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Raman scattering study of iodine intercalated bundles of single-wall carbon nanotubes

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Abstract

We present the results of Raman and field emission studies of the structural and physical features of iodine intercalated bundles of single-walled carbon nanotubes (SWNTs). The periodicity of hexagonally closest-packed pristine nanotubes was destroyed by the intercalation of iodine molecules in interstitial sites of carbon nanotube bundles. The Raman spectra obtained using a 647.1 nm line of Kr-ion laser indicate that I_2 intercalation does affect the electronic state of metallic SWNTs of small diameters of ~ 1.26 nm changing into the insulating state. The turn-on electric fields obtained from the $I-V$ measurements for iodine intercalated SWNTs and pristine SWNTs were 2.43 and 3.41 $V \mu m^{-1}$, respectively, and iodine intercalated SWNTs show higher field emission than pristine SWNTs do.

Keywords: field emission, Schottky emission, CNT

Classification number: 5.14

1. Introduction

Carbon nanotubes have been investigated extensively because of their unique material properties [1]. Various potential applications of these properties, including those in electronic and optoelectronic devices and chemical and biochemical sensors, have been widely discussed [2–5]. The arc-assisted growth of single-wall carbon nanotubes (SWNTs) has been reported to produce bundles of an armchair form of nanotube with a diameter of 1.3 nm. It has previously been demonstrated by Raman spectroscopy and resistivity measurements that SWNT bundles exhibit amphoteric behavior similar to that of graphite; that is, they can be doped with either electron donors (K, Rb) or acceptor (Br_2) [6]. However, little is known about the detailed electronic states or emitting property changes [7] of the doped SWNTs. Charge transfer between intercalants and the SWNTs were studied previously by Raman scattering by Rao *et al* [8]. The charge transfer between the nanotubes and the guest species can be

used as a design parameter to optimize and study quantum transport phenomena in carbon nanotubes [9]. The geometric characteristic of nanotubes, together with high chemical stability and high mechanical strength is advantageous for field electron emitters [10]. Indeed, extensive studies of the field emitting property of multi-walled nanotubes (MWNTs) and SWNTs have been carried out in recent years due to the potential applications of electron emitters in field emission display (FED) devices. The detailed emission mechanism of each kind of carbon nanotube (CNT) remains, however, a controversial issue [11].

In this paper, we report the results of resonance Raman and field emission studies on the influence of iodine intercalation in SWNT bundles in terms of structure and material properties. We found that iodine intercalation in SWNTs does affect the electronic structure of metallic ones, unlike the previous Raman results, from resonance Raman spectroscopic measurements and field emission measurements.



2. Experimental

SWNTs synthesized by the arc-discharge method were obtained from a commercial source (ILJIN Nanotech Co.). To intercalate iodine, we place pristine SWNTs in a small-size quartz tube of 5 mm diameter and this tube is placed in a 10 mm diameter quartz tube with an excess amount of iodine, and vacuum-sealed and heated at 250 °C for 3 days. After reaction, in order to remove excess physisorbed iodine, one end of the quartz tube containing the I_2 -intercalated SWNTs was kept at 120 °C for 2–4 h, while the other end was submerged in liquid nitrogen to collect the vaporized iodine. The resulting I_2 -intercalated SWNT samples were found to be stable under ambient conditions, permitting measurements to be carried out in air (hereafter, we refer to this sample as intercalated SWNTs). To check reversibility, I_2 -intercalated SWNT samples were heated to 700 °C for 6 h under flowing N_2 gas (hereafter we refer to this sample as de-intercalated SWNTs). Thermogravimetric (TG) analysis experiments show that weight loss commenced at 80 °C and the intercalated iodine was completely removed at 230 °C.

Powder x-ray diffraction (XRD) data were collected from a Rigaku x-ray diffractometer equipped with a monochromated beam of Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$, 40 kV and 20 mA). The powder of the product was spread on the slide glass as a thin layer.

Raman spectra of the SWNTs were measured at room temperature in a back scattering geometry using an Ar-ion laser line (514.5 nm) and a Kr-ion laser line (647.1 nm). The scattered light was analyzed by a triple spectrometer (Jobin Yvon T64000) equipped with a liquid-nitrogen cooled CCD detector. The laser power used was kept at less than 5 W mm^{-2} in order to minimize the possible damage to the samples during measurements.

Current–voltage (I – V) curves of the samples were measured using an ampere meter (Keithley 2400). Before the first emission measurement of each sample, a bias voltage in the range of 0–1500 V was applied for several tens of minutes to reach a stable emission condition. A maximum of 2000 V was applied between the CNT (cathode) and ITO electrode (anode), and the spacer distance was 500 μm with an emission area of $0.8 \times 0.8 \text{ cm}^2$.

3. Results and discussion

3.1. Powder XRD analysis

Figure 1 shows the powder x-ray diffraction (PXRD) patterns of pristine SWNTs and I_2 -intercalated SWNTs. An arc-produced pristine SWNTs sample has a strong peak at 6.2° and two weak peaks at 10.4° and 16.1° , which are indexed as the d_{100} , d_{110} and d_{210} reflections of a hexagonal lattice with unit cell dimension $a = 16.7 (\pm 0.2) \text{ \AA}$. The hexagonal lattice is the cross section of the closest-packed nanotube bundles. The estimated diameter of pristine SWNTs from the hexagonal lattice parameter was $14.2 (\pm 0.1) \text{ \AA}$ and this value is consistent with the previously reported value [12]. Upon further iodine intercalation, the intensities of the diffraction peaks corresponding to the hexagonal lattice fell below the diffraction limit. However, in the de-intercalated

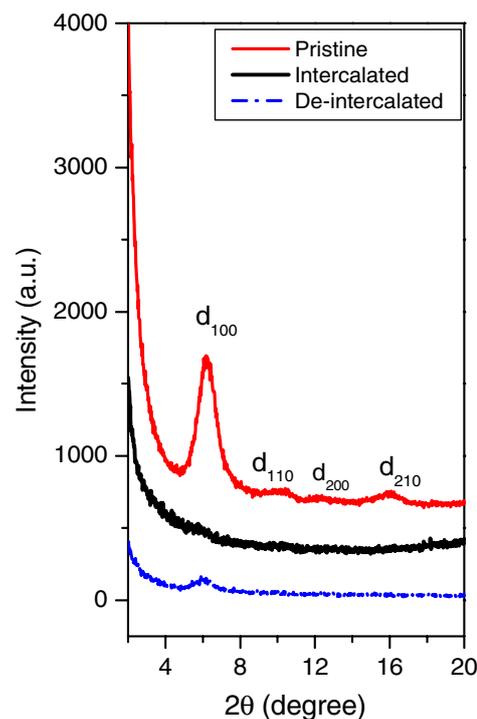


Figure 1. XRD patterns of pristine SWNTs and I_2 -intercalated SWNTs.

sample, the peak observed in pristine powder reappears at near its original position at $2\theta \sim 6^\circ$. The x-ray data indicate that iodine acts as a chemical wedge entering the interstitial channels between nanotubes. At high iodine uptake levels, the lattice expands, and a long-range ordering within the hexagonal packing disappears. A similar result was reported in the case of K and Cs doped SWNTs [13,14].

The x-ray data indicate that iodine is intercalated and de-intercalated reversibly into the interstitial channels between nanotubes. At a high iodine uptake level, a long-range ordering is destroyed. When iodine is removed, the long-range ordering comes back again. TGA measurement indicates that the composition of I_2 intercalated SWNTs is close to IC_{12} , which is consistent with previous work [12].

3.2. Raman spectroscopy analysis

Charge transfer between intercalants and SWNTs was studied previously by Raman scattering by Rao *et al* [8]. They measured SWNT bundles intercalated with various guest species; potassium, rubidium, iodine and bromine using the 514.5 nm laser excitation. Among them, only I_2 was found to be non-effective in intercalation. Raman scattering by SWNTs is known to be a resonant process. The energy, or the wavelength, of the excitation light for the Raman measurements is sensitive to the diameter and metallic or insulating character of the SWNTs.

In this Raman study, we focus on the effect of I_2 intercalation into SWNT bundles using different wavelengths of the excitation light. In brief, we found that I_2 intercalation does change the metallic SWNTs of small diameter into an insulating state. This is in contrast with the previous finding by Rao *et al*, where little change was seen for I_2 intercalation [8].

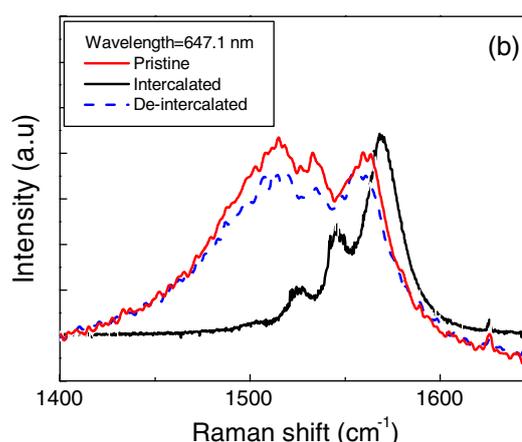
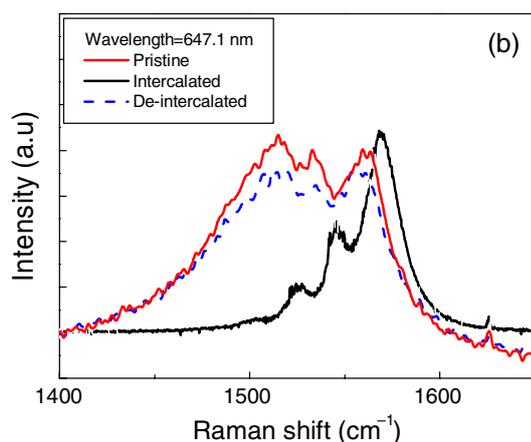
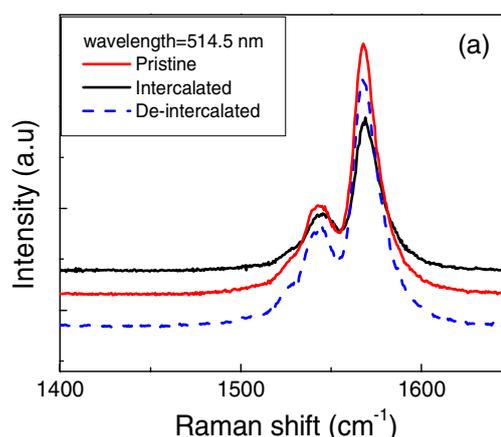
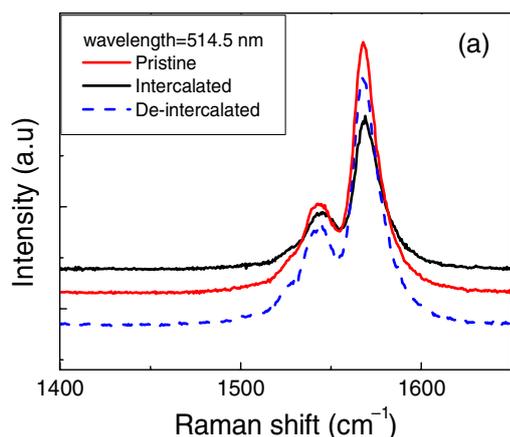


Figure 2. Raman spectra of pristine, intercalated, and de-intercalated SWNTs in the low frequency (below 400 cm^{-1}) range, measured by the 514.5 nm Ar-ion line (a) and 647.1 nm Kr-ion line (b).

Figure 3. Raman spectra of pristine, I_2 -intercalated, and de-intercalated SWNTs in the tangential mode range (between 1400 and 1650 cm^{-1}), measured by the 514.5 nm line of an Ar-ion laser (a) and the 647.1 nm line of a Kr-ion laser (b).

Figure 2 shows the Raman spectra of pristine, intercalated, and de-intercalated SWNTs in the low frequency (below 400 cm^{-1}) range, measured by the 514.5 nm Ar-ion line (a) and 647.1 nm Kr-ion line (b). Pristine and de-intercalated SWNTs show the strong radial breathing modes (RBMs) in the range of $140\text{--}200\text{ cm}^{-1}$. Grigorian *et al* [12] attributed the strong peak at 175 cm^{-1} of I_2 -intercalated SWNTs to resonant Raman scatterings from charged (I_5)- and (I_3)-linear chain complexes. Their photoluminescence (PL) spectrum of I_2 -intercalated SWNTs indicates a strong resonance in the wavelength range of $600\text{--}650\text{ nm}$. Thus, we have used the 647.1 nm Kr-ion line in measuring the Raman spectra of I_2 -intercalated SWNTs, as shown in figure 2(b). The relative intensity of the 175 cm^{-1} mode with respect to those of RBM of pristine- and/or de-intercalated SWNTs is indeed resonant with the 647.1 nm Kr-ion line. However, the Raman spectra of pristine and de-intercalated SWNTs excited by the 647.1 nm Kr-ion line do show the contribution from the SWNTs of smaller diameter than those measured by the 514.5 nm Ar-ion line. It is known that the Raman frequency of the RBMs are closely related to the diameter d (in nm) of the SWNT bundles by the phenomenological equation; $\nu\text{ (cm}^{-1}\text{)} = 6.5 + 232/d$. The Raman spectra of pristine and de-intercalated SWNTs excited by the 647.1 nm Kr-ion line show peaks at 190 cm^{-1} higher than the peak frequency (at 175 cm^{-1}) of the Raman spectra excited by the

514.5 nm Ar-ion line. The 647.1 nm excitation seems to be more sensitive to the SWNTs of smaller diameter (1.26 nm) than that (1.38 nm) of those SWNTs excited by the 514.5 nm excitation.

Figure 3 shows the Raman spectra of pristine, I_2 -intercalated, and de-intercalated SWNTs in the tangential mode range (between 1400 and 1650 cm^{-1}), measured by the 514.5 nm line of an Ar-ion laser (a) and the 647.1 nm line of a Kr-ion laser (b). The spectra of all samples shown in figure 3(a) are composed of symmetric Lorentzian-type peaks, while the spectra of pristine and de-intercalated SWNTs shown in figure 3(b) are asymmetric peaks. The asymmetry of the tangential phonon modes is a Breit–Wigner–Fano (BWF) lineshape, and it is due to coupling between discrete phononic excitation and continuum excitation of any origin. This continuum is likely the electronic continuum of metallic SWNTs. Therefore, we interpret that the 647.1 nm line is sensitive to the metallic SWNTs of small diameters. These observations are in agreement with a previous Raman result [15]. However, the striking fact is that the tangential phonon mode, measured using a 647.1 nm Kr-ion line, of I_2 -intercalated SWNTs are symmetric. The corresponding spectra of the same sample after thermal treatment for de-intercalation are asymmetric. The change in asymmetric shape to a symmetric one due to I_2 -intercalation appears to be a thermally reversible process. It is interpreted that the

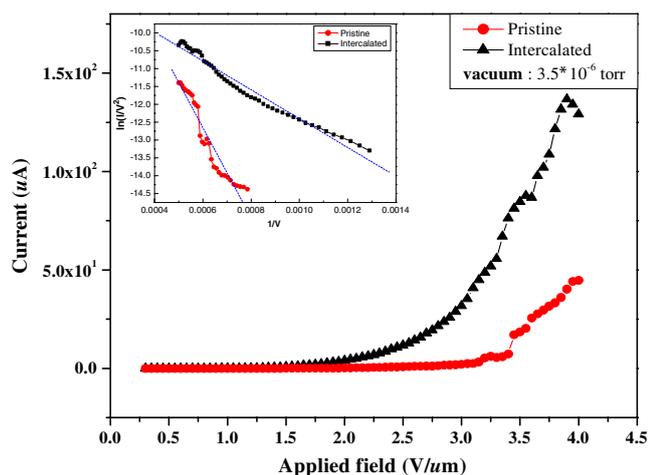


Figure 4. FE currents from I_2 -intercalated and pristine SWNTs. The inset shows the F–N plot.

I_2 -intercalation does change the metallic SWNTs of small diameters (1.26 nm) into an insulating (or semiconducting) state, and the intercalation effect can be removed by thermal treatment. This is in contrast with the previous conclusion by Rao *et al* [8], where little change is seen for I_2 intercalation using the 514.5 nm Ar-ion line.

The apparent paradox can be resolved if the I_2 -intercalation effect into SWNTs is dependent on the diameter. The sample is composed of SWNTs of different diameters, including metallic SWNTs with diameters of around 1.26 nm. The 647.1 nm line of the Kr-ion laser in the Raman measurement is sensitive in probing the SWNTs of small diameters. The finding from the Raman measurement using the 647.1 nm line is that the I_2 -intercalation does affect the metallic SWNTs to become insulating. Previous Raman measurement using a 514.5 nm line might simply have been inefficient in detecting such changes in SWNTs of diameters around 1.26 nm due to the different resonant behavior of the laser excitation lines.

3.3. Field emission

Figure 4 shows the field emission (FE) currents from I_2 -intercalated and pristine SWNTs. For field emission measurement, grounded indium tin oxide (ITO) served as an anode above the CNT cathode plate, which was biased with a negative potential. A homemade 500 μm thick alumina spacer was used in between the cathode and the anode. FE current was monitored with a precise multimeter (Keithley 6517) connected to the cathode plate. Each current density in figure 4 is the average value of ten measurements from each sample under pressure of 3.5×10^{-6} Torr. The turn-on electric fields V_{TO} for iodine intercalated SWNTs and pristine SWNTs were 2.43 and 3.41 $\text{V} \mu\text{m}^{-1}$, respectively. The inset of figure 4 is the Fowler–Nordheim (F–N) plot of the two samples, and the calculated field enhancement factor β is 9162 for I_2 -intercalated SWNTs and 3001 for pristine SWNTs, respectively.

The I_2 -intercalated SWNTs can be regarded as a p-type semiconductor since iodine molecules accept electrons from the SWNTs. In the p-type semiconductor, electron

concentration in the conduction band is very low. So the F–N theory only holds at low applied voltage. At high voltage, the emission current is limited by the electron supply, and hence, the observed saturation. At even higher extraction voltage, the current increases rapidly with the voltage [16]. A previous study argued that this phenomenon is probably due to electron emission from the valence band [17]. To elucidate the exact emission site of I_2 -intercalated SWNTs, it is necessary to measure the field emission energy distribution (FEED). The lower V_{TO} value and the higher β value of I_2 -intercalated SWNTs suggest a good electron emitter for future FEED devices.

4. Conclusions

We found that I_2 intercalation does affect the electronic state of metallic SWNTs of small diameters changing into the insulating state. Unlike previous Raman works, where no effect of I_2 intercalation was observed, we used the 647.1 nm line of a Kr-ion laser resonant with metallic SWNTs of small diameters. The effect of the I_2 intercalation is thermally reversible. This reversibility is consistent with the results of both thermogravimetric (TG) and x-ray powder diffraction analyses. The turn-on electric fields obtained from the field emission measurements for iodine intercalated SWNTs and pristine SWNTs were 2.43 and 3.41 $\text{V} \mu\text{m}^{-1}$, respectively, and iodine intercalated SWNTs show higher field emission than the pristine SWNTs do.

Acknowledgments

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