Conversion of semiconducting behavior of carbon nanotubes using ball milling

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Abstract

This paper proposes a novel chemo-mechanical method to in-situ functionalize carbon nanotubes (CNTs). Ball milling in the presence of ammonium bicarbonate allowed the introduction of amine and amide groups onto the surface of CNTs, resulting in the conversion of the semiconducting behavior of CNTs from p-type to n-type. The corresponding electrical conductivity of CNT increased gradually with ball milling time, presenting a remarkable 250% increase after 9 hrs of milling. These interesting observations are attributed to the nitrogen compounds introduced on CNTs, which function as the electron donor in the material.

1. Introduction

The electrical properties of carbon nanotubes (CNTs) have attracted much attention since their discovery in 1991 [1]. Theoretical and experimental studies have shown that CNTs can behave like semiconductors or metals, depending on their conformation and features of each coaxial carbon shell [2-4]. This property can be very useful for applications such as chemical sensors [5], gas storage [6], optical limiter [7], field transistor [8], solar cell [9], organic light-emitting diodes [10-12], etc. Several methods have been successfully developed to treat CNTs by introducing impurities inside the tube or on the surface in an effort to change the electrical properties of CNTs. For example, the intercalation of potassium and bromine into single walled CNTs has shown to increase the electrical conductivity of the CNT [13]. The substitution of carbon atoms by boron [14] or nitrogen [15] modified the room-temperature resistivity and optoelectronic switching behavior of CNTs, respectively, while forming characteristic bamboo-shaped structures. Compounds containing nitrogen, such as butylamine [16], hydrazine [17], polyamine [18], have been successfully employed to alter the chemical gating and charge transfer behavior of CNTs. However, the above modification processes have major disadvantages, involving either tedious chemical treatment or complicated CNT fabrication processes, resulting in a high cost of the final products for practical applications.

In this paper, a simple but efficient method to modify the electrical and semiconducting properties of CNTs is proposed. CNTs are in-situ functionalized using ball milling in the presence of ammonium bicarbonate (NH_4HCO_3). The surface chemical information and electrical conductivity along with the semiconducting behavior of CNTs are reported.

2. Experimental

Materials and ball milling of CNTs: CNTs used in this study were multi-walled carbon nanotubes, the same as those studied previously [19]. They were prepared through chemical vapor deposition and supplied by Iljin Nanotech Ltd. The diameter and length ranged between 10-20 nm and 10-50 μm , respectively, according to the supplier's specification. For the ball milling of CNTs, typically, 1.58 g of NH_4HCO_3 and 0.25 g of CNTs were put into a stainless steel ball milling container. It contained a total of 450 ZrO_2 milling beads, comprising 150 pieces each with diameters of 5.5, 3.0 and 2.0 mm. The container was rolled at a rolling speed of 250 rpm and the milling was continued for durations of 1, 2, 4, 6 and 9 hrs. After ball milling, the container was put into a vacuum oven at 100 °C for 24 hrs to remove the residual gases. CNTs were also milled without NH_4HCO_3 for different durations to investigate the ball milling effect on the properties of CNTs.

Characterization: X-ray photoelectron spectroscopy (XPS) was employed to evaluate the elemental compositions and chemical status of the CNT surface. In the XPS analysis (Surface analysis PHI5600, Physical Electronics, Inc.), a monochromatic Al $K\alpha$ X-ray was used at an electron voltage of 14 kV. Time-of-flight secondary ion mass spectroscopy (Physical Electronics 7200 ToF-SIMS spectrometer) was used to identify the functional groups on the CNT surface. The primary Cs^+ ion source was operated at 8 keV and the scanning area was 200 μm square. A field emission analytical transmission electron microscope (TEM, JEOL 2010F) was used to characterize the dispersion state and surface morphology of CNTs before and after treatment. The influence of amino groups on the semiconducting properties of CNTs, including electrical conductivity, carrier type and concentration, were evaluated by employing a four-probe resistivity/Hall measurement system (HL5500PC, Bio-Rad). Sheet samples with thickness of 40-60 μm were prepared by pumping 5 mg of CNT particles between two iron plates at a pressure of 150 KN/cm^2 . Measurements were made at five different positions on a given sample, and the mean values are reported here.

3. Results and discussion

The elemental compositions and the functional groups introduced on the CNT surface were evaluated after ball milling in the presence of NH_4HCO_3 . Fig. 1 shows the variations of O/C and N/C ratios of CNTs determined by XPS as a function of milling time. The nitrogen content increased continuously as the ball milling time increased, suggesting the attachment of

nitrogen compounds onto the CNT surface via covalent bonding and/or physical adsorption. In contrast, the oxygen content decreased in the first 4 hrs, followed by showing an upward trend upon further treatment beyond 4 hrs. The pristine CNTs already contained a high O/C ratio of about 1.4%, arising mainly from ambient moisture or oxidation occurred during the purification process [19]. In summary, i) in the first 4 hrs of ball milling, the oxygen attached onto the CNTs was desorbed; and ii) upon ball milling beyond 4 hrs, the oxygen and water molecules arising from the decomposed NH_4HCO_3 formed covalent bonds with the broken -C-C- bonds.

ToF-SIMS results are incorporated here to verify the chemical states of nitrogen on CNT surface after ball milling. Judging from the ToF-SIMS results shown in Fig. 2 for CNTs ball milled with NH_4HCO_3 for 2 hrs (where N = 0.37 at% as determined by XPS), three different types of nitrogen compounds were identified. They include i) the ammonium gas adsorbed onto the CNT surface, as verified by $m/z = 18$; ii) the amines that were verified by the peaks of $-\text{CH}_4\text{N}$ ($-\text{CH}_2\text{NH}_2$), $-\text{C}_2\text{H}_6\text{N}$ ($-\text{CH}_2\text{CH}_2\text{NH}_2$) and $-\text{C}_3\text{H}_8\text{N}$ ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$) at $m/z = 30, 44$ and 56 , respectively; iii) the amide which was present in the form of $-\text{C}_3\text{H}_6\text{NO}$ ($-\text{CH}_2\text{CH}_2-\text{CO}-\text{NH}_2$) at $m/z = 72$. The comparison between the relative intensities of these nitrogen compounds suggested that only a small amount ($\sim 15\%$) of NH_3 gas was adsorbed onto the CNT surface while the majority of these compounds were covalently bonded to the CNT.

The underlying mechanism behind the successful attachment of nitrogen compounds on the CNT surface is schematically illustrated in Fig. 3. During milling, NH_4HCO_4 is decomposed into NH_3 gas, water and CO_2 . The ball milling process also introduces defects and breaks the -C-C- bonds of the CNT surface [20-23], which is further promoted by the presence of NH_4HCO_4 (see below). These in turn allow the amine and amide groups to form covalent bonds with the broken -C-C- bonds of the CNT surface.

To confirm the cutting effect of ball milling with NH_4HCO_3 , CNT samples were examined using TEM. Fig. 4 shows typical TEM images of pristine CNTs and those milled for 9 hrs. The pristine CNTs were severely agglomerated (Fig. 4A) and the end tips were almost all closed (see inset). After ball milling along with NH_4HCO_3 (Fig. 4B), agglomeration was significantly reduced and there were many individual CNTs separated from the agglomerates. The shortened CNTs tended to cluster again, indicating secondary agglomeration of CNTs particularly after prolonged ball milling. The end part of CNTs was widely opened indicating a fragmented CNT piece, and even the wall was partially damaged. Amorphous materials produced during ball milling were also found near the end and inside the cavity of CNTs (see inset). In sharp contrast, the CNTs milled without NH_4HCO_3 were present mainly in the form of agglomerates although their lengths were to a certain extent shortened (Fig. 4C). The end tip was only partially opened (see inset), where there was little evidence of amorphous materials. The above observations confirmed that adding NH_4HCO_3 during ball milling enhanced dispersion and cutting effects of CNTs for a given ball milling duration.

The electrical conductivity of milled CNTs was measured to evaluate the effects of amino functionalization on the semiconducting properties of CNTs, and the results are presented in Fig. 5. It was noted that with an increase in the ball milling time, the electrical conductivity of CNTs milled with NH_4HCO_3 increased gradually: a remarkable 250% increase after 9 hrs of treatment was achieved. In sharp contrast, no obvious increase or reduction in electrical conductivity was found of the CNTs milled without this chemical. These contrasting behaviors strongly suggested that NH_4HCO_3 played an important role for the improvement of electrical conductivity of CNTs during milling. Ball milling conducted in the absence of any chemicals created defects and amorphous materials [20-23], resulting in a negative effect on electrical properties of CNTs due to the destruction of the graphite layer and perturbation of the π electron system on the CNT walls. However, the current study revealed a positive effect of ball milling on electrical conductivity. To explain this phenomenon, the carrier concentration of CNTs was measured and the results are summarized in Table 1.

The pristine CNTs were found to be a kind of semiconductor with a positive carrier concentration. A slight decrease in carrier concentration was found for the CNTs milled in the absence of NH_4HCO_3 , suggesting some damages to the CNT structure. The electrical carrier of these CNTs was positive, being identical to the pristine CNTs. It should be emphasized here that the carrier concentration became negative upon ball milling in the presence of NH_4HCO_3 , and its absolute value increased gradually with an increase in milling time. The positive and negative carrier concentrations are closely related to different types of semiconductor, i.e. p-type and n-type, respectively: the pristine CNTs and those obtained after ball milling without NH_4HCO_3 are a p-type semiconductor, whereas those produced after ball milling along with NH_4HCO_3 are of n-type. It is well-known that the major carriers are holes with positive charges and electrons with negative charges, respectively, for the p-type and n-type semiconductors. The latter CNTs with negative charges were shown to contain amine and amide functional groups attached on the surface (Fig. 2). Because the nitrogen atoms in these groups contain lone-pair electrons that can function as the electron donor, charge transfer occurred between these groups and the CNTs [17], which in turn resulted in the conversion of the semiconducting behavior of CNTs from p-type to n-type along with a concomitant increase in electrical conductivity (Fig. 5).

Converting the semiconducting behavior of CNTs leads to many potential applications, for example, rectifying p-n junctions, bipolar junctions, photovoltaic devices and field-effect transistors, all of which require accurate control of electrical properties for different functions. Apart from being capable of converting the semiconducting behavior of CNTs, the present in-situ functionalization technique possesses several unique advantages over the other established methods, including the simplicity and ease of application as well as cost effectiveness.

4. Conclusions

A new chemo-mechanical method is proposed for in-situ amino functionalization of CNTs. The use of ball milling in the presence of ammonium bicarbonate allowed functional groups like amine and amide to be introduced on the surface of CNTs. After the ball milling, the semiconducting behavior of CNTs was converted from p-type to n-type as verified by the change in carrier type and concentration. The corresponding electrical conductivity of CNTs increased as ball milling time increased, with a remarkable 250% increase after 9 hr milling. These phenomena are attributed to the nitrogen compounds that are covalently-bonded onto the CNTs, functioning as electron donors and being responsible for charge transfer to CNTs. The CNTs in-situ functionalization based on the current technique [may find wider](#) applications in the fields requiring accurate control of electrical properties of CNTs. The CNT length can also be controlled by choosing an appropriate milling time and other processing conditions, such as type of chemicals added. The whole process is simple, convenient to use and cost effective.

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Fig. 1. Variations of the O/C and N/C ratios of CNT after ball milling with NH_4HCO_3 .

Fig. 2. ToF-SIMS results of CNTs after ball milling for 2 hrs.

Fig. 3. Schematics showing attachment of amine and amide groups on CNTs during the ball milling process.

Fig. 4. TEM images of pristine CNTs and these milled after 9 hrs. (A: Pristine; B: Milled with NH_4HCO_3 ; C: Milled without NH_4HCO_3)

Fig. 5. Electrical conductivity of CNTs after ball milling with and without NH_4HCO_3 .

TableTable 1. Carrier type and concentration of CNTs after ball milling without and with NH_4HCO_3 .

Sample	Without NH_4HCO_3 (cm^{-3})	With NH_4HCO_3 (cm^{-3})
Pristine CNTs	$+ (3.28 \pm 0.27) \times 10^{20}$	$+ (3.28 \pm 0.27) \times 10^{20}$
1 hr	$+ (1.93 \pm 1.55) \times 10^{20}$	$- (1.74 \pm 0.77) \times 10^{19}$
2 hr	$+ (1.98 \pm 0.78) \times 10^{20}$	$- (6.84 \pm 1.02) \times 10^{19}$
4 hr	$+ (2.75 \pm 0.31) \times 10^{20}$	$- (4.17 \pm 1.47) \times 10^{20}$
6 hr	$+ (2.62 \pm 1.20) \times 10^{20}$	$- (6.54 \pm 0.88) \times 10^{20}$
9 hr	$+ (1.63 \pm 1.21) \times 10^{20}$	$- (9.39 \pm 1.25) \times 10^{20}$

Figures

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