High yield purification of multiwalled carbon nanotubes by selective oxidation during thermal annealing

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Abstract

Multiwalled carbon nanotubes were synthesized by electric arc discharge method in helium ambient with the pressure of 400 Torr and then purified by thermal annealing. During the annealing in air, the quartz tube in which the raw samples were placed was rotated in order to expose evenly the nanotubes and the carbonaceous particles to the air. The carbonaceous particles were presumably etched away by the selective oxidation with faster etching rate than nanotubes. This gives rise to very high yield of about 40%. It was found from Raman scattering measurements that the ratio of the intensity of G-line peak (1583 cm⁻¹) to that of D-line peak (1285 cm⁻¹) increased drastically by this purification process. Our density-functional tight-binding calculations clearly show that the desorption energy barrier of a C-O pair from the nanotube edge is 2.48 eV, higher than 0.32–2.1 eV from an amorphous carbon, confirming the current approach of purification by the selective oxidation.

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1. Introduction

Carbon nanotubes have gained great interests due to its unique and superb properties, such as effective field emission characteristics [1,2], capability for the storage of large amount of hydrogen [3–5], high modulus [6,7], and structural diversities that make it possible for the band gap engineering [8,9]. Electric arc discharge of graphite rods has been considered to be an appropriate method for the synthesis of carbon nanotubes in large quantity [10–12]. However, with this approach, a large amount of unnecessary carbonaceous particles such as fullerenes, nanoparticles, and amorphous phases are always contained in the soots in addition to carbon nanotubes [13,14]. Highly purified nanotubes are in general required for further sophisticated measurements and practical applications.

Purification involves in general the separation and the elimination processes of some carbonaceous particles from nanotubes. Various standard techniques, such as filtration, chromatography, and centrifugation, have been tried for multiwalled nanotubes (MWNTs) [12]. Although carbon nanotubes are separated to some extent from carbonaceous particles, some particles still remain in the purified samples and, to make things worse, the yield is very low in most cases. Gas phase purification method presumably utilizes the fact that different thermal oxidation rates exist between MWNTs and other carbonaceous particles. However, thermal annealing of raw samples in air or oxygen ambient resulted in very low yield of 1 wt% [12,15]. Initially, carbonaceous particles are presumably burned out first due to the selective etching by faster oxidative etching rate than carbon nanotubes. As the time proceeds, more carbon nanotubes are exposed on the surface and have more chance to be attacked by the oxygen molecules. Therefore, carbon nanotubes are also burned out by the oxidative process.
etching, although its oxidation rate is slower than that of carbonaceous particles. This is the main reason for such a low yield. In order to compensate such a drawback, liquid phase purification method in an acidic solution was introduced [12]. Oxygen ions melted in the solution can now attack evenly the network of raw samples and therefore the careful control of oxidation time would provide optimum condition to obtain the high yield of carbon nanotubes. This process give much higher yield (30–50 %) than gas phase oxidation method. Liquid phase purification, however, tends to result in shorter nanotubes and requires quite intricate procedures. Another approach is the purification by intercalation which utilizes the difference in oxidation rates of graphite and intercalated graphite to eliminate from the sample impurities that have open graphitic structures [16]. This method also gives high yield as much as 30–50 %. So the key idea of this study is to take advantage of the existence of different oxidation rates between nanotubes and carbonaceous particles, and even exposure of raw samples viable to the surface oxidation. In addition, we do not want to shorten the tube lengths if possible. This paper is two fold. We first designed annealing apparatus which satisfies the above requirements. Keen control of annealing condition in air gave rise to highly purified samples with high yield of up to 40%. We next performed density-functional based tight-binding total energy calculations in order to verify the existence of different oxidation rates between carbon nanotubes and other carbonaceous particles.

2. Experimental details

Multiwalled carbon nanotubes were prepared by conventional electric arc discharge method. Two graphite rods with a diameter of 10 mm and 25 mm were used as an anode and a cathode, respectively. DC current of 120 A with a voltage of 20 V was applied between two electrodes under helium atmosphere (400 Torr). Soots deposited on the water-cooled chamber wall mostly contained fullerene and carbonaceous particles. The material deposited on the cathode consists of outer hard shell with grey color which is composed of mostly amorphous carbons and soft core with black color which is composed of large quantity of carbon nanotubes and carbonaceous particles. Core parts are separated and ground to make them into small pieces. The ground samples were then transferred to the annealing equipment. We designed the annealing apparatus, where two quartz tubes were used, as can be seen in Fig. 1. The inner tube which contained the ground materials was simply rotated by the outer tube that was connected to a step motor with the rate of 30 rpm during the annealing procedure, such that samples were evenly exposed to the surface in order to have uniform selective etching by different oxidation rates controlled exclusively by the annealing time. The inner tube was initially set to a desired temperature prior to the sample loading. We first tried to determine the annealing temperature for fixed annealing time. For temperatures above 760 °C, all samples were burned out quickly. For temperatures below 700 °C, relatively long annealing time was required. In this work, we fixed the annealing temperature at 760 °C and tried to change the annealing time to obtain highly purified samples with high yield. Each time, 50 mg of raw sample was loaded into the chamber. The yield after the annealing was determined by the weight percentage. The morphology of MWNTs and the degree of purification were observed by scanning electron microscope (SEM) (JEOL, JSM-6400). Fourier Transformed (FT) Raman spectroscopy (BRUKER, RFS 100/S) using Nd:YAG laser (1064 nm) was used to confirm the formation of graphitized carbon nanotubes and to investigate qualitatively the degree of purification.

3. Results and discussion

Fig. 2(a) shows the SEM image of the ground raw sample. MWNTs were rarely seen on the surface after the grinding, since they were mostly embedded inside the carbonaceous particles. We annealed the samples as a function of time at 760°C under air ambient. With annealing for 20 min, some of the carbonaceous particles were removed at the surface and the weight was reduced to about 70% (Fig. 1(b)). With annealing for 40 min, major portion of the carbonaceous particles was removed, as shown in Fig. 1(c) and the weight was reduced to about 35%. One may increase the annealing time but the yield is expected to be low. During the annealing process, the supply of sufficient amount of oxygen is prerequisite for high yield of nanotubes. In this case, however, the temperature of the outer tube was slightly higher at the center than at the edge due to the temperature gradient, prohibiting air flow into the inner tube where the sample was located, although both edges of the outer tube were open to air. In order to improve the oxygen supply, air was blown into the tube by the fan from one side, while the
determined by the annealing time. Now the weight after annealing for 10 min was reduced to about 40%. We estimated from the SEM images that the annealed samples contained nanotubes more than about 80%. We emphasize here that the yield is remarkably improved compared to the previously reported value of about 1% [12,15]. This improvement was achieved by the rotation of the sample which promoted an even exposure of the carbonaceous particles to the surface. TEM images showed that the diameters and lengths are about 50 nm and 5 μm, respectively. Although the relative population of nanotubes to carbonaceous particles should get larger with increasing annealing time due to selective etching by oxidation, too long annealing times will result in over-burning of even nanotubes. Therefore, keen control of annealing time is a key factor for high quality and high yield of nanotubes. The degree of purification can be measured by the Raman spectroscopy [17]. Fig. 4 shows FT-Raman spectra of raw and purified MWNTs with the rotation of the quartz tube. The thermal annealing was done in air at 760°C for 40

Fig. 3. SEM images of multiwalled carbon nanotubes annealed with an air blowing for an annealing time of (a) 5 min and (b) 10 min.

Fig. 2. SEM images of multiwalled carbon nanotubes; (a) raw sample, (b) annealed for 20 min, and (c) annealed for 40 min.
Raman spectra of both raw and annealed MWNTs clearly show the peak centered at 1583 cm\(^{-1}\) (G-line), indicating the formation of well graphitized carbon nanotubes. The D\(^{-}\)-line peak located at 1605 cm\(^{-1}\) and no second order scattering peak near 1740 cm\(^{-1}\) suggest that these carbon nanotubes are multiwalled [18–20]. Multiwalled structure was also confirmed by TEM measurements. Raman spectrum of raw sample shows a relatively large peak at 1285 cm\(^{-1}\) (D-line), which was attributed to defects such as pentagons and heptagons in graphite and amorphous carbon [21,22]. After the annealing, the intensity of the D-line peak was decreased, whereas the intensity of the G-line peak was increased drastically, as shown in the figure. The intensity ratio of the G-line peak to the D-line peak of the annealed sample is about five times larger than that of the raw material. This again suggests that structures with pentagons and heptagons and amorphous carbon are etched away first by the selective oxidation, as will be argued in the next paragraph. Purification of carbon nanotubes by selective oxidation presumes that the oxidation rate of carbon nanotubes is slower than those of carbon clusters and amorphous carbon [12,15], although this statement has never been confirmed. In order to verify the above assumption, we here performed density-functional tight-binding (DFTB) total energy calculations. The DFTB method uses a basis of numerically obtained \(s\), \(p\), and \(d\) atomic orbitals. Hamiltonian overlap matrix elements are evaluated by a two-center approach. Charge transfer is taken into account through the incorporation of a self-consistency scheme for Mulliken charges based on the second-order expansion of the Kohn–Sham energy in terms of charge density fluctuations. The diagonal elements of the Hamiltonian matrix employed are then modified by the charge-dependent contributions in order to describe the change in the atomic potentials due to the charge transfer. Accurate description of charge transfer is necessary for C–O systems. Further details of the DFTB method have been published elsewhere [23]. For nanotube calculation, we chose (5,5) armchair and (9,0) zigzag nanotubes with 10 layers along tube axis where the dangling bonds of the bottom layer were saturated by the hydrogen atoms. We first calculate an \(O_2\) molecular adsorption on the nanotube walls. The adsorption energy can be defined,

\[
E_{\text{ads}} = E_{\text{tot}}(O_2 + \text{CNT}) - E_{\text{tot}}(O_2) - E_{\text{tot}}(\text{CNT})
\]

where \(E_{\text{tot}}\) is the total energy of a given system, \(E_{\text{tot}}(O_2)\) the total energy of an \(O_2\) molecule, and CNT stands for carbon nanotube. We tried various adsorption sites for an \(O_2\) molecule on both tubes. All the adsorption energies were within \(-0.5–0.6\) eV, depending on different sites [24]. An \(O_2\) molecule was not broken apart, with the bond length varying from 1.48 to 1.53 Å. This suggests that an \(O_2\) molecule adsorbs on the nanotube edge with relatively small adsorption energy and migrates easily to the nanotube edge. An \(O_2\) molecule was then adsorbed to the armchair edge to find optimum adsorption sites. Fig. 5(a) shows the minimum energy geometry for \(O_2\) adsorption at the armchair edge. An \(O_2\) molecule first adsorbs on top of the dimers with an adsorption energy of \(-4.04\) eV, as a precursor with a weak O–O bond [24] and finally gains the energy of \(-7.98\) eV by having the seat and top sites, as shown in Fig. 5(a). On the zigzag edge, however, an \(O_2\) molecule first dissociates without an activation barrier and adsorbs on two top sites with adsorption energy of \(-8.39\) eV, as shown in Fig. 5(b). This is expected, since the edge energy of a zigzag nanotube is higher by 0.8 eV than that of an armchair nanotube [25–27]. In order to show the difference in oxidation rate between nanotubes and other carbonaceous particles, we choose amorphous carbon. We first generated \(a\)-carbon network using melting-quenching molecular-dynamics simulation technique [24,28]. 144 carbon atoms in a supercell were used to generate \(a\)-carbon network with periodic boundary conditions. The periodic boundary condition along \(z\) axis was then removed to open the \(a\)-carbon surface and annealed again at 1000 K, followed by the quenching process, until the forces on each atom became less than 0.01 a.u. Only one two-fold coordinated atom is shown on the surface and the rest of them are three-fold coordinated, i.e., mostly graphitized [24]. Fig. 5(c) shows the typical local equilibrium geometry, when an \(O_2\) molecule adsorbs on top of \(C_1–C_1\) site, where \(C_0\) stands for an \(n\)-fold coordinated carbon atom. An intermediate state exists but the activation barrier is small (0.36 eV). The final adsorption energy is much larger with \(-11.0\) eV, compared to those of nanotube edges. Fig. 5(d) shows the typical local geometry of an \(O_2\) molecule adsorbed on top of \(C_1–C_1\) bond. In this case, the \(O_2\) molecule dissociates first without an activation barrier and adsorbs on the surface with strong C–O bonds with bond lengths around 1.2 Å. This involves one C–C backbond-breaking but more strain energy is involved during the
relaxation, resulting in large adsorption energy of $-11.7$ eV. Thus, the adsorption of an $O_2$ molecule on $a$-carbon surface is strongly site-dependent with relatively large adsorption energy. We expect $O_2$ molecules more likely to be adsorbed on $a$-carbon than nanotube edges. So far we have carried out energetics of $O_2$ adsorption on various species. In order to describe the oxidative etching, one needs to evaluate a desorption barrier of a CO molecule from the adsorbed phases, which governs the kinetics of the system. We first try to desorb the C–O pair from the pentagon site. The corresponding potential barriers for concerted pathways are shown in Fig. 6(a). We move up the carbon atom below a oxygen atom at the pentagon site by 0.2 Å along the $z$ axis and then fix $z$ coordinate of the chosen carbon atom and relax all other atoms. The C–O bond becomes stronger as the carbon atom move further from the edge. The barrier height of 2.48 eV is observed at the step (iii), where the C–O pair loses bonds with the adjacent carbon atoms. The oxygen atom at the next top site rebonds with the carbon atoms at the pentagon site, gaining the energy by 2.0 eV. One can imagine the desorption of a C–O pair from the top site first. However, this requires relatively large barrier height of about 4.0 eV [24]. Desorption pathways from the zigzag edge were relatively simple. The carbon atom below the oxygen atom was moved upward, giving rise to the energy barrier of 2.44 eV. This barrier height is similar to that of armchair edge. One can also evaluate desorption barriers of C–O pairs from $a$-carbon surface. Since $a$-surface is very complicated, various pathways can be chosen. Fig. 6(b) shows the pathways which give the minimum activation barriers. The desorption barrier from the $C_1$–$C_1$ site (Fig. 6(b)) is 2.1 eV, as shown in the step (iii), where most energy cost results from the bond-breaking of a strong C–C bond. In the case of desorption from the $C_2$–$C_2$ site, the barrier height was 0.25 eV, relatively low due to two weak C–C bonds. The desorption energy barrier was found to vary largely from 0.3 eV to about 2 eV, depending on the site. The desorption will take place from the site which requires the smaller activation barrier. We can now argue
the selective etching based on our calculations. Adsorption of an O₂ molecule on nanotube edges gains significant energy, whereas this energy gain is much larger from that on α-carbon. Furthermore, the desorption barriers of C–O pairs from the α-carbon are much lower than those at nanotube edges. This clearly demonstrates that the etching will occur more easily on α-carbon than nanotubes. One may also consider the etching from the graphitic nanoparticles which can also exist in the samples. In principle, the local arrangement of dangling bonds at the edge of graphitic nanoparticles should not be different significantly from the edge of nanotubes. The etching rate of nanoparticles will therefore be about the same as that of nanotubes. However, the surface area per unit mass is much larger in nanoparticles than in nanotubes. An accurate control of etching time will eventually remove these nanoparticles.

4. Conclusions

In summary, multiwalled carbon nanotubes were synthesized by electric arc discharge method under helium atmosphere, and purified by the thermal annealing process. During the annealing, the quartz tube in which the nanotubes were placed was rotated for the sake of even burning of the samples. It was found that the rotation of quartz tubes was effective for the purification with very high yield above 40%. It was demonstrated by the FT-Raman spectra that well graphitized multiwalled carbon nanotubes were produced by arc discharge, and that purification of multiwalled carbon nanotubes was realized by the thermal annealing. We also demonstrated from the DFTB calculations that the etching rate of nanotubes by O₂ molecules are much faster than that of amorphous carbons.

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References