Tuning of hole doping level of iodine-encapsulated single-walled carbon nanotubes by temperature adjustment†

Zhiyong Wang,[a] Lu Wang,[b] Zujin Shi,*[a] Jing Lu,*[b] Zhennan Gu[a] and Zhengxiang Gao[b]

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We present a simple approach of tuning the hole doping level of iodine-doped single-walled carbon nanotubes by adjusting temperature, utilizing the structural conversion of iodine species encapsulated in SWNTs.

Due to their outstanding electronic and mechanical properties, single-walled carbon nanotubes (SWNTs) are promising materials for creating new-generation nanodevices.[1] The modulation of SWNTs' properties is a crucial step toward their applications. A great deal of interest focuses on the doping of SWNTs.[2] Experiments and theoretical calculations have demonstrated that SWNTs can be doped by either electron donors (*e.g.* alkali metals[2a,b]) or electron acceptors (*e.g.* halogens[2c,d]). One of the goals of doping is to control/tune the carrier concentration of SWNTs. Previous studies reported that the amount of transferred charge can be tuned *via* changing the species and amount of dopant,[3] but it is difficult to realize continuous tuning by this method. Electrochemical doping of SWNTs[4] is advantageous in tuning the doping level continuously, however it requires complex operation. Thus, simple methods for tuning the doping level of SWNTs continuously are still highly desired.

Recently we have observed the conversion between polyiodide chains and iodine molecules inside SWNTs upon electron beam irradiation.[5] The polyiodide chains and iodine molecules might have different doping effects on SWNTs, suggestive of a route to tune the doping level of SWNTs by utilizing the conversion of different doping species encapsulated in SWNTs. Because electron beam irradiation inevitably gives rise to a thermal effect, the observed conversion between polyiodide chains and iodine molecules is probably caused by temperature change. In the present study, we investigated the effect of temperature on the hole doping level of I-doped SWNTs using Raman spectra as a probe. We found that the hole doping level of I-doped SWNTs can be tuned by adjusting the temperature. The change of hole doping level with temperature is ascribed to the conversion between polyiodide chains and iodine molecules.

SWNTs were prepared and purified as described previously.[6] Encapsulation of iodine into SWNTs was achieved by immersing SWNTs in molten iodine at 150 °C for 48 h.† After the encapsulation process, the SWNTs were heated at 60 °C for 1 h under dynamic vacuum (10^{-1} Pa) to remove excess iodine molecules. Raman measurements were performed using a Jobin Yvon HR-800 spectrometer with excitation wavelengths at 488 and 632.8 nm, a Jobin Yvon T64000 spectrometer at 532.1 nm and a Renishaw 2000UK system at 514.5 nm. The Raman spectrometer was calibrated before measurements with reference to the F_{1g} line of Si at 520.7 cm^{-1}.

Raman spectra for pristine SWNTs and I-doped SWNTs excited with an excitation wavelength of 532.1 nm are shown in Fig. 1. An intense peak at 172 cm^{-1} and its overtones (indicated with arrows) arise after the encapsulation of iodine. There is still controversy regarding the origin of these peaks. Grigorian *et al.* assigned the peak at 172 cm^{-1} to I_5^-, according to the Raman band position of I_5^- in other systems;[2c] while Kim and co-workers argued that it should be the radial breathing mode (RBM) of SWNTs, because the expected resonant Raman scattering behavior of I_5^- with a laser of 647.1 nm was not observed.[7]

We have found that the Raman peak at 172 cm^{-1} is resonant with the excitation source of 532.1 nm after performing Raman measurements with a series of lasers with different wavelengths. Fig. 2 depicts the RBM region of Raman spectra for SWNTs and I-SWNTs excited by lasers at 488, 514.5 and 632.8 nm, respectively. There is no obvious difference between the Raman spectra for SWNTs and I-SWNTs excited at 488 nm except for slight frequency shifts, as well as at 632.8 nm.

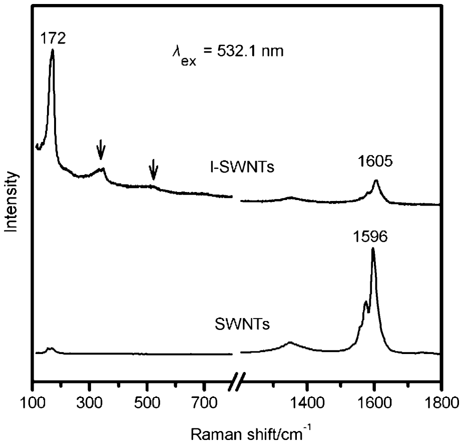

Fig. 1 Raman spectra for SWNTs and I-SWNTs excited at 532.1 nm. The peak at 172 cm^{-1} and its overtones (indicated with arrows) originate from charged polyiodide chains.

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[a] *Beijing National Laboratory for Molecular Sciences, State Key Lab of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, PR China. E-mail: zjshi@pku.edu.cn; Fax: 86-10-62751708; Tel: 86-10-62751495*
[b] *State Key Laboratory for Mesoscopic Physics and Department of Physics, Peking University, Beijing, 100871, PR China. E-mail: jinglu@pku.edu.cn; Fax: 86-10-62751615; Tel: 86-10-62756393*

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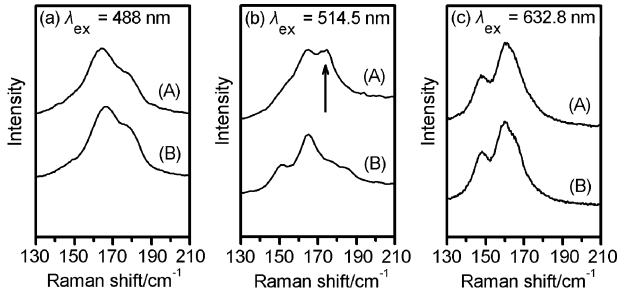

Fig. 2 Low-frequency region of Raman spectra for I-SWNTs (A) and SWNTs (B) excited at 488 nm (a), 514.5 nm (b) and 632.8 nm (c). The arrow indicates the newly appearing peak from charged polyiodide chains.

However, when the I-SWNTs sample is excited at 514.5 nm, a peak at 174 cm^{-1} (indicated with an arrow) with intensity comparable to that of the RBM of SWNTs appears. When using an excitation wavelength of 532.1 nm, as shown in Fig. 1, the intensity of the Raman signal at 172 cm^{-1} is extremely strong. It is apparent from the above results that the Raman band at 172 cm^{-1} is in strong resonance with the excitation wavelength of 532.1 nm. Taking into account that the resonant energy lies in the range of the absorption band of I_5^-,[8] it is reasonable to assign the resonant component to I_5^-. Moreover, the presence of polyiodide chains of seven iodine atoms has been observed directly by high-resolution transmission electron microscopy in our previous study (see ref. 5, right part of the image with a time of "10s" in Fig. S1(a) in supporting information). Due to the similarity of I_7^- and I_5^- in the position of Raman and absorption bands,[8,9] the Raman signal at 172 cm^{-1} may also contain contributions from I_7^-.

Furthermore, we performed density functional theory (DFT) calculations for the vibrational properties of isolated iodine molecules I_2 and isolated charged linear polyiodide chains I_3^-, I_5^- and I_7^-.† The strongest Raman-active frequencies are 188.4, 95.6, 148.8 and 152.4 cm^{-1} and the corresponding Raman activities are 18, 42, 395 and 2894 Å^4 amu^{-1} for I_2, I_3^-, I_5^- and I_7^-, respectively. The much smaller frequency rules out I_3^- as the origin of the observed Raman peak at 172 cm^{-1}. The calculated 148.8 and 152.4 cm^{-1} frequency for I_5^- and I_7^- supports the assignment of the Raman peak at 172 cm^{-1} to the two polyiodides. The deviation between the calculated Raman frequency and the experimental peak may come from the interaction between the polyiodide chains and SWNTs.

It is known that the frequency of the tangential band (G band) of SWNTs is sensitive to doping, as a consequence of expansion or contraction of C–C bonds in SWNTs.[10] Generally, p-doping of SWNTs induces an upshift of the G band.[10] The quantitative relation between charge transfer and the upshift of G band was found to be 320 cm^{-1} per hole per C-atom from electrochemical p-doping of SWNTs.[11] For I-doped SWNTs in the present study, the frequency of the G band upshifts by 9 cm^{-1} (Fig. 1) compared to pristine SWNTs, resulting from electron transfer from SWNTs to iodine molecules, generating negatively charged polyiodide chains (I_5^- and I_7^-).

In order to investigate the structural transition of iodine in SWNTs upon temperature variation and the subsequent change of doping level, we performed Raman scattering measurements on I-doped SWNTs using the laser of 532.1 nm at temperatures ranging from 30 to 90 °C. Because temperature also affects the frequency of Raman bands, we measured Raman spectra of pristine SWNTs at the same temperature range for comparison.

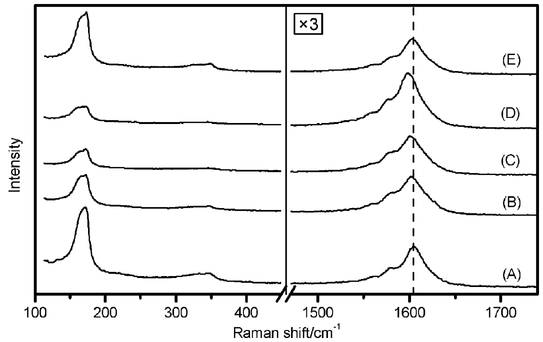

Fig. 3 Raman spectra for I-SWNTs heated to 30 °C (A), 50 °C (B), 70 °C (C), 90 °C (D) and cooled to 30 °C from 90 °C (E). The vertical dashed line indicates the initial position of the G band maximum for I-SWNTs at 30 °C.

Raman spectra for I-doped SWNTs in Fig. 3 show that the peak from polyiodide chains at 172 cm^{-1} decreases dramatically with increasing temperature; meanwhile, the frequency of G band downshifts gradually. The shift of the G band for I-doped SWNTs and pristine SWNTs as functions of temperature are plotted in Fig. 4. It is apparent that the G band for I-doped SWNTs downshifts more rapidly than that of pristine SWNTs with increasing temperature. The decreasing difference of G band between doped and pristine SWNTs indicates a decreasing doping level in I-doped SWNTs with increasing temperature. From the change of doping level and the intensity reduction of the Raman band from I_5^- and I_7^-, we infer that the negatively charged polyiodide chains transform into iodine molecules (I_2) in the heating process. The absence of a Raman signal from I_2 can be attributed to the low Raman activity of I_2, *i.e.*, one and two orders of magnitude lower than that of I_5^- and I_7^-, respectively, as presented above. To test the reversibility of the transformation, Raman spectra for I-doped SWNTs cooled from 90 to 30 °C were taken (Fig. 3(E)). It can be seen that the peak from polyiodide chains is recovered and the frequency of the G band shifts

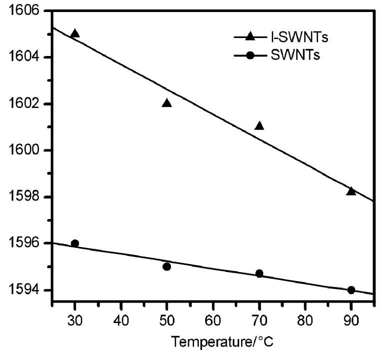

Fig. 4 Temperature dependence of the frequency of the G band maximum for I-SWNTs and pristine SWNTs.

Table 1 The charges per iodine atom of iodine molecules and polyiodide chains confined in SWNTs

Charge (|e|/I)	I_2	I_5	I_7
(8, 8)	−0.16	−0.18	−0.16
(14, 0)	−0.07	−0.15	−0.13

back to 1603 cm^{-1}. Although the hole doping level of SWNTs after one heating and cooling cycle is not recovered completely, it is unambiguous that the hole doping level decreases with increasing temperature and *vice versa*. These results indicate that the doping level of I-doped SWNTs can be tuned by adjusting temperature.

Since iodine molecules are easily sublimed, the loss of iodine in the heating process must be considered. According to a previous report, sublimation of iodine molecules in I-doped SWNTs commences at around 100 °C.[2c] Thus we herein choose the temperature range of 30–90 °C as a higher temperature would result in loss of iodine. We found that the Raman peak from polyiodide chains disappears at 190 °C, and its intensity after cooling to 30 °C is significantly weaker than the initial signal (Fig. S2, ESI†), which is in contrast to the sample cooled to 30 °C from 90 °C. This indicates that the polyiodide chains have transformed into iodine molecules completely at 190 °C and only a small quantity of iodine molecules remain in the SWNTs. Consequentially, the change of hole doping level of I-doped SWNTs is irreversible due to considerable loss of iodine molecules.

The tendency of charge transfer between iodine and SWNTs is associated with the energy levels in their electronic structures. The SWNTs sample used here consists of a variety of (*n*, *m*)-types of SWNTs that are of different Fermi energies or valence band positions,[12] thus the electron transfer between SWNTs and iodine is complex and the result is an overall average. In the case of a specific (*n*, *m*)-type of SWNT, its charge transfer behavior with iodine is expected to be characteristic of its unique electronic band structure. The research on isolated iodine-encapsulated SWNT is now ongoing.

For further understanding the charge transfer between SWNTs and iodine species, we theoretically studied I_2, I_5 and I_7 confined in the metallic (8, 8) and semiconducting (14, 0) SWNTs (see ESI†). The calculated charges per iodine atom from Mulliken population analysis[13] are listed in Table 1. The polyiodide chains I_5 and I_7 have total charges of −0.90 and −1.12 |e| in the (8, 8) SWNT, respectively, and −0.75 and −0.91 |e| in the (14, 0) SWNT, respectively, suggesting that the identification of I_5^- and I_7^- is reasonable. On the other hand, the total charges of I_2 are −0.32 and −0.14 |e| in the (8, 8) and (14, 0) SWNTs, respectively. The electrons transferred from the metallic (8, 8) SWNT to I_5 are 0.02 |e| per iodine atom larger than that to I_2, while the electrons to I_7 per iodine atom are almost equal to that to I_2. On the other hand, the electrons transferred from the semiconducting (14, 0) SWNT to I_5 and I_7 are 0.08 and 0.06 |e| per iodine atom larger than that to I_2. The actual SWNTs are mixtures of metallic and semiconducting tubes, and semiconducting SWNTs account for 2/3 of the sample. Therefore the charges on SWNTs are generally reduced when the polyiodide chains transform into iodine molecules, and it is reasonable to ascribe the change of the doping level in the experiments to the conversion between these two iodine species.

In conclusion, we have found that the hole doping level of I-doped SWNTs decreases with increasing temperature and *vice versa*. We ascribe the temperature-dependent hole doping level of SWNTs to the conversion between polyiodide chains and iodine molecules. The former can accept more electrons than the latter from SWNTs according to DFT calculations. Our study opens a simple path toward controlling of carrier concentration of SWNTs.

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