Structural improvement of CVD multi-walled carbon nanotubes by a rapid annealing process

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A B S T R A C T

Generally, due to structural disorders in multi-walled carbon nanotubes (MWCNTs) synthesized by chemical vapor deposition (CVD), most of their properties are much below the expected values. A novel technique has been developed in this investigation for structural improvement of CVD MWCNTs using a rapid annealing process. Direct observation by transmission electron microscope (TEM) indicates obvious structural changes in the nanotubes after a rapid annealing process between 2000 °C and 2800 °C, while nanotubes with twisty shells and kinked walls have been observed as the annealing temperature approaches 3000 °C. Decrease of ID/IG ratio in Raman spectra, increase of the starting oxidation temperature observed in Thermogravimetric analysis (TGA), as well as increase in electrical conductivity of nanotube powders suggests the reconstruction toward more ordered nanotube structure after a rapid high temperature annealing process.

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1. Introduction

Carbon nanotubes have emerged as an extraordinary material in the past two decades due to their unique structure and outstanding properties [1,2]. Carbon nanotubes as a nanomaterial is very promising for a variety of potential applications, such as high strength materials [3], conductive composites [4,5], nanoscale semiconductor devices [6,7], energy storage devices and sensors [8–11].

Due to large scale production of high purity, and low cost CVD MWCNTs, this nanomaterial is now quite affordable and available for large volume commercial applications. However, it is well known that CVD MWCNTs have very disordered structures and a high content of defects including vacancies, dangling bonds, edges and dislocations, as a result of the idiosyncrasy of CVD conditions at temperatures below −1000 °C [12]. Defects within the structure of MWCNTs may significantly induce the increase in electrical resistivity [13,14]. Residual metal catalyst particles in MWCNTs affect not only the electrical, thermal and mechanical properties, these residual particles can even induce toxicity in CNTs. High temperature annealing method has been reported to alter the nanotube structural order to improve CNT properties and purify the carbon content of CNTs using rather complicated high vacuum and air-proof furnaces [15–20]. For example, S. Musso et al. used high temperature to anneal the aligned MWCNTs to improve their mechanical properties [15]. R. Jin et al. revealed the electrical and thermal transport properties of macroscopic bundles of long MWCNTs, which were significantly enhanced after high-temperature annealing treatment [16]. S.C. Ray et al. enhanced the field emission properties of carbon nanotubes after annealing process [17]. However, drawbacks in these high temperature annealing methods include excessive energy consumption to raise the furnace temperature and excessive time conducting heat to the annealing sample.

Raman spectroscopy is well regarded as a powerful structural analytical tool to characterize the graphitization or structural ordering of carbon nanotubes [21–25]. There are three characteristic bands in the Raman spectra of carbon nanotubes: the radial breathing modes (RBM) (100–400 cm⁻¹), the D mode (~1350 cm⁻¹) and the tangential stretching G mode (1500–1600 cm⁻¹), which are sensitive to the structural changes in CVD MWCNTs [21–23]. The RBM Raman feature associated with small-diameter nanotubes is normally too weak to be observed for large-diameter MWCNTs [22]. The D-band observed in the Raman spectra can be attributed to nanocrystalline and disordered graphite, amorphous carbon, and defective or damaged nanotube structures [22,23]. The G-band is related to the tangential mode vibrations of the C atoms, including intramolecular vibration between C atoms and the tangential in-place stretching of C=C bonds in graphite sheets [19,22]. The intensity ratio of ID/IG is usually used as diagnostic characteristic for determining the structural perfection of MWCNTs, which has been widely used as a structural parameter for evaluating the degree of graphitized structure content of CNTs as well as a disorder parameter for carbon materials [22,24,25]. As the value of ID/IG becomes larger, the CNT structure is more defective. In addition, TEM images of MWCNTs before and after treatments can give the direct-viewing CNT structural changes. TGA has been always used to study the oxidative stability of nanotubes. These tests can be used to illustrate the changes in the structures for as-prepared and treated MWCNTs.
In this paper, a novel technique has been developed for the structural improvement of CVD MWCNTs using a rapid annealing process. Features of the process include rapid heating, low energy consumption, convenient and practical application by imposing electric current directly through MWCNTs for fast heating to high temperature. As-prepared and treated samples have been studied using TEM, Raman spectroscopy, TGA and electrical resistance measurements in order to characterize the structural improvement of MWCNTs through different rapid annealing temperatures.

2. Experimental

MWCNTs of high purity used in this study were synthesized by CVD using nanoscale sized Fe catalyst at 850 °C. The typical diameters of MWCNTs ranged from 20 to 30 nm while the lengths were mostly from 5 to 15 μm.

The schematic representation of rapid annealing process in a graphite tube system is presented in Fig. 1. The nanotube powders were compacted in the graphite tube, and then embedded in two graphite bricks under a constant pressure of 50 kPa. The graphite tube was wrapped in carbon felts for thermal insulation. Rapid annealing process at an appropriate temperature was carried out using a direct heating mechanism of DC current and voltage of 150–200 A and about 25–30 V between the two graphite bricks for 10 min under an argon gas atmosphere. A pyrophotometer was used to measure the center temperature from a hole through the carbon felt.

Compared with the rapid annealing process, samples of as-prepared MWCNTs were treated in 100 mL of a 3:1 mixture of concentrated H₂SO₄/HNO₃ and refluxed at 80 °C for 1 h, and then, centrifuged and subsequently washed with the distilled water until pH reached 7. After that, the treated MWCNTs were dried at 110 °C for 12 h in the oven.

The electrical conductivity of MWCNT powders was measured by a method of filling MWCNT powders into a quartz tube, and then pressing into a cylindrical pellet by two stainless steel bars as electrodes, under a stable pressure against each other during the measurement process.

TEM analysis was carried out using a JEM-2100 (JEOL Ltd., Japan). Raman spectra were recorded at room temperature on a Renishaw inVia Raman spectrometer with two laser excitation wavelengths of 532 nm (40 mW) and 785 nm (25 mW), respectively. TGA and differential thermogravimetric (DTG) were measured using a Perkin-Elmer Pyris thermal analyzer. The samples were heated from 50 to 900 °C at 10 °C/min with 20 sccm air flow.

3. Results and discussion

Typical TEM images of the as-prepared and treated MWCNTs are shown in Fig. 2. Table 1 shows the treatment of as-prepared and treated CNTs in the TEM images. Fig. 2(a) shows the defects commonly detected within the hollow cores and at the ends of as-prepared MWCNTs, which are due to the presence of residual metal catalyst particles. After the rapid annealing processes at 2000 °C and above, the residual metal catalyst particles have been completely removed from both within the hollow cores and at the ends of nanotubes by diffusion, as shown in Fig. 2(c) and (e). In addition, metal catalyst particles as shown in Fig. 2(i) are hardly found in the MWCNTs after mixed acid treatment, since they are dissolved during the acid treatment. However, it is clearly observed that the MWCNTs are cut into different shorter lengths due to etching by the mixed acid. After the mixed acid treatment, the acid solution of carbon nanotubes must be filtered, washed and dried.

The insets in Fig. 2(a) and (e) show clearly the cross-section TEM images of as-prepared and treated MWCNTs at 2800 °C. A polygonal shape cross section of a dislocated graphite-like stacking is present in the as-prepared MWCNT. After high temperature rapid annealing process, the polygonal shape cross section becomes more marked. Similar observation has been described in ref. by T. Katayama, H. Araki, and K. Yoshino [26]. This result indicates that MWCNTs have a more distinct polygonal cross section after high temperature annealing treatment.

HRTEM images of the as-prepared and treated tubes at 2000 °C, 2800 °C and 3000 °C are shown in Fig. 2(b), (d), (e) and (g), respectively. It can be seen from Fig. 2(b) that high defect density including vacancies, edges and dislocations along the nanotube wall can be found. Graphite sheets of the treated MWCNTs become stiffer and more continuous after rapid annealing treatment at 2000 °C (Fig. 2(d)). It reveals the small fringes of MWCNTs becoming more aligned along the tubes, due to the effects of rapid annealing process at 2800 °C (Fig. 2(e)). Intuitively the nanotubes have been restructured by the rapid annealing process. As the annealing temperature reaches up to 3000 °C, it is observed that defects such as twisty graphite shells and kinked walls of the MWCNTs are formed due to appearance of perturbing effects at excessively high temperature, as shown in Fig. 2(h).

In order to study the effect of rapid annealing on the structural enhancement in MWCNTs, Raman spectroscopic investigation has been performed. A stronger peak at about 1580 cm⁻¹ (G-band) shown in Raman spectra indicates the formation of well-graphitized structure of carbon nanotubes, while noncrystalline carbon species have a different peak at about 1350 cm⁻¹ (D-band). The intensity ratio of IG/IL can be used to show characteristics of structural reconstruction. The Raman spectra of the as-prepared and annealed MWCNTs at different temperatures with 532 nm excitation wavelength are presented in Fig. 3. It can be seen that the as-prepared MWCNTs have a very high IG/IL ratio as 0.99, resulting from high density defects and poor structural ordering. The IG/IL ratio of the rapidly annealed CVD MWCNTs decreases from 0.78 to 0.39 as the annealing temperature increases from 2000 °C to 2800 °C. The gradual decline of IG/IL ratio indicates the structural reconstruction toward ordering by the high temperature annealing process. However, as the annealing temperature reaches as high as 3000 °C, the value of IG/IL reaches to 0.72, which is attributed to the nanotube structural distortion due to perturbing effects at excessively high temperature, (see Fig. 2(h)). For the shortened MWCNTs by mixed acid treatment, the IG/IL ratio is 0.46, which means that many disordered parts in the structures were etched away, as shown in Fig. 2(i).

More detailed observations of the G-band changes by using Raman spectra of MWCNTs in the as-prepared state and after thermal
increases. Similar result has been reported in ref.[19] by K. Behler et al. The investigated by the TGA technique. Fig. 5 shows TGA (a) and DTG (b) successively high annealing temperature. Tube defects results in the increase structural distortion due to excessive high annealing temperature. The effect of annealing on the oxidative stability of MWCNTs was investigated by the TGA technique. Fig. 5 shows TGA (a) and DTG (b) thermographs for the as-prepared and annealed MWCNTs at 2000 °C, 2400 °C, 2800 °C and 3000 °C. No strikingly oxidation-induced weight loss is observed below about 550 °C. TGA is an effective tool to detect the combustion temperature in air. MWCNTs samples before and after the rapid annealing processes from 2000 °C to 2800 °C show combustion temperatures at 752 °C, 816 °C, 840 °C, and 850 °C, respectively. The combustion temperature of carbon nanotubes can be raised approximately 100 °C after the rapid annealing process at 2800 °C. It is generally agreed that the combustion temperature is related to the degree of graphitization [27]. Therefore, these results clearly indicate an improvement of thermal stability with more resistance against oxidation, resulting from structural reconstruction towards more ordering in the nanotube structure. As the annealing temperature is raised to 3000 °C, the oxidation peak shifts to lower temperature at 839 °C. The thermal stability of nanotubes annealed at 3000 °C decreases due to structural transformation to more disorder at such excessively high annealing temperature. These thermal analysis results are in good agreement with the TEM and Raman spectral characterizations and observations.

Normally, the annealing effects are sensitive to the structure of MWCNTs and thus can be investigated by comparing the changes in the intrinsic physical properties. Considering the macro changes can be readily visualized through a cursory evaluation of structural changes by measuring the electrical resistivity of MWCNT powders. Electrical resistivity in the pressed powder state has been measured to evaluate the contribution by both the intrinsic resistivity of the carbon nanotubes and the interface contact resistivity between CNTs. Electrical resistivity was measured by putting MWCNT powders into a quartz tube of 6 mm in diameter. Two stainless steel bars in both end of the quartz tube were used as the electrodes for measuring electrical resistivity. MWCNT powders jumped to 96.7% of as-prepared MWCNT powders, which means a corresponding nanotube structural transformation of the resistivity and a constant pressure of 340 kPa was applied to the MWCNTs between the two bars. Fig. 6 shows the electrical resistivity of as-prepared and annealed MWCNTs powders. The electrical resistivity of as-prepared nanotube powders is about 0.42 Ω·cm. For the MWCNTs annealed at 2000 °C, there was a decline of about 15.4% in electrical resistivity of MWCNT powders, which can be attributed to the better structural order of MWCNTs through the rapid high temperature annealing treatment. For tubes annealed from 2000 °C to 2800 °C, a small but continuous decrease of the electrical resistivity was measured from 83.2% to 79.3% of as-prepared MWCNT powders. These indicate the enhancement of structural order of MWCNTs with the reflection of a higher electrical conduction. However, when the annealing temperature reaches 3000 °C, the electrical resistivity of MWCNT powders jumped to 96.7% of as-prepared MWCNT powders, which means a corresponding nanotube structural transformation of

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**Table 1** Treatment of CNTs displayed in the TEM images of Fig. 2.
more disorder at such excessively high temperature. This phenomenon is reproducible during this investigation, but has not been reported by other groups. It is suggested that a perturbing effect results as electric current transporting through the MWCNTs: electrically induced high temperature would most certainly perturb the nanotube structure, leading to the increase of electrical resistance due to electron scattering as electric current transports through the MWCNTs.

4. Conclusions

A rapid high-temperature annealing technique has been developed, demonstrating a great potential for defects reduction and structural enhancement of CVD MWCNTs. High resolution TEM, Raman spectra, TGA and electrical resistivity measurement of nanotube powders have been employed in order to evaluate the rapid high temperature annealing effects. The results show that the structure becomes more ordered and stable as a result of the rapid annealing process at the high temperature range within 2000 °C and 2800 °C. As the annealing temperature reaches an excessively high temperature of 3000 °C, the structural order of the MWCNTs would be perturbed, resulting in a more disordered state.

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References


Fig. 5. Spectra of TGA (a) and DTG (b) for the as-prepared (square) and annealed MWCNTs at 2000 °C (circle), 2400 °C (triangle up), 2800 °C (triangle down) and 3000 °C (diamond) in air atmosphere. The inset of (a) shows the detail with enlarged graph. ‘W’ in Y-coordinate of (b) is the abbreviation of ‘Weight’.

Fig. 6. The electrical resistivity of MWCNT powder annealed at 2000 to 3000 °C. The inset shows a two-point probe apparatus for measuring the electrical resistivity of MWCNT powders.