LETTER TO THE EDITOR

n-diamond from catalysed carbon nanotubes: synthesis and crystal structure

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Abstract
The phase composition and morphology of black powder samples synthesized by pyrogenation of carbon nanotubes and colloidal $Fe(OH)_3$ were investigated using x-ray diffraction (XRD) and transmission electron microscopy. A new kind allotrope of carbon, 'new diamond' (n-diamond), was obtained in the final black powder when the treatment temperature was higher than $1000\,^{\circ}\text{C}$. As the treatment temperature reached $1400\,^{\circ}\text{C}$, the peak intensity of the n-diamond achieved its maximal value and the estimated yield rate was about 20%. The average size of the n-diamond nanometric particles was around 20 nm. Using the least squares refinement method and XRD pattern simulation technology, the crystal structure of n-diamond was studied.

There has long been interest in synthesizing diamond from other allotropes of carbon [1]. However, there are still many unclear issues in the process of transformation from the sp^2 or sp^1 allotropes to sp^3 diamond. In order to understand the transition mechanisms and to explore new pathways to diamond, Hirai and Kondo [2] designed a unique procedure based on rapid cooling of shock compressed graphite sheets. A possible new allotrope of carbon was found and this was referred to as n-diamond ('new diamond'), since its lattice parameter is close to that of diamond. Many reflections in its electron diffraction pattern match those of cubic diamond (space group: $Fd\bar{3}m$) except for some additional forbidden reflections indexed at (200), (222) and (420). In 2001, Konyashin and co-workers studied its crystal structure by means of electron diffraction (ED) [3, 4] and found that n-diamond has a face-centred cubic (fcc) lattice structure (space group: $Fm\bar{3}m$) with lattice parameter $a = 0.3563$ nm.

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To date, a variety of techniques have been developed for the production of n-diamond, including radio-frequency plasma aided decomposition of hydrocarbon [5], plasma assisted chemical vapour deposition using diluted hydrocarbons [6], transformation of graphite under shock compression [2], transformation of C_{60} films under shock compression [7], transformation of graphite at high pressure and temperature [8], plasma–chemical synthesis with the aid of a carbon plasma jet [4], treatment of the diamond surface in hydrogen plasma [3] and annealing of silica wafer embedded with carbon atoms [9–11]. In 2003, we discovered that n-diamond could also be synthesized by the method of catalysing carbon black at atmospheric pressure and at the temperature of $1100\,°C$ [12–14].

Like other soots and fullerenes, carbon black is composed of fragments of carbon network, either single layers (bent, curved or flat) or small, assembled packs [15, 16]. Before the discovery of fullerenes [17], the idea that graphene sheets contain pentagonal or heptagonal rings as defective sites was not considered for carbon black. However, soon after the discovery of fullerenes, it was found that fullerenes could also form in flames. Thus, it is naturally to think that pentagonal or heptagonal rings must be present in the carbon black resulting from flames [18]. In fact, both theoretical [19–21] and experimental results [22–27] have evidenced the presence of fullerene-like structures in carbon black. After the pentagon and heptagon rings were first found by lijima in 1991, transmission electron microscopy (TEM) study of the carbon nanotube (CNT) morphology revealed that they play key roles in governing the tube-tip shapes [28–31]. Since n-diamond could be synthesized from carbon black as a carbon source and as both carbon black and CNTs contain pentagonal or heptagonal rings, one could speculate that n-diamond might be transformed from CNTs instead of carbon black. To validate this notion, we designed a unique experimental procedure for synthesizing n-diamond using CNTs as the carbon source in this work.

The present method of synthesis of pristine CNTs was a chemical vapour deposition (CVD) method and it is the same as that used in [32]. The CNTs obtained were multi-walled carbon nanotubes, approximately 20–50 nm in diameter, $\sim 1\,\mu m$ in length. After preparation, CNTs were washed with acid. The final CNTs were almost 100% tubules.

Colloidal $Fe(OH)_3$ was prepared from the reaction between saturated $FeCl_3$ solution and saturated NaOH solution at room temperature, and then it was stirred into CNT powder using a blender. After being dried in an oven at $110\,°C$, the admixture was compressed into an open stainless steel tank (capacity 100 ml). The mass ratio of CNTs to iron in the mixture was 10:1. The tank was maintained at a given temperature for 10 min in flowing nitrogen, and then cooled to room temperature. The heating rate and cooling rate were 10 and $-30\,°C\,min^{-1}$ respectively. Then the phase composition of the heat-treated reactant was analysed using an XRD-6000 diffractometer with Cu Kα radiation (wavelength 0.154 nm). Afterwards, the products were washed with $6\,mol\,l^{-1}$ H_2SO_4, rinsed with distilled water and dried in an oven at $110\,°C$. These dried powders were finally analysed with transmission electron microscopy (TEM, JEM-100CXII with 80 kV accelerating voltage).

Figure 1 shows the x-ray diffraction (XRD) patterns of the powders heat treated at given temperatures. As shown in figure 1, when the treatment temperature was below $400\,°C$, NaCl and CNTs were detected by the x-ray diffractometer, and the NaCl was a remnant of the $FeCl_3 + NaOH$ reaction. When the temperature reached $600\,°C$, Fe_2O_3 was detected, as a result of pyrogenation of colloidal $Fe(OH)_3$. When the treatment temperature was $800\,°C$, the Fe_2O_3 disappeared from the final reaction products. The XRD results on the $800\,°C$ specimen demonstrated the presence of amorphous carbon, α-Fe and NaCl in the final reaction products, while the (002) peak of the CNTs disappeared. The above results indicated that the α-Fe was the product of a deoxidization reaction of Fe_2O_3 + carbon. When the treatment temperature was $1000\,°C$, the XRD patterns indicated that NaCl, n-diamond and α-Fe exist in
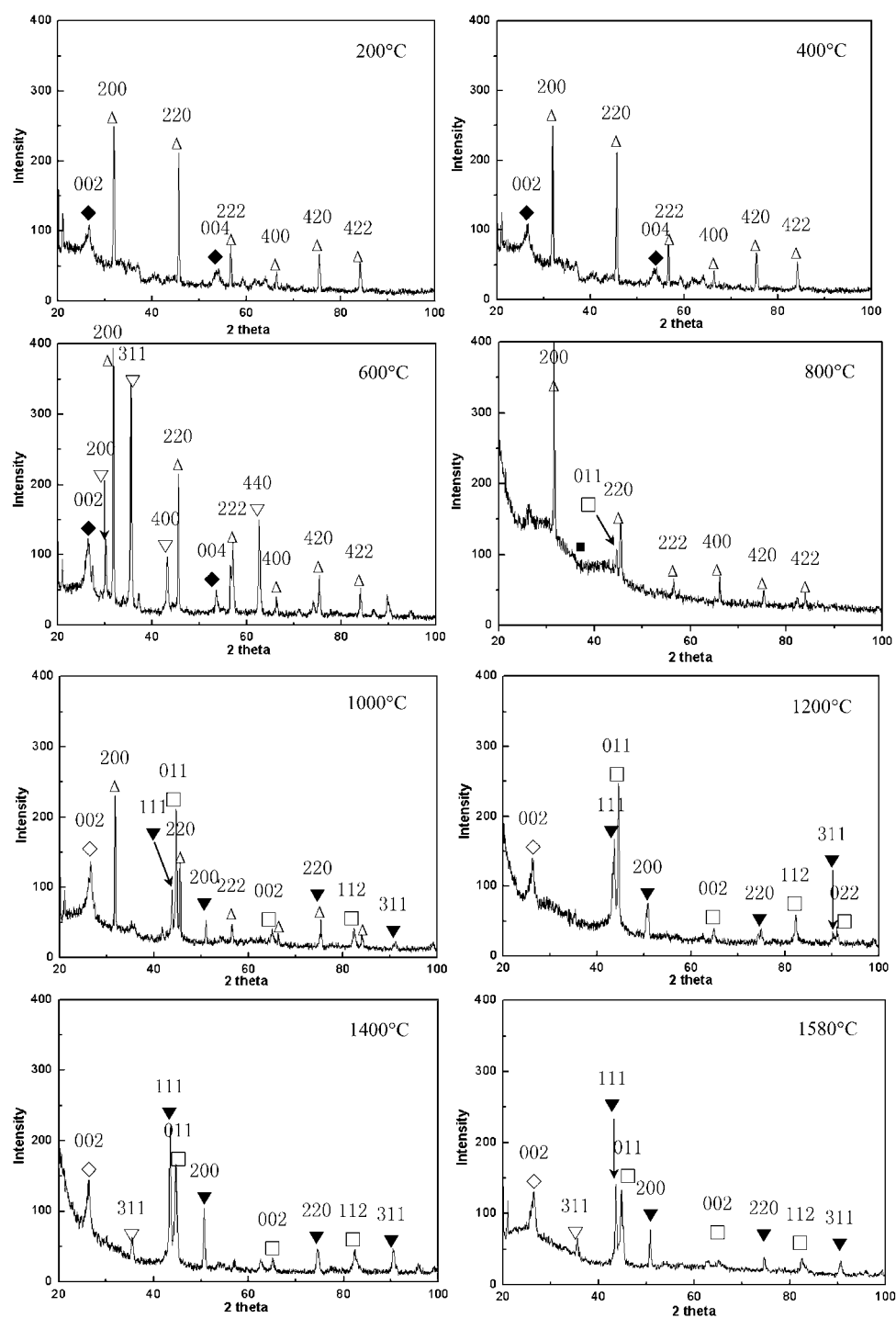
Figure 1. X-ray diffraction pattern following sample heat treatment at various temperatures; ◆, carbon nanotubes; ▼, n-diamond; ◇, graphite; □, α-Fe; △, NaCl; ▽, Fe_2O_3.
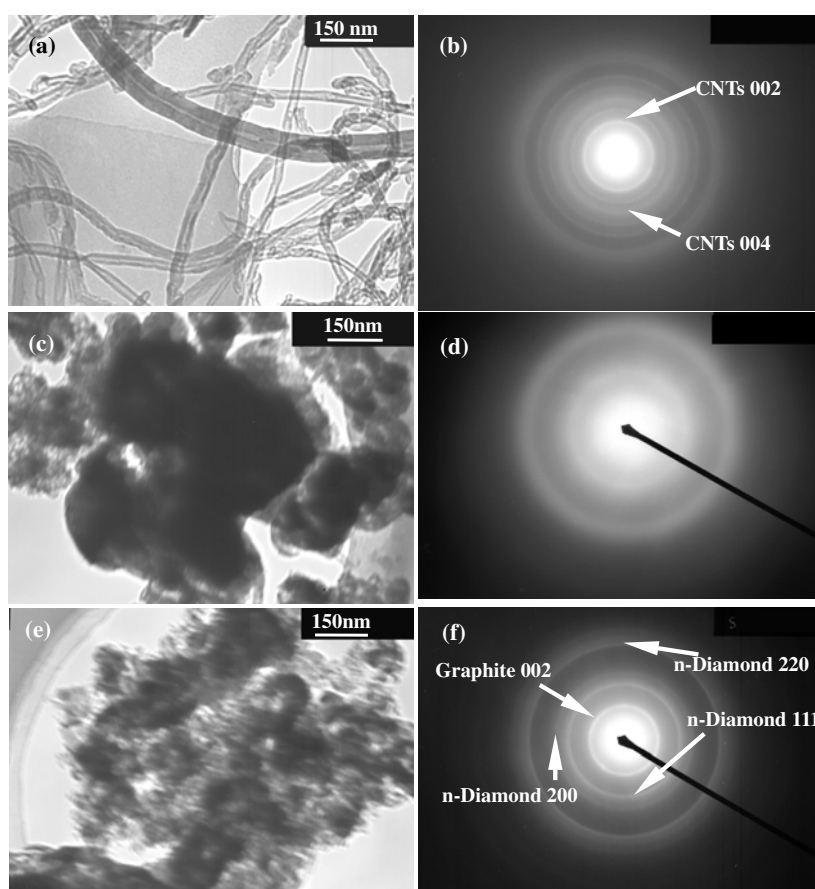
Figure 2. Bright-field TEM images ((a), (c), (e)) and the corresponding SAED patterns ((b), (d), (f)) of final products that have been heat treated at various temperatures: ((a), (b)), 200 °C; ((c), (d)), 800 °C; ((e), (f)) 1580 °C.

the final reaction products. With increasing treatment temperature, the peaks of the n-diamond increased in intensity. As the treatment temperature reached 1400 °C, the peak intensity of n-diamond achieved its maximal value. The yield of n-diamond at 1400 °C was estimated as about 20% from the integral area of the XRD peaks of n-diamond. On the other hand, the presence of graphite-like carbon in the final reaction products was proved by the XRD patterns when the treatment temperature was above 1000 °C. When the treatment temperature was above 1200 °C, no NaCl was found in the final reaction products, owing to its evaporation. When the treatment temperature was above 1400 °C, Fe_2O_3 was found in the final powder, as a result of oxygenation of Fe.

To further clarify the morphology of the amorphous carbon and graphite-like carbon, TEM was used to characterize the sample. Figure 2 shows the TEM picture of the final products that have been heat treated at various temperatures. For the products with 200 °C treatment temperature, the bright image (figure 2(a)) and corresponding electron diffraction (figure 2(b)) show that the final product consists of CNTs. A bright-field image of the final powder that has been heat treated at 800 °C is shown in figure 2(c); it indicates that the CNTs had decomposed into nanoparticles. The corresponding electron diffraction pattern (figure 2(d)) of the nanoparticles shows two broad rings, typical characteristics for amorphous carbon. When
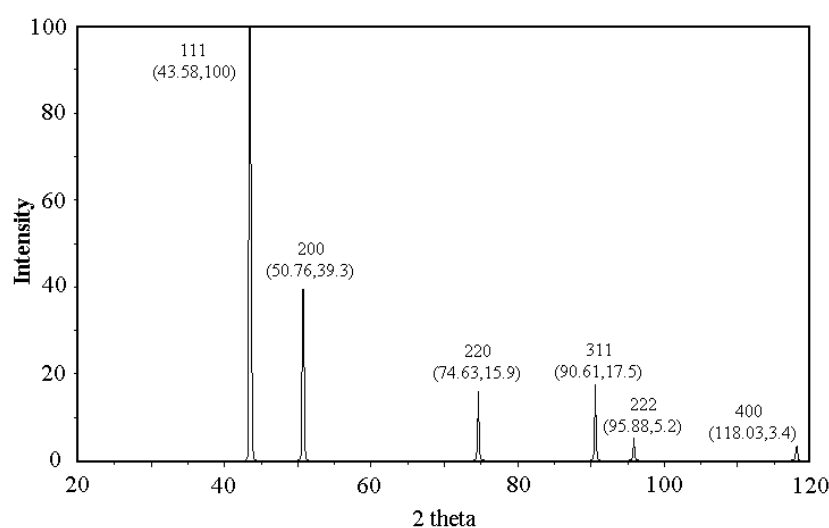
Figure 3. Simulated x-ray diffraction pattern of the fcc carbon with the lattice parameter $a = 0.3594$ nm.

Table 1. The XRD reflection intensities of the n-diamond. d_{obs}: the spacing of XRD reflections observed in the experiment; I/I_{111}: the intensity ratio of each reflection peak with respect to the (111) peak; d_{cal}: the spacing of XRD reflections calculated from simulation.

	Experiment		Simulation	
hkl	d_{obs}	I/I_{111}	d_{cal}	I/I_{111}
111	2.068	100	2.075	100
200	1.792	39.8	1.797	39.3
220	1.267	18.3	1.271	15.9
311	1.081	16.5	1.084	17.5

the heat treatment temperature reaches 1580 °C, the bright image and corresponding electron diffraction of the sample shown in figures 2(e) and (f) respectively indicate that the CNTs transform into nanocrystal graphite and n-diamond.

In order to validate the previously proposed crystal structure of n-diamond, CELREF[5] and CaRIne Crystallography 3.1[6] were employed to analyse the XRD patterns observed experimentally in this work. CELREF analysis indicates that the four stronger peaks of n-diamond at 43.57°, 50.765°, 74.69° and 90.77° can appear for fcc structure crystal with the lattice parameter $a = 0.3594$ nm. This result is very close to those in [3] and [4]. Indeed, the peaks at 43.57°, 50.765°, 74.69° and 90.77° come from the 111, 200, 220 and 311 reflections in the fcc structure crystal. To further investigate the structure of n-diamond, an XRD pattern of fcc carbon with the lattice parameter $a = 0.3594$ nm was simulated using the CaRIne Crystallography 3.1 program. The XRD patterns obtained from our simulation are shown in figure 3. In table 1, the simulated intensities for each characteristic peak associated with

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[5] CELREF is a crystal cell parameter refinement program for application to powder x-ray or neutron diagrams, using a least squares refinement method.

[6] The CaRIne Crystallography 3.1 program comes from the crystallographic software for research and teaching distributed by C Boudias and D Monceau.

n-diamond are summarized and compared with the observed intensities; the simulated results agree quantitatively with the experimental data. In addition, the admixture is composed of C, H, O, Na, Cl and Fe elements, and there are no elements to enlarge the austenitic (γ-Fe, fcc crystal structure with lattice parameter $a = 0.36$ nm) region [33]. Estimated from the integral area of the XRD peaks of α-Fe, the content of α-Fe in the final powder is about 10 wt%, which is the same as the initial quantity of iron in our experiment. The coincidence basically excludes the formation of iron carbide in the final sample and indicates that the Fe element in the final powder exists as α-Fe. Furthermore, the n-diamond is characterized by its (200) peak which is absent for normal diamond, and its lattice constant is 0.3594 nm, which falls close to the reported values[7]. On the basis of the above analysis, n-diamond can be considered as fcc carbon with the lattice parameter $a = 0.3594$ nm, instead of γ-Fe with fcc crystal structure and a 0.36 nm lattice parameter. However, first-principles calculations on fcc carbon crystal led to some controversies regarding the crystal structure of n-diamond [34–38]. For example, according to the calculations by Pickard *et al* [34], if a carbon allotrope with fcc crystal structure exists, the equilibrium lattice parameter would be about 3.08 Å, i.e. quite different from that of diamond and the observed lattice parameter for n-diamond [2]. To evaluate the structural stability of carbon fcc crystal, Murrieta *et al* [35] computed the total energy as a function of the isotropic, tetragonal and trigonal deformation and found that the carbon fcc structure with the lattice parameter of 3.57 Å is not a true local minimum on the potential energy surface. It was suspected that the interaction between n-diamond and the substrate as well as the impurities inside n-diamond crystals contribute to the temporary stability of n-diamond [35]. Therefore, the true crystal structure of n-diamond is still a confused question, and work is still needed.

To summarize, we have examined the synthesis of n-diamond nanopowders via the route of an Fe-catalysed process from CNTs at atmospheric pressure, on the basis of the XRD and TEM results. The final products following heat treatment at different temperatures (from 200 to 1580 °C) have been analysed. The maximal yield of n-diamond (about 20%) can be realized at a treatment temperature of 1400 °C. The crystal structure of the n-diamond was studied by analysis of the experimental XRD patterns and CaRIne Crystallography simulation. However, the details of the crystal structure and mechanism of formation of n-diamond from carbon nanotubes still need more comprehensive investigation and will be the subject of our future work.

References

[1] Prawer S, Peng J L, Orwa J O, McCallum J C, Jamieson D N and Bursill L A 2000 *Phys. Rev.* B **62** R16360
[2] Hirai H and Kondo K I 1991 *Science* **253** 772
[3] Konyashin I, Zern A, Mayer J, Aldinger F, Babaev V, Khvostov V and Guseva M 2001 *Diamond Relat. Mater.* **10** 99
[4] Jarkov S M, Titarenko Ya N and Churilov G N 1998 *Carbon* **36** 595
[5] Amaratunga G, Putnis A, Clay K and Milne W 1989 *Appl. Phys. Lett.* **55** 634
[6] Frenklach M, Kematick R, Huang D, Howard W and Spear K E 1989 *J. Appl. Phys.* **66** 395
[7] Yoo C S, Nellis W J, Sattler M L and Musket R G 1992 *Appl. Phys. Lett.* **61** 273
[8] Endo S, Idani N, Oshima R, Takano K J and Wakatsuko M 1994 *Phys. Rev.* B **49** 22
[9] Orwa J O, Prawer S, Jamieson D N, Peng J L, McCallum J C, Nugent K W, Li Y J, Bursill L A and Withrow S P 2001 *J. Appl. Phys.* **90** 3007
[10] Peng J L, Bursill L A, Jiang B, Orwa J O and Prawer S 2001 *Phil. Mag.* B **81** 2071

[7] See the supplementary x-ray data (Joint Committee on Powder Diffraction Standards (JCPDS) 43-1104).

[11] Peng J L, Orwa J O, Jiang B, Prawer S and Bursill L A 2001 *Int. J. Mod. Phys.* B **15** 3107
[12] Wen B, Li T, Dong C, Zhang X, Yao S, Cao Z, Wang D, Ji S and Jin J 2003 *J. Phys.: Condens. Matter* **15** 8049
[13] Wen B, Li T, Dong C, Zhang X, Yao S, Cao Z, Wang D, Ji S and Jin J 2004 *J. Phys.: Condens. Matter* **16** 2991
[14] Wen B, Li T, Dong C, Zhang X, Yao S, Cao Z, Wang D, Ji S and Jin J 2004 *J. Phys.: Condens. Matter* **16** 6891
[15] Doherty S P, Buchholz D B, Li B J and Chang R P H 2003 *J. Mater. Res.* **18** 941
[16] Buchholz D B, Doherty S P and Chang R P H 2003 *Carbon* **41** 1625
[17] Kroto H W, Heath J R, O'Brien S C, Curl R F and Smalley R E 1985 *Nature* **318** 162
[18] Cataldo F 2002 *Carbon* **40** 157
[19] Berezkin V I, Kholodkevich S V and Konstantinov P P 1997 *Phys. Solid State* **39** 1590
[20] Berezkin V I 2000 *Phys. Solid State* **42** 580
[21] Berezkin V I 2001 *Phys. Solid State* **43** 967
[22] Donnet J B, Johnson M P, Norman D T and Wang T K 2000 *Carbon* **38** 1885
[23] Kholodkevich S V, Berezkin V I and Davydov V Yu 1999 *Phys. Solid State* **41** 1291
[24] Papirer E, Brendle E, Ozil F and Balard H 1999 *Carbon* **37** 1265
[25] Krishnan A, Dujardin E, Treacy M M J, Hugdahl J, Lynum S and Ebbesen T W 1997 *Nature* **388** 451
[26] Howard J B, Chowdhury K D and Sande J B V 1994 *Nature* **370** 603
[27] Howard J B, Mckinnon J T, Makarovsky Y, Lafleur A L and Johnson M E 1991 *Nature* **352** 139
[28] Lijima S 1991 *Nature* **354** 56
[29] Lijima S, Ichihashi T and Ando Y 1992 *Nature* **356** 776
[30] Lijima S, Ajayan P M and Ichihashi T 1992 *Phys. Rev. Lett.* **69** 3100
[31] Popov V N 2004 *Mater. Sci. Eng.* R **43** 61
[32] Jose-Yacaman M, Miki-Yoshida M, Rendon L and Santiesteban J G 1993 *Appl. Phys. Lett.* **62** 202
[33] Christian J W 1965 *The Theory of Transformations in Metals and Alloys* (Oxford: Pergamon) p 678
[34] Pickard C J, Milman V and Winkler B 2001 *Diamond Relat. Mater.* **10** 2225
[35] Murrieta G, Tapia A and de Coss R 2004 *Carbon* **42** 771
[36] Yin M T and Cohen M L 1983 *Phys. Rev. Lett.* **50** 2006
[37] Mailhiot C and McMahan A K 1991 *Phys. Rev.* B **44** 11578
[38] Broughton J Q and Mehl M J 1999 *Phys. Rev.* B **59** 9259