# Behavior of carbon nanotubes under high pressure and high temperature

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The structural changes of carbon nanotubes induced by high pressure and high temperature were investigated by means of x-ray diffraction, Raman scattering, scanning electron microscopy, and transmission electron microscopy. It is shown that, with increasing pressure and temperature, the lattice constant  $d_{002}$  of tubes shortens, and then tubes collapse into tapelike ones; at the same time the C–C bonds at high curvature break, which lead the tapelike tubes to break into graphite sheets as diamond crystallization centers. Compared with graphite, the diamond particles from carbon nanotubes have many defects as the trace of tubes.

### I. INTRODUCTION

Since their discovery in 1991,<sup>1</sup> carbon nanotubes have attracted more and more interest for their unique morphology and exceptionally physical and chemical properties.<sup>2–6</sup> Theoretical studies of carbon nanotubes suggest that their properties depend sensitively on their morphology and structure.<sup>7–9</sup> Therefore high pressure, which can vary the interatomic distance of substance and thus change its phase transition, was employed as an important probe of the relation between the structure and the property of carbon nanotubes. On the basis of graphite, the transformation from carbon nanotubes to diamond under high pressure and high temperature was realized already,<sup>10,11</sup> but the behavior of carbon nanotubes under high pressure and high temperature is not clear yet even though much experimental work has been done in this aspect. For example, Zhou et al.<sup>12</sup> studied defects in carbon nanotubes through the average radial compressibility calculated from the pressure-induced shift in  $d_{002}$ . Zhang et al.<sup>13</sup> investigated the thermal stability of carbon nanotubes under 5.5 GPa. Zhu et al.<sup>14</sup> investigated the structural change of carbon nanotubes under shock waves. In this paper, we investigate the behavior of carbon nanotubes under high pressure (up to 7.0 GPa) and high temperature (up to 1800 °C) by means of x-ray diffraction, Raman scattering, scanning electron microscopy, and transmission electron microscopy. The structural change of the sample induced by high pressure and

high temperature reveals that the tubes first become tapes and then graphitelike sheets as nuclei of diamond growing into diamond particles.

#### **II. EXPERIMENTAL**

In our experiments, multiwalled carbon nanotubes, loosely entangled and most highly graphitized, were prepared by modified arc discharge.<sup>15</sup> The subsequent purification by the oxidizing process made the carbon nanotubes free of contaminating nanoparticles and amorphous carbon [Fig. 3(a)]. The high pressure was created by a 600-ton oil pressure machine, and the pressuretransmitting medium was pyrophyllite. The samples were indirectly heated by the electrical current through a graphite furnace. As insulator, two BN sample cells (4-mm diameter) were put into the graphite furnace. In one of the BN sample cell carbon nanotubes (about 10 mg) were loaded, and in the other BN sample cell graphite sample was loaded for comparing. The two samples were covered with a piece of nickel-base alloy as catalyst. After that, the sample was heated for several seconds at the desired temperature under a certain pressure, and then temperature was decreased and pressure released to ambience in 1 min. The structural changes were characterized by x-ray diffraction, Raman scattering, scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

#### **III. RESULTS AND DISCUSSION**

The x-ray diffraction spectra of the pristine material (purified carbon nanotubes) [Fig. 1(a)] and the samples under the different pressure and temperature [Figs. 1(b)

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and 1(c)] were performed on D/Max-2400 with Cu  $K_{\alpha}$ radiation. Compared with the x-ray diffraction spectra of the pristine material [Fig. 1(a)], the (002) peak and the other three peaks [Fig. 1(b)] are broader and more symmetric in the case of the sample after the treatment at 6.0 GPa and 1600 °C for 7 s. This change indicates that some irreversible processes took place in this sample and might be attributed to the smaller diameters and enhanced interlayer interaction as well as pressure-induced defects of carbon nanotubes after being treated at 6.0 GPa and 1600 °C. Judged from Fig. 1(c), the samples treated at 7.0 GPa and 1800 °C for 7 s were mainly transformed to diamond. At the same time, we found that most of the graphite in the same furnace of 7.0 GPa and 1800 °C has also been transformed into diamond but the graphite in the furnace of 6.0 GPa and 1600 °C was not transformed.

As shown in Fig. 2(a), Raman spectra of the purified carbon nanotubes are characterized by a strong band at approximately  $1580 \text{ cm}^{-1}$  (G line) and a very weak band at approximately  $1350 \text{ cm}^{-1}$  (D line), which is similar to data previously reported.<sup>16</sup> The sample after the treatment of 6.0 GPa and 1600 °C gives a slightly stronger D line in its spectra, which represented more defects in this sample.<sup>17</sup> Figure 2(c) shows that there is only a strong D line (1332 cm<sup>-1</sup>) without the G line, which gives the same conclusion as that from x-ray diffraction.

To investigate the structural change of carbon nanotubes in more detail, SEM and TEM observations of the samples taken after the treatment under different pressures and temperatures are performed. Figure 3(a) shows the SEM image of purified carbon nanotubes, which are free of nanoparticles and amorphous carbon and have remarkably uniform diameters (about 20 nm). The SEM images of the sample after the treatment at 6.0 GPa and 1600 °C indicate that carbon nanotubes were broken and



FIG. 1. X-ray diffraction spectra of (a) purified carbon nanotubes and carbon nanotubes treated (b) at 6.0 GPa and 1600  $^\circ$ C and (c) at 7.0 GPa and 1800  $^\circ$ C.



FIG. 2. Raman spectra of (a) purified carbon nanotubes and carbon nanotubes treated (b) at 6.0 GPa and 1600  $^\circ$ C and (c) at 7.0 GPa and 1800  $^\circ$ C.





(b)

FIG. 3. (a) SEM image of purified carbon nanotubes and (b) SEM image of the sample treated at 6.0 GPa and 1600  $^{\circ}$ C.

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compacted, but the tubelike structure of most carbon nanotubes was kept down in spite of the accumulation of some graphitelike materials on their surfaces [Fig. 3(b)]. Figure 4(a) is the TEM image of a carbon nanotube before the high-pressure treatment, which is free of defects and highly graphitized with uniform innermost diameter. The TEM image [Fig. 4(b)] of a tube in this sample (at 6.0 GPa and 1600 °C) shows that the layer-structure of the tip, external surface, and inner surface was badly destroyed. From the TEM image of another tube in this sample [Fig. 4(c)], we found that the innermost diameter decreased markedly in some places, which indicates that the tube become a tapelike one, and the bent sections, as well as the tips, are more labile under high pressure and high temperature. We believe that the atoms at these sections with high curvature (tips, interior surfaces, and bend sections) and external faces have much higher energy and the C-C bonds are much more easily broken, especially under high pressure and high temperature.

Though both carbon nanotubes and graphite can be transformed to diamond under 7.0 GPa at 1800 °C, the products have different morphologies and structures. The



FIG. 4. TEM image of carbon nanotubes (a) before the pressure treatment and (b, c) after treated at 6.0 GPa and 1600 °C. In (b) the layer structures of the tip, external surface, and inner surface were badly destroyed. In (c) the decreased innermost diameter indicates that the tube becomes a tapelike one.

SEM image of the carbon nanotubes after the treatment at 7.0 GPa and 1800 °C [Fig. 5(a)] shows that besides diamond particles there are many graphitelike sheets in this sample. To get rid of catalysts and unconverted carbon the samples were etched with aqua regia (HCl and HNO<sub>3</sub> with the volume rate of 3:1) and HClO<sub>4</sub>. Figure 5(b) shows the morphology and structure of diamond transformed from carbon nanotubes, from which we can see that diamond particles do not have as fine a crystal form as that from graphite in the same graphite furnace. In addition, the crystal faces of the diamond particles from carbon nanotubes have many defects as the trace of tubes, which can be considered as the agglomeration of the tapelike diamond. So, these diamond particles with defects should be much softer which was confirmed in our experiments.

## **IV. CONCLUSIONS**

In summary, with increasing pressure and temperature, the interlayer interaction was enhanced, which corresponds to the lattice constant  $d_{002}$  to be shortened. On the





FIG. 5. (a) The SEM image of the rupture face of the sample after the treatment at 7.0 GPa and 1800 °C and (b) the SEM image of this sample after being treated with aqua regia and HClO<sub>4</sub>.

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other hand, high pressure also induced the stress accumulation at the interior face and at the region with high curvature. When the pressure is beyond elastic region, the plastic deformation of the tubes made the tubes become ellipsoidal and at last they collapsed into the tapelike ones. At the same time, the C-C bonds at high curvature and external surface were broken first, for example, at the edge of the sheets; the tapelike sheets collapsed from carbon nanotubes into small graphitelike sheets, and then transformed into diamond, keeping the forms before transformation. It was worth noticing that the carbon nanotubes are not a better carbon source for getting diamond than graphite, no matter how much the  $sp^{2+\delta}$  bond structure in the carbon nanotubes is closer to the  $sp^3$  of diamond than graphite  $(sp^2)$ . In fact the interlayer interaction and intertube interaction are much weaker than that of the interlayer in graphite with its tubular structure, which might be responsible for the distinct behavior of carbon nanotubes and graphite.

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