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Synthesis of Multi-Walled and Bamboo-like Well-Crystalline CN_x Nanotubes with Controllable Nitrogen Concentration ($x = 0.05–1.02$)

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The multi-walled and bamboo-like well-crystalline CN_x nanotubes with controllable nitrogen concentration ($x = 0.05–1.02$) were synthesized. The stoichiometry of as-prepared CN_x ($x \cong 1.02$) is close to that of the theoretically predicted graphite-like CN.

In 1991, carbon nanotubes (NTs) were discovered by Iijima while examining carbon soot using electron microscopy.[1] Subsequent work has shown that nanotubes could be produced from a wealth of materials that are also featured by a layered structure, such as BN, MX_2 (M = Mo, W, Nb, Hf; X = S, Se), ZrS_2, TaS_2, $NiCl_2$, and VO_x.[2] The synthesis of nanotubes from new layered materials is currently a subject of intensive research. Graphitic−C_3N_4 and −CN are ideal compounds with two-dimensional layered structures that are analogous to graphite. Cohen's group predicted theoretically that graphitic −C_3N_4 and −CN most probably have tubular forms in 1997.[3] Since then, the study of CN_x NTs with controlled composition has attracted much attention, due to their advantages in the fabrication of materials with tailored electronic[3] and mechanical properties.[4]

Rao's group reported the synthesis of CN_x ($x < 0.09$) NTs by pyrolyzing pyridine over Co powder in an argon atmosphere in 1998.[5] Since then, there have been a variety of techniques applied to prepare CN_x NTs, with notable examples including chemical vapor deposition (CVD),[6−8] arc discharge,[9] and magnetron sputtering.[10] However, the average concentration of nitrogen in well-crystalline CN_x NTs is typically less than 13%.[11−13] Recently our group prepared poor-crystalline C_3N_4 NTs via a benzene thermal process,[14] and CN_x NTs ($x = 0.01−0.33$) by the reactions between carbon halides and sodium azide.[15] In this Communication, we demonstrate that multi-walled and bamboo-like well-crystalline CN_x nanotubes with controllable nitrogen concentrations ($x = 0.05−1.02$) were synthesized. Note that the stoichiometry of as-prepared CN_x ($x \cong 1.02$) is close to that of the theoretically predicted graphite-like CN. To our best knowledge, this is the highest nitrogen concentration in the reported crystalline CN_x NTs.

In a typical synthesis of $CN_{1.02}$ NTs, 2.05 g of metal magnesium (Mg), 3.10 g of urea ($CO(NH_2)_2$), and 2.00 g of sodium azide (NaN_3) were placed in a 15 mL stainless steel autoclave. The autoclave was sealed, warmed at a rate of 0.5 °C/min and maintained at 550−600 °C for 24−36 h, and then allowed to cool to room temperature naturally. The precipitate was filtered off and washed with diluted acid, distilled water, acetone, and absolute ethanol in turn twice. The resulting brown powders were dried in a vacuum at 50 °C for 3 h.

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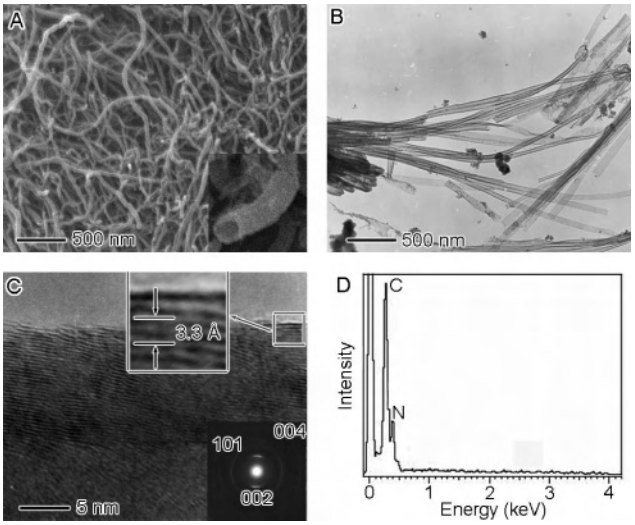

Figure 1. (A) FE-SEM image, (B) TEM image, (C) HRTEM image, and (D) EDX spectrum of the as-synthesized multi-walled $CN_{1.02}$ NTs. The inset of panel A is a magnified SEM image of the open end of a nanotube. The inset of panel C is ED pattern of the nanotube.

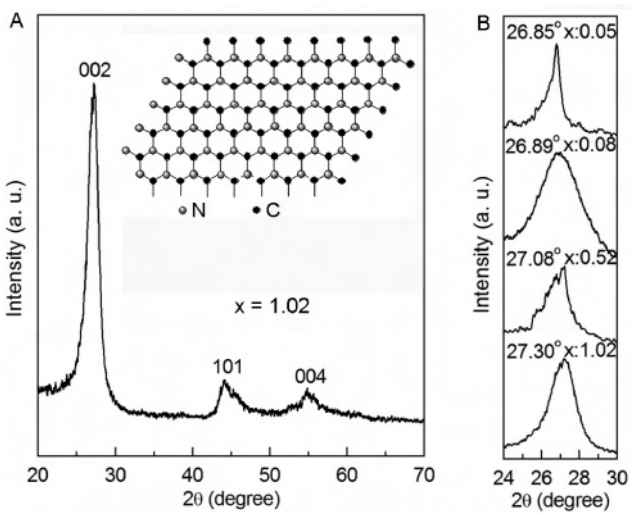

Figure 2. (A) XRD pattern of the as-synthesized $CN_{1.02}$ sample. The inset is the ideal atomic structure of a graphite-like CN single layer. (B) The (002) peaks in the XRD patterns of CN_x sample with different x values.

The morphology of as-obtained products was observed by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). From the FE-SEM image (Figure 1A), it can be seen that these $CN_{1.02}$ NTs have diameters of 50−100 nm and lengths of 2−3 μm. Some of the nanotubes have open ends, shown in the inset of Figure 1A, giving the most direct evidence of tubular structures. TEM image (Figure 1B) shows that the wall thickness of nanotubes ranges from 5 to 10 nm. The content of nanotubes in the sample is 50−60%, while there exist 20−25% nanosheets and 20−25% nanoparticles.

A further investigation on the tubular structure by HRTEM (Figure 1C) reveals that the nanotubes are multi-walled and that the fringes are separated by about 3.3 Å, consistent with the (002) plane lattice parameter of graphite-like CN.[16] The electron diffraction (ED, inset of Figure 1C) pattern also confirms its tubular structure growing along (002) plane. The energy-dispersive X-ray (EDX) analysis (Figure 1F) on nanotubes shows the content of nitrogen in $CN_{1.02}$ NTs. The ratio of carbon to nitrogen is determined to be 1.00:1.02. More precise data for their composition were determined by element analysis, revealing that the N/C ratio is 1.01, which is in good agreement with the CN stoichiometry.

The phase of product is determined by X-ray diffraction (XRD) pattern. Figure 2A shows a typical XRD pattern of the product. In comparison with the XRD data of graphite and carbon nanotubes for (002),[16] the strongest sharp peak is shifted to high angle at 27.3° (d = 3.27 Å), which is very similar to the XRD patterns of graphite-like CN in the previous works.[17]

More information about their bonded structure is provided by X-ray photoelectron spectroscopy (XPS) analysis.The structure of graphite-like CN can be regarded as CN single layers aligned relative to each other along the hexagonal c axis (inset of Figure 2A).[3,18,19] All the N atoms in each graphite-like CN single layer are of one type.[3,18,19] XPS measurements (Figure S1) show that the C1s and N1s binding energies of the sample are 288.15 and 399.02 eV, respectively, which can be attributed to sp^2 C and sp^2 N in atomic structure of graphite-like CN. The observed C1s and N1s binding energies are very similar to those of the C−N bonds in graphite-like CN.[20] All the above results reveal that the structure of the products should be close to that of graphite-like CN.

By changing the added amount of sodium azide, the nitrogen concentration of multi-walled CN_x NTs (i.e., the value of x) can be continuously adjusted. For example, the $CN_{0.52}$ NTs (Figure S2) were also prepared by adding half amount of sodium azide. It was found that the CN_x NTs with lower nitrogen concentration have similar properties to carbon NTs. As examples, many $CN_{0.52}$ NTs with large bending angles were observed; there also exist some Y-structural and subdivided NTs in the products.

The replacement of sodium azide by sodium amide ($NaNH_2$), while other experimental parameters were kept constant, afforded bamboo-like $CN_{1.01}$ NTs (Figure 3A−D). This type of nanostructure has been observed in the case of CNTs.[21] The diameters of the bamboo-like $CN_{1.01}$ NTs range from 50 to 100 nm, and their wall thickness is 5−10 nm. The content of bamboo-like $CN_{1.01}$ NTs is 40−50%, while the sample contains 50−60% nanoparticles. HRTEM image (Figure 3F,G) and ED pattern (inset of Figure 3E) reveal that the walls of the bamboo-like $CN_{1.01}$ NTs are along (002) plane, and the inner tubes are subdivided by some layers along (002). The nitrogen concentration of bamboo-like CN_x NTs can also be continuously adjusted by changing the added

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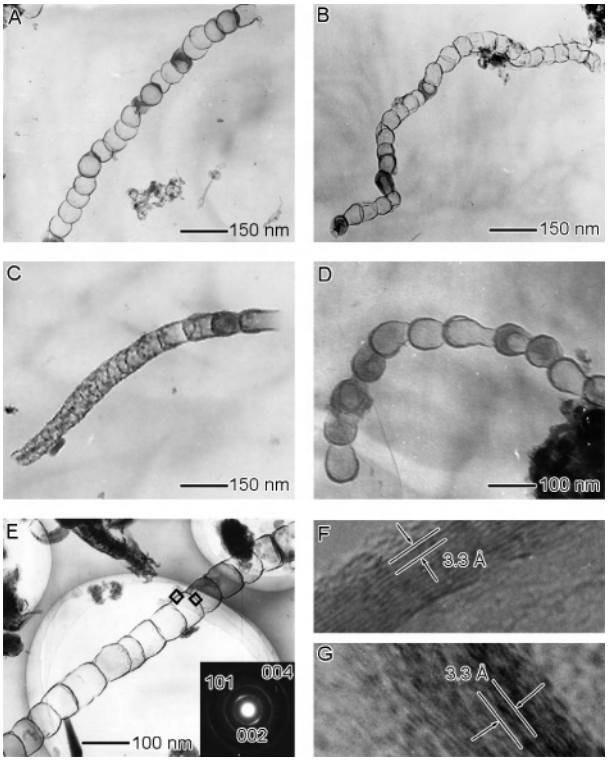

Figure 3. (A−E) TEM images of the as-synthesized bamboo-like $CN_{1.01}$ NTs. The inset of panel E is ED pattern of the bamboo-like nanotube. (F) HRTEM image of the wall (marked by the box in panel E). (G) HRTEM image of the subdivision layers (marked by the box in panel E).

amount of sodium amide. For example, bamboo-like $CN_{0.49}$ NTs (Figure S3) were obtained by adding half amount of sodium amide.

We found that the reaction between $CO(NH_2)_2$ and Mg without azide or amide could produce $CN_{0.08}$ NTs (Figure S4). It indicates that the urea acted as both carbon and nitrogen source in the reactions. The nitrogen concentration could further be controlled below $x = 0.08$ by adding ethanol (C_2H_5OH) to the reaction (see Supporting Information). C_2H_5-OH acts as an additional carbon source in this reaction. Unfortunately, we found that the x value of CN_x NTs cannot be adjusted to be higher than 1.02, even when larger amounts of sodium azide or amide are added. As a typical result, non-graphitic C_3N_4 sub-microcrystals (Figure S6) rather than graphitic $-CN_x$ nanotubes were obtained in the presence of more azide.

The XRD observations of CN_x NTs with different x value ranging from 1.02 to 0.05 show that their (002) peaks are shifted to low angles toward 26.8° with the decrease of nitrogen concentrations (Figure 2B). It was reported that the (002) peak of carbon NTs is about at 26.8°.[16] It indicates that the (002) plane distances of CN_x NTs are more and more close to that of carbon NTs with the decrease of nitrogen concentration.

The formation mechanism of CN_x NTs in our present work is unclear at present. However, some reaction conditions play crucial roles in the formation of CN_x NTs as follows; (1) The reaction temperature appears to be the key parameter, and at a temperature <530 °C, no nitrogen concentration was found in the products; at temperatures >620 °C, nitrogen concentration decreased strongly. (2) 36−51 MPa is the crucial pressure for the formation of $CN_{1.02}$ NTs. In the experiments, the pressure can be controlled by adjusting appropriate autoclave volume and reagent amount. The high pressure is supposed to be the reason the nanotubes with high nitrogen doping have good crystallinity. (3) Metal magnesium played an important role, most probably acting as reducing agent to remove the oxygen in urea. (4) Sodium azide or amide was found to be indispensable for the production of CN_x NTs with high nitrogen concentration, providing a rich-nitrogen system.

In summary, the synthesis of multi-walled and bamboo-like well-crystalline CN_x nanotubes (NTs) with controllable nitrogen concentrations ($x = 0.05-1.02$) was reported. Future research will further reveal the detailed mechanism.

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Supporting Information Available: Table of the experimental parameters and results of all reactions; XPS spetra of $CN_{1.02}$ NTs; TEM and SEM images of CN_x NTs ($x = 0.05-0.52$); XRD pattern and SEM image of the product when larger amounts of NaN_3 were added; instrumentation. This material is available free of charge via the Internet at http://pubs.acs.org.

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