catalysts transported by HCN gas. The pre-existing C–N bonds during catalytic decomposition thus may play a key role for the incorporation of N in C nanotubes.

Based on the above considerations, we now suggest that some precursors containing =C–N units linked by sp² carbons may be catalytically converted to sp² CN_x nanotubes. Importantly, the precursors should not contain the N–H bond because it has considerable stability (bond length ~100 pm) at elevated temperatures and needs some specific catalysts to break the bond linkage. Therefore, a commonly used organic solvent, *i.e.* *N,N*-dimethylformamide (HOCN(CH₃)₂, DMF), was chosen as the desired precursor for the N-rich CN_x nanotube growth in this study. Nitrogen in DMF links to one sp² carbon (C–N bond length ~137 pm) and two sp³ carbons (C–N bond length ~147 pm), thus meeting our selection criteria. In order to depress the C–N bond break, we adopted an aerosol assisted vapour synthesis method to transport the precursor: the aerosol droplets of DMF heated to 60 °C were transported by a continuous Ar carrier gas into a quartz tube inside a tubular furnace. Dry ammonia was fed simultaneously into the furnace.

Fe₂O₃ and MoO₃ composite particles embedded into an Al₂O₃ matrix film on a Si substrate were used as the support catalysts for the CVD synthesis of CN_x nanotubes. The catalysts were prepared in a conventional sol–gel method. 5 mL of tri-sec-butoxide was dissolved in the mixed solution of 41 mL of 2-propanol and 1 mL of acetylacetone under vigorous stirring for 30 minutes, and an aqueous solution of iron nitrate and ammonium heptamolybdate with a molar ratio Fe/Mo = 1 was added drop by drop to form the desired sol. A few drops of the sol were coated onto an n-type Si (100) substrate to form after several minutes a transparent gel. A catalyst film was obtained after aging and drying.

After the aerosol-assisted CVD reaction at 800 °C for 30 minutes, CN_x nanotube fibers grew in a direction normal to the substrate surface. Fig. 1 depicts a scanning electron microscopy (SEM) micrograph of the product on the substrate. The product consists of numerous cracked flakes, each composed of aligned nanotube fibers. The densely packed and aligned fibers are clearly seen in the inset of Fig. 1. The highly oriented growth results from the weak van der Waals forces between the tubular fibers,¹¹ resulting in the formation of aligned CN_x tubular arrays with the individual fiber of approximately the same length.

Shown in Fig. 2, are the transmission electron microscopy (TEM) micrographs of N-rich CN_x nanotube fibers and the corresponding electron energy loss spectrum (EELS) measured by using a stationary focused 0.5-nm electron probe. Fiber diameters range from several nanometers to ~50 nm. Some metal particles containing Fe and Mo are encapsulated into fibers, indicating that the base growth, rather than top growth, is the plausible mechanism for the formation of CN_x nanotube fibers. We also note that the present fibers reveal a distinctly different morphology compared to previously reported CN_x nanotubes with the lower N content. The nanotube fibers are polymerized through linking compartmentalized units (nanobells),⁷ which consist of an interlinking cap and a short cylindrical shell of a nearly constant outer diameter. The unique characteristic of the present N-rich CN_x nanotubular fibers is their “pearl necklace-like” morphology with characteristically uniform adjacent spheres.

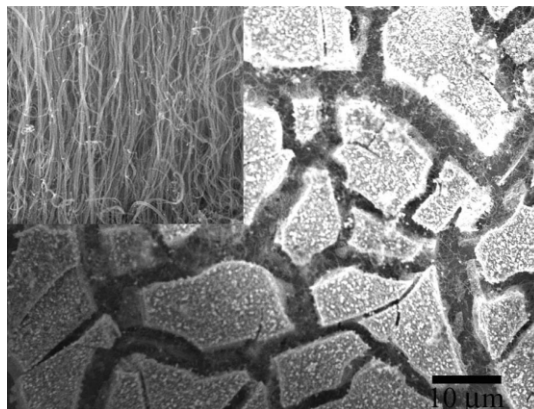


Fig. 1 Low-magnification SEM image displaying the aligned N-rich CN_x nanotubular fibers with a uniform length. (inset) high-magnification SEM image for the densely-packed and aligned nanotubular fibers.

Previous works indicated that the N content is directly related to the microstructure of CN_x nanotubes; the tube cap region appeared to always have a higher N content than that of a cylindrical part.^{5,7-9} Therefore, the “necklace-like” morphology may allow a higher N content. In fact, numerous EELS taken on the “necklace-like” nanotubular fibers (e.g. Fig. 2) typically revealed the N/C atomic ratios in the range of 0.19 to 0.25, independent of the electron probe positioning on the nanostructures. The N K edge shows a well-developed σ^* feature with a notable peak splitting. The unusual double-peak structure has been observed by Han *et al.*,⁸ with the interpretation that high-N-content CN_x fibers do not undergo a transition from graphite-like to a fullerene-like phase. The σ^* of the C K edge also exhibits a relatively sharp feature in Fig. 2 and suggests a graphitic-like stacking rather than disordering within the walls, thus clearly verifying a well-crystallized CN_x nanostructure. We have not detected a pronounced antibonding π^* on the N K edge; and the existing π^* peak of the C K edge leads only to a relatively smooth shoulder. This indicates that the intensity of the π^* peak, peculiar to all previously reported low-N-content CN_x nanotubes, is significantly depressed in the present N-rich fibers. Such a depression indeed agrees with the theoretical predictions on N electron filling of the antibonding π^* state in N-rich CN_x .¹

Doping carbon nanotubes with N may enhance their electron field emission due to the presence of additional lone pairs of electrons. Therefore we particularly examined the field emission properties of the synthesized N-rich CN_x nanotube fibers. The field emission current was measured as a function of applied voltages in a vacuum of $\sim 10^{-9}$ Torr at different distances between the aligned CN_x fiber film and an anode probe. The distance was accurately adjusted by a linear-motion step controller. The measurement details and data analytic method were reported elsewhere.¹³ Fig. 3 displays the field emission current–voltage curves. The average turn-on field, defined as the applied electrical field needed to produce a current density of 0.01 mA cm^{-2} , is as low as $1.32 \pm 0.29 \text{ V } \mu\text{m}^{-1}$. The current density of 0.08 mA cm^{-2} can be obtained for an applied field of $1.8 \text{ V } \mu\text{m}^{-1}$ by curve fitting. The results indicate that the present N-rich CN_x nanotubular fibers exhibit better field emission performances than most of the previously reported low-N-containing CN_x nanotubes and undoped carbon nanotubes (for instance,¹¹ $CN_{<0.09}$ nanotubes: turn-on field of $1.5 \text{ V } \mu\text{m}^{-1}$, $80 \text{ } \mu\text{A cm}^{-2}$ at $2.6 \text{ V } \mu\text{m}^{-1}$; carbon nanotubes: turn-on field of $2.6 \text{ V } \mu\text{m}^{-1}$, $14 \text{ } \mu\text{A cm}^{-2}$ at $4.8 \text{ V } \mu\text{m}^{-1}$).

In summary, the present study documented that N content in CN_x nanotube fibers can be effectively increased through selecting appropriate organic precursor and synthesis conditions such as catalyst and vapour transport routes. DMF used here is one of the possible candidates. EELS analyses indicated

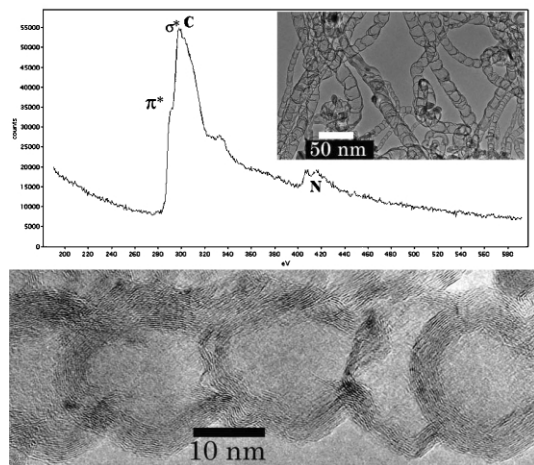


Fig. 2 Low-magnification TEM image and EELS spectrum of the N-rich CN_x nanotubular fibers. (up); and high-resolution TEM image of an individual fiber (bottom).

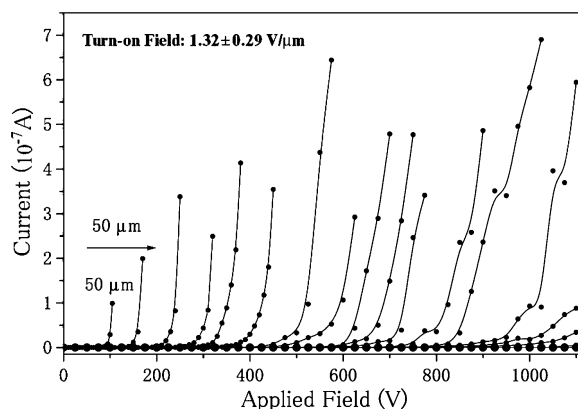


Fig. 3 Field emission current–voltage curves recorded on the aligned N-rich CN_x nanotubular fibers at different anode–sample distances; the distance was gradually changed in $50 \text{ } \mu\text{m}$ steps.

that the N content along and across the CN_x nanotube fibers is high and uniform, $\sim 20 \text{ at.}\%$, which corresponds to a C_5N stoichiometry. The high N content affects the resultant nanotube morphology, a novel “pearl necklace-like” tubular morphology was observed here. The characteristically low turn-on field and high emission current density suggest intriguing prospects for practical applications of the N-rich nanostructure.

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