Graphical abstract

The modification of electronic structure of SWCNH with iodine molecules should lead to the change of the electrical conductivity of SWCNH. The electrical conductivity of SWCNH proportionally increases with the iodine coverage, indicating the charge transfer interaction between SWCNH and iodine molecules.

Electronically Modified Single Wall Carbon Nanohorns with Iodine Adsorption

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Abstract

Tailoring electronic properties of single wall carbon nanohorn (SWCNH) is expected to develop the application potential in various fields. SWCNH is efficiently modified with iodine molecules by liquid phase adsorption. The adsorption isotherm of iodine on SWCNH was Langmuirian with the saturated adsorption amount of $185 \pm 10 \text{ mg g}^{-1}$ (coverage 0.18), indicating a specific interaction between SWCNH and iodine. The DC electrical conductivity of SWCNH film prepared by dip-coating method increased with the iodine adsorption amount almost by a factor 10.

1. Introduction

Single wall carbon nanotubes (SWCNT) have recently received a widespread attention due to their distinctive nanoporosity and outstanding electronic properties [1,2]. Current works have been focused on controlling electronic properties of SWCNT in order to develop new application to future electronic devices [3-5]. Single-walled carbon nanohorn (SWCNH) belongs to single wall nanocarbon family, although it is more defective than SWCNT. An individual SWCNH has a closed horn-shaped tip with an average cone angle of about 20° and the mean diameter of tubular part and length are 2-4 nm and 40-50 nm, respectively. SWCNH particles associate to form spherical aggregates such as dahlia-, bud-, and seed-types [6-8]. The tube space of SWCNH is closed in the as-grown state. The hole-opening through oxidation significantly increases the surface area and pore volume, widening the applications [9]. SWCNH have no metallic impurities, being favorable in surface chemical studies. Basically, SWCNH exhibits n-type semiconductivity, being different from SWCNT. Urita et al. reported that opening hole of SWCNH changes the electrical conductivity response of SWCNH on gas adsorption from n-type to p-type semiconductivity [10]. Accordingly, an intensive study on electronic properties of SWCNH from the view point of surface chemistry is indispensable to extend their potential application. Chemical doping is expected to substantially increase the density of charge carrier and thereby enhance the electrical conductivity. Recent studies showed that chemical modification leads to a dramatic enhancement in electrical conductivity of carbon nanotubes owing to the electronic structure change [11]. The charge transfer between the nanotubes and the dopant molecules can be used as a design parameter to study the charge transport phenomena in carbon nanotubes [12]. For example, it was reported that encapsulation of electron acceptor dopants such as iodine compounds (KI, polyiodine, and I_2) into carbon nanotubes intensively affected the conjugated π -electron system of carbon nanotubes [13-15]. Furthermore, Eklund et al. found that intercalation of iodine molecules in the SWCNT bundle by immersing SWCNT in molten iodine showed a remarkable electrical conductivity enhancement [16]. Gotovac et al. reported that adsorption from solution was simple and efficient method to modify the

property of SWCNT [17,18]. Iodine adsorption on SWCNT in the solution is a promising method [19]. Study of iodine adsorption on SWCNH having defective nature should provide a valuable guideline for the electronic structure control of single wall nanocarbon families. This article describes the modification of electronic properties of SWCNH with iodine molecules through liquid phase adsorption.

2. Experimental

The dahlia-flower type of SWCNH was used in this study. The tube structure was opened before adsorption experiment by oxidation at 823 K in Ar and O₂ mixed gases. The detailed procedure for opening tube of SWCNH is found in our previous report [9]. SWCNH of 0.5 mg was dispersed ultrasonically in iodine-ethanol solution over the iodine concentration range of 0.10 to 60 mg L⁻¹ at 298 K for adsorption measurement. The adsorption isotherm of iodine on SWCNH was determined by measurement of the iodine concentration change using the maximum absorbance at 440 nm with the aid of UV-NIR spectroscopy (JASCO; V-670). The dispersed SWCNH samples were filtered and washed by ethanol to remove any non-adsorbed iodine molecules. The nanoporosity change of SWCNH with iodine adsorption was examined by measurement of nitrogen adsorption isotherm at 77 K with a volumetric apparatus (Quantachrome 3). The nanopore width distribution was evaluated with the DFT method. The structural change of SWCNH with iodine adsorption was examined with field-emission scanning electron microscopy (FE-SEM; JEOL, JSM-6330F) and high resolution transmission electron microscopy (HR-TEM; JEOL, JEM-2100F). X-ray powder diffraction patterns were measured at room temperature using the synchrotron X-ray with a radiation wavelength of 0.09976 nm at the Super Photon Ring (Spring-8, Hyogo, Japan); the powder samples were set in a Lindemann glass capillary of 0.50 mm in an external diameter.

The electronic property change of SWCNH with iodine adsorption was measured through following spectroscopic methods. Raman spectra were obtained using Raman spectrometer (JASCO; NRS-3100) with the excitation laser wavelength of 532 nm (power 0.1 mW). X-ray photoelectron spectra were measured with X-ray photoelectron spectrometer (JEOL; JPS-9010MX) using monochromatized MgK α

radiation. The optical absorption spectra were measured using UV-Vis-NIR microspectroscope (JASCO, MSV-370). The fabrication of SWCNH and iodine-adsorbed SWCNH films was carried out by dip-coating method in order to measure the electrical conductivity, where the SWCNH and iodine-adsorbed SWCNH dispersions were coated on polyethylene terephthalate (PET) substrate. The sheet resistance at room temperature was measured using a four-point probe method [20,21].

3. Results and Discussion

3.1. Iodine adsorption on SWCNH

The iodine adsorption isotherm on SWCNH at 298 K is shown in Fig. 1. The adsorption isotherm of iodine on SWCNH is Langmuirian. Iodine adsorption is almost saturated around 15 mg L⁻¹ of iodine concentration, indicating the presence of a specific interaction between iodine and SWCNH. The saturated adsorption amount is 185±10 mg g⁻¹, corresponding to the maximum surface coverage of 0.18 using the molecular complex model. The surface coverage calculated with the molecular complex model was used in this paper after the preceding article [19].

3.2. Morphology and nanopore structural changes on iodine adsorption

The SEM images of SWCNH and iodine-adsorbed SWCNH are shown in Fig. 2. It shows the spherical forms of SWCNH assemblies with the uniform size. The SWCNH particles associate each other to give rise to a jelly like structure of many voids. After iodine adsorption, the morphological structure of SWCNH tends to be more dense, whereas possibly iodine should be adsorbed in the interfacial spaces of SWCNH assemblies to strongly bind SWCNH assemblies. Fig. 3 shows TEM images of SWCNH and iodine-adsorbed SWCNH (coverage 0.18). The horn and single wall structures in SWCNH particles are clearly shown in Fig. 3a; there are many kinks in the SWCNH particles, indicating the presence of morphological defects. The TEM image of iodine-adsorbed SWCNH (coverage of 0.18) is close to that of SWCNH. As SWCNH is more defective than SWCNT, it is difficult to observe directly the adsorbed iodine in the internal tube space of SWCNH as reported for SWCNT [22,23].

The X-ray diffraction pattern of SWCNH showed the peaks originating from the graphite-like

structure (SI-Fig. 1). The broad peak at 14.2° typically derived from the aggregate structure of SWCNH. The diffraction peaks at $2\theta = 16.8^\circ$, 27.8° , and 48.5° coming from the residual graphites of SWCNH were assigned to the reflections from the graphite lattice planes of (002), (10), and (11), respectively [29-31]. The XRD pattern of iodine-adsorbed SWCNH did not show any patterns coming from adsorbed iodine, indicating that iodine molecules do not form fine crystals on SWCNH. In case of oxidized SWCNH, the predominant adsorption sites were internal tubes spaces and interstitial spaces among SWCNH tubes [32,9]. Therefore, it can be suggested that some iodine molecules are adsorbed in the internal tubes spaces and/or interstitial spaces. The decrease of X-ray scattering below $2\theta=10^\circ$ on iodine adsorption should be ascribed to adsorption of iodine molecules in the internal tube and/or interstitial spaces.

The nanoporosity changes of SWCNH affected by iodine adsorption can be determined from the adsorption isotherm of nitrogen at 77 K, as shown in Fig. 4. Here, the abscissa of Fig. 4b is expressed by the logarithm of P/P_0 . The iodine adsorption decreases the nitrogen adsorption amount over the whole pressure ranges, in particular, below the $P/P_0 = 10^{-3}$. Then, the nitrogen adsorption in nanopores of SWCNH with iodine molecules should be partially blocked. Consequently, the iodine adsorption also reduces the surface area as well as nanopores volume of SWCNH, as listed on the table 1. The pore width distribution clearly shows that SWCNH without adsorbed iodine has a sharp distribution of micropores pore width of < 2 nm and a portion of mesopores with pore width of 2 to 4 nm, evaluated by the DFT method (Fig. 5). The iodine adsorption (coverage 0.18) induces a notable decrease in micropore volume; broadening the pore width distribution. Accordingly, iodine molecules should partially block the interstitial and/or internal tubes spaces of the SWCNH assemblies, as indicated by the X-ray scattering. The blocking mechanism can be also supported by the large decrease in micropore volume of 0.10 mL g^{-1} on iodine adsorption compared with the possible exclusion volume of 0.02 mL g^{-1} by iodine molecules. An illustration of iodine adsorption on SWCNH is shown in Fig. 6. As SWCNH has diameter range of 2 to 4 nm, the iodine atoms having small atomic size (0.25 nm^2) are possibly adsorbed on the holes and in the interstitial and/or internal tubes spaces of SWCNH.

3.3. Electronic properties of iodine-adsorbed SWCNH

The Raman spectra of SWCNH and iodine-adsorbed SWCNH in the frequency range of 1100 – 1800 cm^{-1} is shown in Fig. 7. The spectrum of SWCNH (Fig.7a) exhibits two typical bands at 1335 and 1591 cm^{-1} corresponding to the disorder feature and tangential modes, which are assigned to D and G bands, respectively[2]. An additional weak band at 1618 cm^{-1} stems from defective graphene wall and oxygen terminated holes resulted from the oxidation treatment. Saito et al. reported that the broader weak signal around G band is assigned to dispersive phonon mode activated from defective structure. Accordingly, the peak located at 1618 cm^{-1} could be assigned to phonon mode, generally indicated as D' band [24-25]. Iodine adsorption does not affect significantly the D and G bands. Probably Raman bands of SWCNH having many defects are not sensitive to adsorption, compared with SWCNT. However, iodine adsorption decreases the G-band intensity and the G/D ratio, as shown in Table 2.

The optical absorption spectra provide an explicit information on electronic structure in case of SWCNT. However, SWCNH is highly defective compared with SWCNT as understood from an intensive D band in the Raman spectrum and thereby we could not observe the interband transitions similar to those of SWCNT. Also any optical absorption peak coming from charge transfer between iodine and SWCNH was not observed (SI-Fig.2). This should stem from the absence of the van Hove singularity in the electronic structure of SWCNH.

The modification of electronic structure induced by the charge transfer interaction between SWCNH and iodine molecules should lead to the change of the electrical conductivity of SWCNH. Fig. 8 shows the dc electrical conductivity change of SWCNH with iodine coverage. The electrical conductivity of SWCNH proportionally increases with the iodine adsorbed concentration. Urita et al. reported that oxidized SWCNH showed p-type semiconductivity, while original SWCNH had n-type semiconductivity. Therefore, SWCNH used in this study must exhibit p-type semiconductivity and thereby the majority carriers are holes. The electron transfer from SWCNH to the acceptor iodine molecules should create the hole-carriers, enhancing the electrical conductivity. The increase of electrical conductivity of SWCNH indicates the charge transfer interaction between SWCNH and iodine

1 molecules [14]. Fig. 9 demonstrates the I 3d X-ray photoelectron spectra of SWCNH and iodine-
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3 adsorbed SWCNH. Iodine-adsorbed SWCNH exhibits a very broad I 3d peak at around 620 eV and
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5 thereby we could not observed the clear chemical shift corresponding to the above electrical
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7 conductivity change. As the peak intensity of I 3d proportionally increased with the iodine coverage, the
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9 XPS examination guarantees the adsorption of iodine on SWCNH.
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12 13 4. Conclusion 14

15 The enhancement of dc electrical conductivity verified the electronic properties change of SWCNH
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17 with iodine adsorption. Iodine molecules partially hindered the interstitial spaces and/or internal tubes
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19 spaces of the SWCNH assemblies, reducing the surface area as well as micropore volume. The presence
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21 of the I 3d XPS confirmed that iodine molecules were adsorbed on SWCNH.
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Table 1. Specific surface area and nanopores volume

Sample	S_{BET} [m ² g ⁻¹]	S_{α_s} [m ² g ⁻¹]	V_{α_s} [cm ³ g ⁻¹]
SWCNH	1320	1420	0.49
Iodine adsorbed SWCNH	1070	1160	0.39

S_{BET} = BET surface area; $S_{\alpha} = \alpha_s$ surface area; V_{α_s} = micropore volume

Table 2. The G/D ratio of Raman spectra of SWCNH with different iodine coverage

Iodine coverage	G/D
0	0.96
0.10	0.91
0.18	0.89

Fig. 1. The adsorption isotherm of iodine on SWCNH at 298 K

Fig. 2. SEM images of SWCNH (a) and iodine-adsorbed SWCNH with coverage of 0.18 (b)

Fig. 3. TEM images of SWCNH (a) and iodine-adsorbed SWCNH with coverage of 0.18 (b)

Fig. 4. Adsorption isotherms of nitrogen at 77 K on SWCNH (•), iodine-adsorbed SWCNH with coverage of 0.18 (○); linear plot (a) and logarithm plot (b)

Fig. 5. Pore width distribution of SWCNH (●) and iodine-adsorbed SWCNH with coverage of 0.18 (○)

Fig. 6. Adsorption model of iodine on the nanohole and in the interstitial and internal tube spaces of open SWCNH. (a):Before adsorption, (b) : Iodine-adsorbed SWCNH

Fig. 7. The Raman spectra of SWCNH (a) and iodine-adsorbed SWCNH with coverage of 0.10 and 0.18, respectively (b,c).

Fig. 8. DC electrical conductivity change of SWCNH with various iodine coverage

Fig. 9. The I 3d peak of X-ray photoelectron spectra of SWCNH (a) and iodine-adsorbed SWCNH with coverage of 0.10 and 0.18, respectively (b,c).