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# Ultra-high crystallinity millimeter long multiwall carbon nanotubes fabricated by mechanothermal method

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In this work, multi-walled carbon nanotubes (MWCNTs) with ultra-high crystalline structure have been prepared by mechanothermal (MT) method. The novel super nanostructure is introduced for the first time as an extraordinary fullerene-carbon based material which, due to its special electronic and mechanical properties, can be used to construct unique building blocks for nanoengineering. Initially, high ultra-active graphite powder has been obtained by mechanical activation under Ar atmosphere. Finally, the mechanically activated product is heat-treated at 1350 °C for 3 – 4 h under an Ar gas flow. However, the crystallite size and crystallinity degree of the MWCNTs increased with the increase in annealing temperature.

Keywords: *carbon nanotube, reinforcement, crystallinity, mechanothermal method, HRTEM*



## 1. Introduction

The finding that carbon nanotubes possess diameter- and helicity dependent properties has made this new form of solid carbon one of the most widely studied nanomaterials for a wide range of potential applications [1]. In many cases, it is highly desirable to produce aligned carbon nanotubes so that they could be effectively incorporated into devices and the properties of individual nanotubes maight be readily assessed [2]. Therefore, research on the synthesis of aligned carbon nanotubes has attracted ever-increasing attention since the discovery of carbon nanotubes by Iijima in 1991 [2, 3]. On the other hand, the multiwall carbon nanotubes (MWCNTs) [3], because of their robust structure and flexible atomic conformation, seem to be of great technological importance for many applications; MWCNTs especially have excellent properties as carriers of functionalized molecules [4, 5] field electron emitters [6] conductive wires [7] and bearers of rotational motors [8] etc. Both theoretical predictions [7–12] and experimental results [13–17] suggest that MWCNTs have exotic electronic structures and intriguing transport properties, which are highly dependent on tube chirality. Although various methods have been developed to prepare carbon nanotubes, it is still a challenge to get the high crystalline MWCNTs with limited atomic conformation and obtain the MWCNTs with identical chiralities. More recently, we have suggested that using washable supported catalysts may offer valuable advantages and an extraordinary structure [18, 19]. Herein, we use an efficient method for the controlled synthesis of ultra-high-crystallinity, millimeter long, multiwall carbon nanotubes by mechanical activation assisted with a suitable heat-treatment route.

## 2. Experimental

Elemental graphite flakes (99.9 %<100 μm) with a purity of 99.8 % were mechanically ground in a purified argon atmosphere. Four grams of the powder with ten steel balls of 15 mm diameter were used in the mechanical activation (MA) process. The ball-to-powder weight ratio was kept at 20:1. The mechanical activation was carried out

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at ambient temperature and at a rotational speed (cup speed) of 700 rpm in a planetary ball mill.

The mechanical activation (MA) process was interrupted to take out a small amount of mechanically activated powder to study the changes in the microstructure at different milling durations. The vial containing the powders and the ball were evacuated by a rotary-pump and then back-filled with a pure argon gas (99.99 %) in a glove box. The final gas pressure in the vial was kept at the level of 0.1 MPa. After completed amorphization, the highly chemically active carbon powders were annealed at different temperatures to investigate the formation of multi-walled carbon nanotubes. The crystal phase was determined with powder X-ray diffraction. For these experiments, a Siemens diffractometer (30 kV and 25 mA) with the $K_\alpha 1$, radiation of copper ($\lambda$ = 1.5406 Å), was used. The characterization of the structure of the powder samples was performed by using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (SEM/EDX, XL30), field emission transmission electron microscopy and selected area electron diffraction (FETEM/SAED, Philips CM200 transmission electron microscopy operated at 200 kV). The Raman spectra were taken at room temperature under ambient conditions using an Almega Raman spectrometer with $Ar^+$ at an excitation wavelength of 514.5 nm.

## 3. Results and discussion

XRD patterns of graphite powder, mechanically mixed in argon atmosphere for several activation times, are shown in Fig. 1. Further milling (after 150 h MA) caused no change in the XRD patterns except the broadening of the peaks. So, this broadening can be attributed to the decrease of grain size and increasing strain in the lattice. In general, we can conclude that this method is very successful for producing amorphous graphite powders.

The constitution of the starting powder corresponds to the elemental graphite powder. The diffraction intensities drastically decreased after mechanical activation (MA). The diffraction peaks

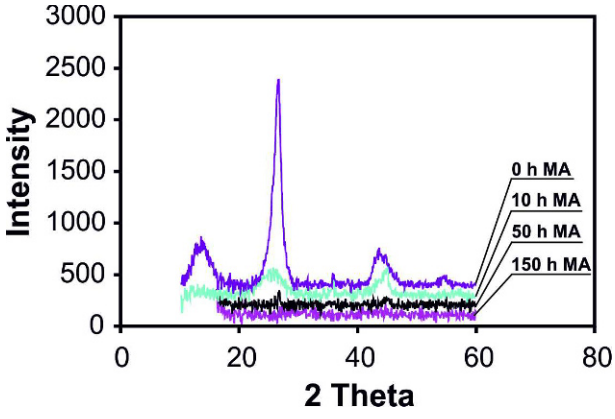



Fig. 1. The X-ray diffraction spectra of mechanically alloyed graphite powders at different milling times with 2 theta angle ranging from 10 to 60°.

corresponding to the graphite (particularly the peak at about $2\theta = 26.6°$) almost disappeared after an activating time of 10 h.

As the milling time increases, the intensities of the peaks of graphite decrease and become unidentifiable. Finally, the formation of amorphous-like particles has been strongly enhanced in the argon atmosphere after an activating time of 150 h.

The nanoparticle size of the carbon milled product was analyzed using a zeta-sizer method. These measurements revealed a wide distribution of the particles sizes (Fig. 2). The milled graphite powders contained the particles with the diameters grouped in two ranges: 7 – 100 nm and 100 – 400 nm.

Fig. 3 shows the transmission electron micrograph (Fig. 3a) and selected area electron diffraction pattern (Fig. 3b) of graphite nanostructures synthesized according to the method described above. It is readily observed that the nanostructures are in a high ultra-fine dispersion and the average crystalline size is 10 nm. The electron diffraction (ED) pattern of the carbon nanotubes (Fig. 3b) exhibits two very weak diffuse rings, indicating highly disordered wall in the milled graphite. On the other hand, the electron diffraction pattern reveals that the carbon nanostructures have an amorphous structure. At the same time, this result is consistent with the

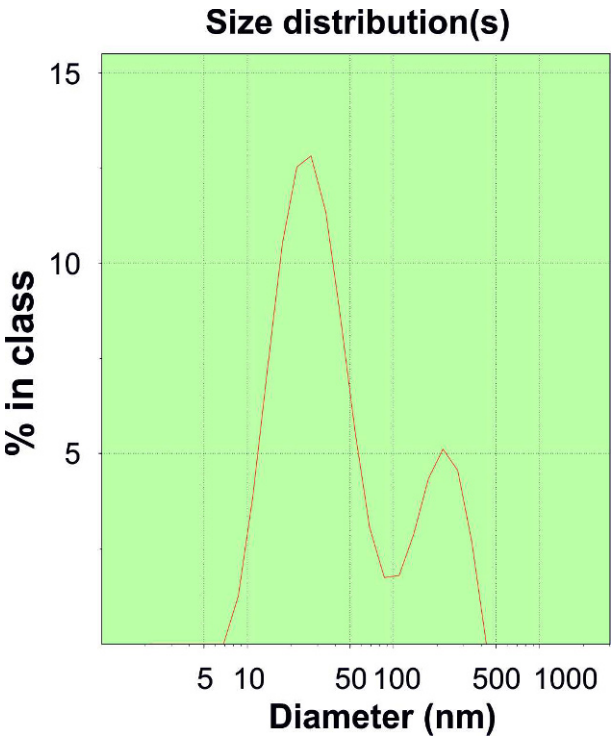
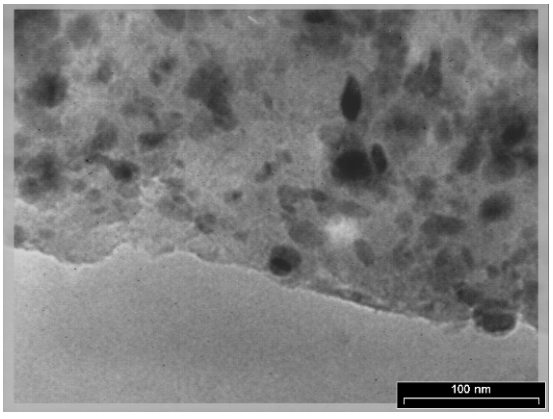
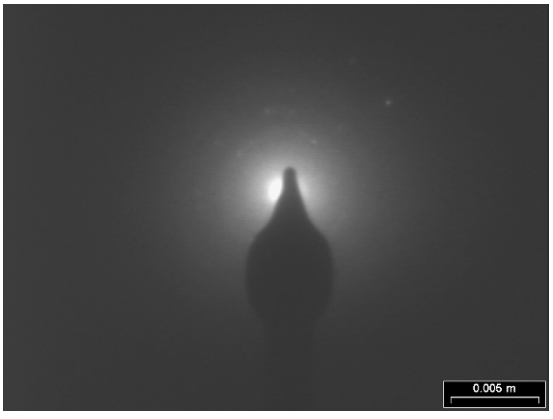



Fig. 2. The nanoparticle sizes of milled carbon measured by zeta-sizer.




(a)

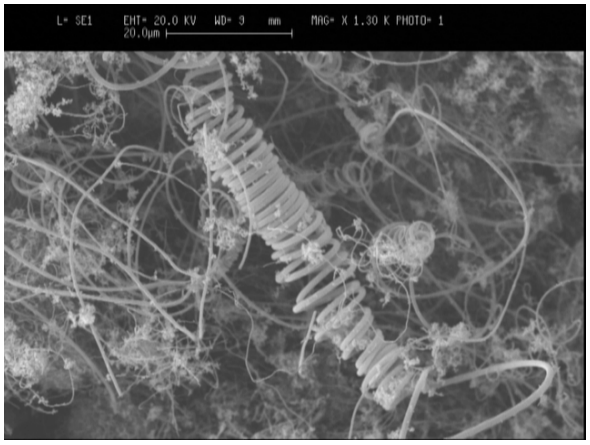



(b)

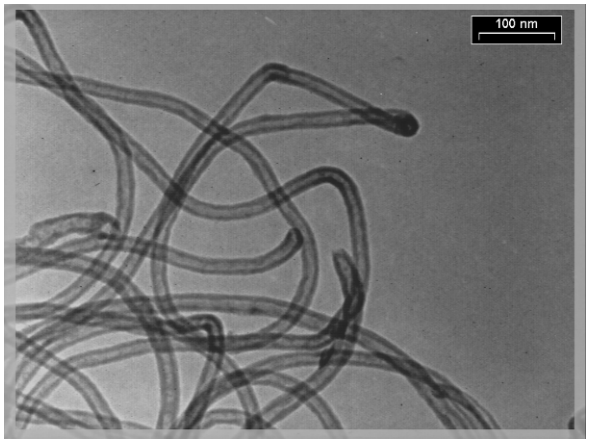
Fig. 3. a) TEM image of graphite powders, b) selected area electron diffraction (SAED) obtained by mechanical activation.

X-ray diffraction (XRD) pattern. We believe that the very small size and the amorphous structure are due to the high energy ball milling of the graphite powders activated by planetary mill. Jiang and Chen [20] recently developed a thermodynamic quantitative model to describe the phase transitions of nanocarbon as a function of its size and temperature, through systematically considering the effects of surface stresses and surface energies. The fine nanosize amorphous structure of pure carbon nanostructures is thermodynamically unstable, owing to the high amount of free energy.

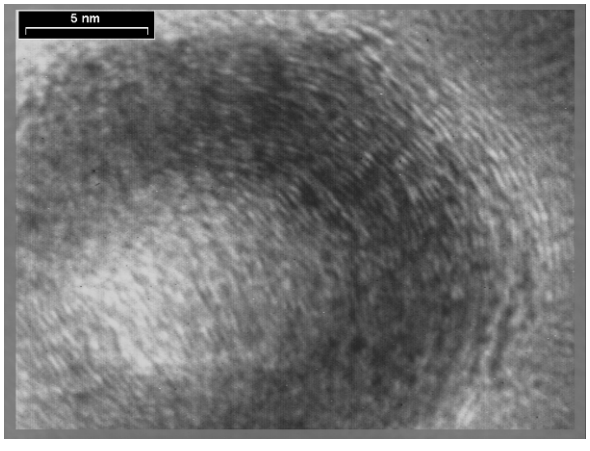
Fig. 4a shows a scanning electron microscopy (SEM) image of the as-synthesized MWCNT obtained by mechanothermal method, which displays the nanotubes with excellent uniformity. The as-synthesized MWCNT sample shows an outstanding morphology, high ordered nanotube structure and high aspect ratio (length/diameter $\approx 10^5$). The high resolution TEM (HRTEM) was used to characterize the MWCNTs. Fig. 4b clearly shows that the product consists of peculiar nanostructures, $30 \pm 10$ nm in diameter and several millimeters in length. The yield of the prepared MWCNTs, estimated by TEM observations, is about 90 % of the yield obtained for the samples on copper grids, while the particles size is in the range of 20 – 30 nm. Thus, high efficiency of the synthesis of MWCNTs with an ultrahigh crystallinity and a better yield than in the previous research can be concluded [20]. In further investigation, the MWCNTs were analyzed by HRTEM in detail, and all nanostructures showed uniform lattice fringes, which could mean that no amorphous product was formed. Fig. 4c shows a HRTEM image of a single CNT with an uniform structure and ultra-high crystallinity. The values of interplanar spacings were calculated from Bragg's




(a)




(b)




(c)

Fig. 4. Images of graphite powders mechanically activated for 150 h after annealing at 1350 °C for 3-4 h, a) SEM, b) TEM and c) high resolution TEM.

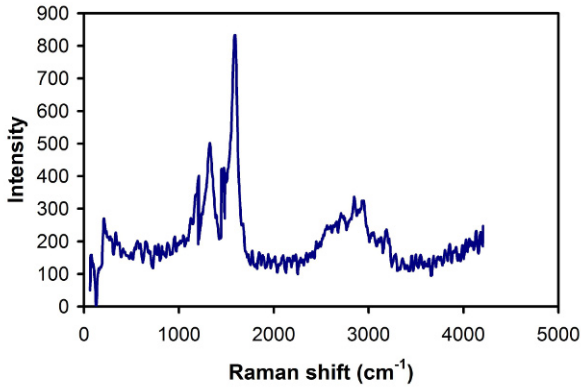



Fig. 5. Raman spectra of the MWCNTs obtained by mechanical activation.

diffraction equation using the diffraction ring diameter and the camera length of the transmission electron microscopy. The interlayer spacing in the walls, about 0.34 nm, corresponds to the (002) interplanar distance of graphitic carbon.

Finally, the Raman spectrum of the prepared sample was also investigated. In the high frequency region the difference in the intensity of the D band (at 1340 $cm^{-1}$) and the G band (close to 1586 $cm^{-1}$) can be noted. The G band indicates original graphite features but the D band is probably associated with disorder features of graphitic sheets. This indicates the ratio of ordered graphite formed during this fabrication process (Fig. 5).

## 4. Conclusion

We have presented a simple method for producing high-yield MWCNTs under mechanothermal conditions. Elemental graphite powder was milled in a planetary ball mill at atmospheric pressure and room temperature. Finally, after annealing at 1350 °C, we obtained high-yield MWCNTs. This method also presents a facile route to high-yield MWCNTs without complex purification processes. The yield and good quality of MWCNTs obtained by the mechanothermal method seem to be very promising for the production of multiwall carbon nanotubes or other graphitic nanocarbons. Indeed,

because of the simplicity and high yield of this route, it may potentially be applied on the industrial scale.

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