

Electronically Modified Single Wall Carbon Nanohorns with Iodine Adsorption

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Abstract

Tailoring of electronic properties of single wall carbon nanohorn (SWCNH) is expected to develop their application potential in various fields. SWCNH is efficiently modified with iodine molecules by liquid phase adsorption. Iodine adsorption isotherm on SWCNH was Langmurian with the saturated adsorbed amount of $185\pm 10 \text{ mg g}^{-1}$ (coverage 0.11-0.18). Iodine adsorption induced the electronic properties change of SWCNH through charge transfer interaction, which is verified by **higher frequency shifts of D, G and D' bands of Raman spectra** and the increase of the electrical conductivity of SWCNH with iodine adsorption.

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 of electronic properties of SWCNT to develop fascinating materials with potential 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 similar structure to a pudgy tube with closed caps with an average cone angle of 20° . The diameter of tubular part of SWCNH is 2-4 nm with length of 40–50 nm. SWCNH particles associate to form spherical aggregates such as dahlia-, bud-, and seed-types [6,7]. The tube space of SWCNH is closed in the as-grown state. The hole-opening through heat treatment in oxygen atmosphere significantly increases the surface area and pore volume, widening the applications [8]. 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 response of SWCNH from n-type to p-type semiconductivity [9]. 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 [10]. 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 [11]. 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 [12-14]. 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 [15]. Gotovac et al. showed that adsorption from solution was simple and efficient method to modify the property of SWCNT [16,17]. Iodine adsorption on SWCNT

in the solution is a promising method [18]. Adsorption study of iodine on SWCNH having defective nature should provide a valuable guideline for the electronic structure control of single wall nanocarbon families. This article describes that iodine molecules are adsorbed on SWCNH with charge transfer interaction in liquid phase adsorption.

2. Experimental

The dahlia-flower type SWCNH was used in this study. The tube structure was open before adsorption experiment by oxidation at 823 K in Ar and O₂ mixed gas atmosphere. The detailed procedure for openings of SWCNH is found in our previous report [8]. 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 dispersion was filtered and washed by ethanol to remove any non-adsorbed iodine molecules. The nanoporosity change of SWCNH by iodine adsorption was examined by nitrogen adsorption isotherm measurement at 77 K with a volumetric apparatus (Quantachrome 3). The nanopore width distribution was evaluated with the DFT method. Their morphological changes were also investigated using scanning electron microscopy (FE-SEM, JEOL JSM6330F).

The fabrication of SWCNH and iodine-adsorbed SWCNH films were carried out by dip-coating method in order to measure the sheet electrical conductivity change on iodine adsorption, where the SWCNH and iodine-adsorbed SWCNH dispersions were coated on polyethylene terephthalate (PET) substrate. The electronic property changes of SWCNH with iodine modification were measured through following spectroscopic methods. Raman spectra were obtained using Raman spectrometer (JASCO; NRS-3100) with the excitation laser wavelength of 532 nm. X-ray photoelectron spectra were measured with X-ray photoelectron spectrometer (JEOL; JPS-9010MX) using monochromatized Mg K α radiation. 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 Figure 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 iodine adsorbed amount is 185±10 mg g⁻¹. The surface coverage of SWCNH is estimated under the assumption of single iodine molecule and iodine-ethanol molecular complex as the adsorbed model. The surface coverages are 0.11 and 0.18 corresponding to the adsorption models of single molecule and complex form, respectively.

3.2. Morphology and nanopore structural changes on iodine adsorption

The morphological change of SWCNH on iodine adsorption is 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 gelly 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 bind SWCNH assemblies more strongly. 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. 3. Here, the abscissa of Fig 3b is expressed by logarithm of P/P₀. The iodine adsorption decreases the nitrogen adsorption amount over the whole pressure ranges, in particular, below the P/P₀ = 10⁻³. Then, the fractional hindering of SWCNH nanopores in smaller pores of SWCNH with iodine molecules should be induced. The iodine adsorption also reduces the surface area as well as nanopore volume of SWCNH, as listed on the table 1. The pore width distribution predominantly shows that SWCNH without adsorbed iodine has a sharp distribution of micropores having pore width of < 2 nm and a portion of mesopores with pore width of 2 to 4 nm, calculated by the DFT method (supporting information). The iodine adsorption gives rise to a notable decrease in micropore volume; the sharp distribution transforms into the broad one with the iodine adsorption. Accordingly, iodine molecules should partially block the interstitial and internal pore spaces of the SWCNH assemblies.

3.3. Electronic properties of iodine-adsorbed SWCNH

The electronic property change of SWCNH with the iodine-adsorption treatment was studied by Raman spectroscopy. A series of Raman spectra of SWCNH and iodine-adsorbed SWCNH in the frequency range $1100 - 1900 \text{ cm}^{-1}$ is shown in Fig. 4. The band of Raman spectrum was deconvoluted by Lorentzian function. The spectrum of SWCNH (Fig. 4a) exhibits two characteristic bands at 1329 and 1575 cm^{-1} , corresponding to the disorder-induced feature and tangential modes, which are assigned to the D and G bands, respectively [2]. An additional weak band at 1604 cm^{-1} stems from defective graphene wall and oxygen terminated holes resulted from the oxidation treatment. The defective structure can activate the Raman scattering of phonon mode [19]. Saito et al. was theoretically studied the intrinsic modes of graphite and SWCNT with double resonance Raman method. They reported the broader weak signal around G band is assigned to dispersive phonon mode. Accordingly, the peak centered at 1604 cm^{-1} could be assigned to phonon modes, usually denoted as the D' band [24].

Figure 4b-e show the Raman spectra change of SWCNH with various iodine coverage, whereas the higher frequency shifts of D, G and D' band gradually increase with the enhancement of iodine coverage. A detailed of band shift is listed in the Table 2. These shifts indicate the increase of disorder and defect structure of SWCNH with iodine molecules, which reflect to the notable modification of electronic structure of SWCNH upon iodine adsorption. Bandow et al. was investigated the charge transfer in halogen (Br_2) doped SWCNH. They found that the higher frequency shift in band position upon acceptor doping is reflected to the important effect of the C-C bond contraction upon removal of electrons from the graphene wall [11]. Consequently, the observed higher frequency shift indicates charge transfer from the graphene wall of SWCNH to iodine molecules.

The charge transfer interaction between SWCNH and iodine molecules should lead to the change of the electrical conductivity of SWCNH. Figure 5 shows the dc electrical conductivity change of SWCNH with iodine surface coverages. The electrical conductivity of SWCNH proportionally increases with the surface coverage. 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, as observed. The remarkable increase of electrical conductivity of SWCNH indicates the intensive charge transfer interaction between SWCNH and iodine molecules [13], agreeing with the Raman spectroscopic results.

Figure 6 shows the C 1s and O 1s X-ray photoelectron spectra deconvoluted by the Gaussian-Lorentzian mixed function after background subtraction with the Shirley method. The C 1s peak of SWCNH has the strongest peak at 284.3 eV assigned to carbon double bonding (sp^2 carbon) and the sub-peak at 285.4 eV corresponding to the single carbon bonding (sp^3 carbon). Other sub-peaks in the relatively high binding energy region are assigned to the carbon oxide groups as C-O, C=O, and COO at 286.2, 287.1 and 289.0 eV, respectively [23]. **Iodine adsorption changes the peak position of C=C and C-C by 0.1 eV and C-O by 0.2 eV.** The relative intensity of these peaks varies slightly on the iodine adsorption. The sp^2 carbon/ sp^3 carbon and C/O ratios of SWCNH are slightly smaller than those of iodine adsorbed SWCNH (Table 3). As the sp^3 carbon is mainly associated with included in the surface oxygen groups, adsorption of iodine on the surface functional group should shield the sp^3 carbon, inducing the decrease of the peak intensity of the sp^3 carbon. The above XPS results indicate that iodine molecules can interact with the oxygen functional groups of SWCNH in addition to the interaction of iodine with the conjugated π -electron frame. The O 1s peak supports clearly the presence of oxygen functional groups illustrated by two deconvoluted peaks, which are assigned to oxygen single bonding of C-O at 533.8 eV and double bonding of C=O at 532.4 eV [22,23]. These data support the above discussion.

4. Conclusion

Raman spectroscopic and electrical conductivity data evidence the charge transfer interaction between iodine and SWCNH. Iodine molecules should be mainly adsorbed on the graphene-like walls. X-ray photoelectron spectroscopic examination showed that some of iodine molecules are adsorbed on the

surface functional groups. Surface modification of SWCNH using liquid phase iodine adsorption can control efficiently the electronic properties control of SWCNH.

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

Figure 2. SEM images of SWCNH (a) and iodine-adsorbed SWCNH (b)

Figure 3. Adsorption isotherms of ●: SWCNH, ○: iodine-adsorbed SWCNH

Figure 4. The deconvoluted Raman spectra of SWCNH (a) and SWCNH with various iodine surface coverages of 0.05, 0.10, 0.14, and 0.18, respectively (b-e).

Figure 5. DC electrical conductivity change of SWCNH with iodine surface coverages

Figure 6. The deconvoluted C 1s and O 1s of X-ray photoelectron spectra of SWCNH (a,c) and iodine-adsorbed SWCNH (b, d).

Table 1. Specific surface area and nanopores volume

Table 2. The peak shift of Raman spectra of SWCNH with various iodine coverages

Table 3. Peak intensity ratio of sp^2 carbon/ sp^3 carbon and C/O ratios determined from XPS

Figure 1.

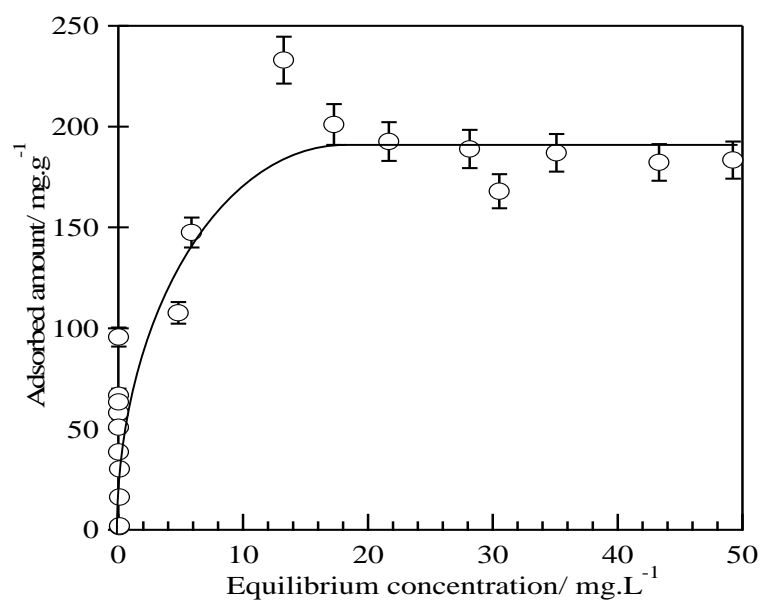


Figure 2

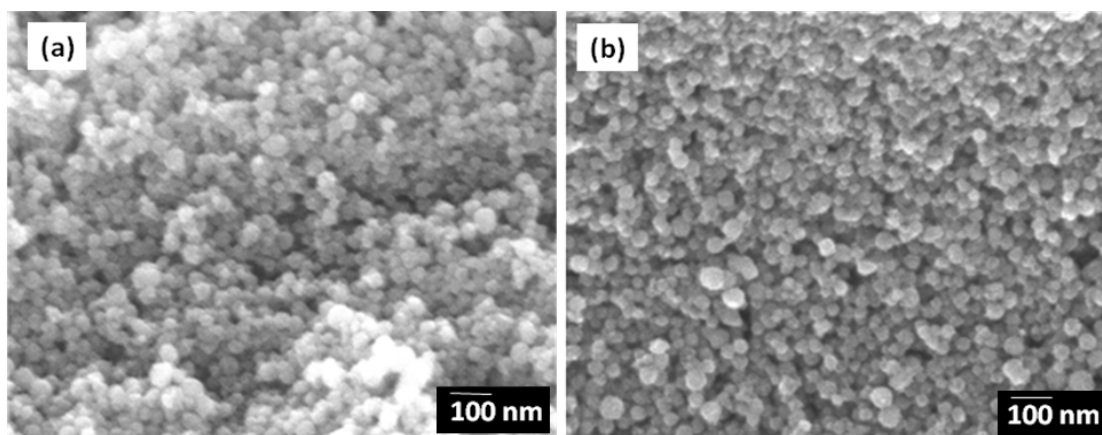


Figure 3

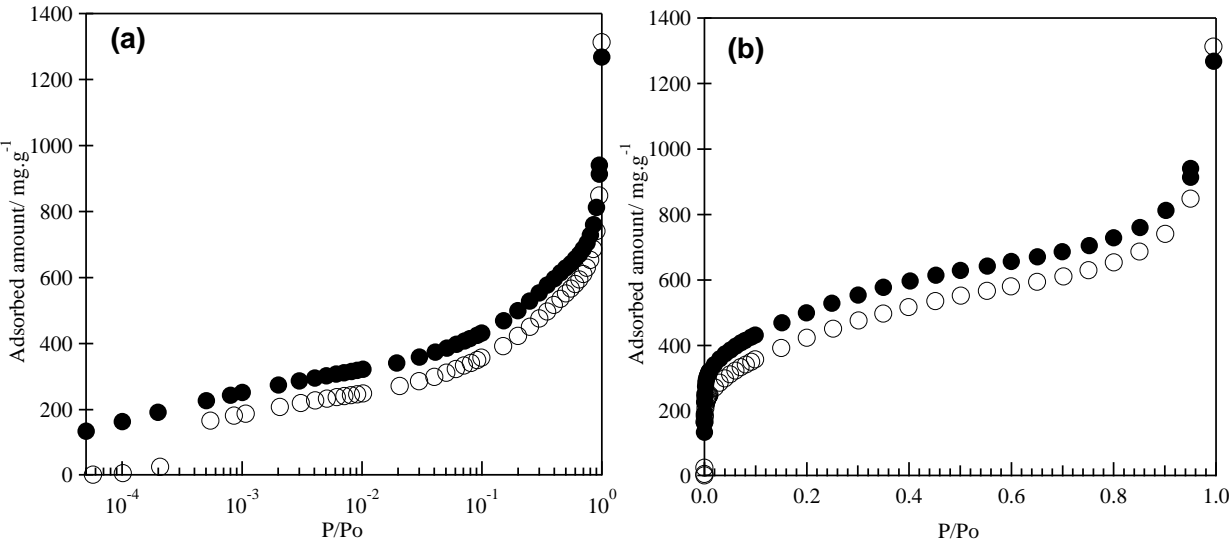


Figure 4

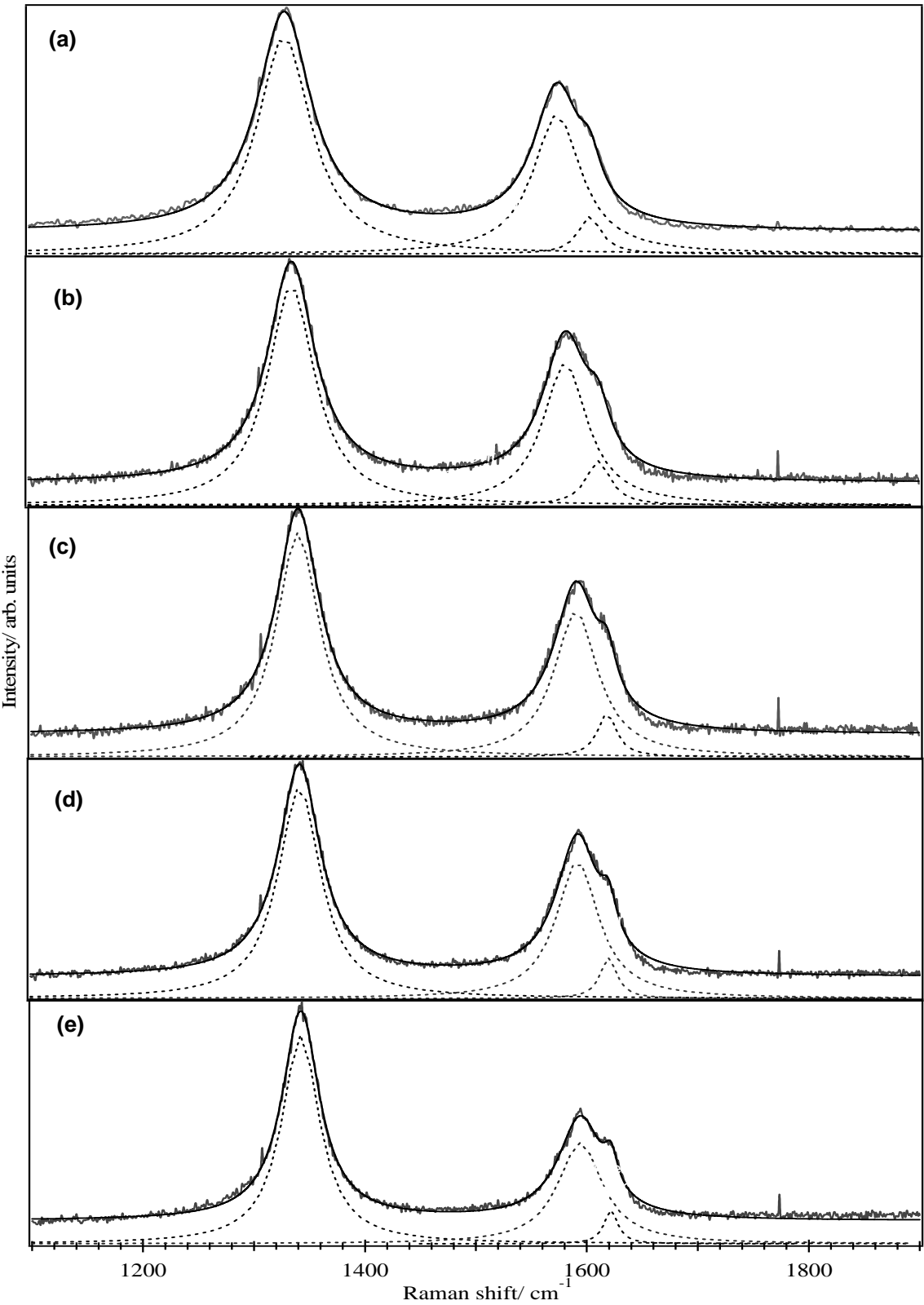


Figure 5

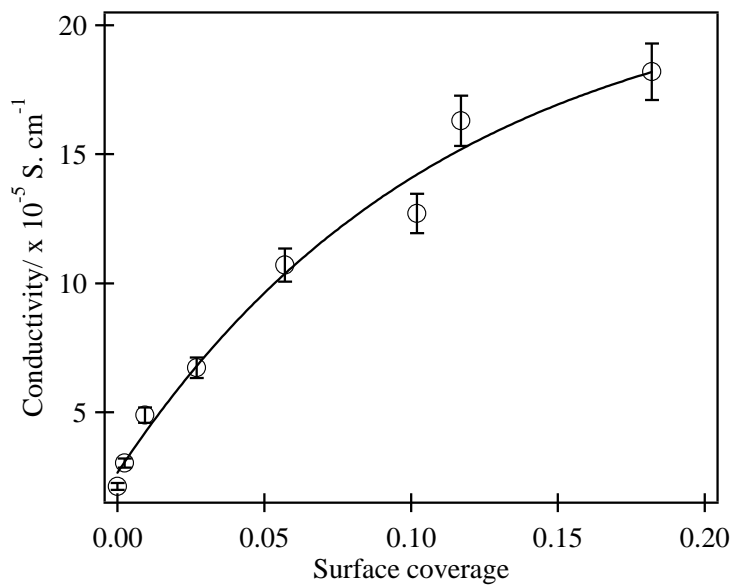


Figure 6

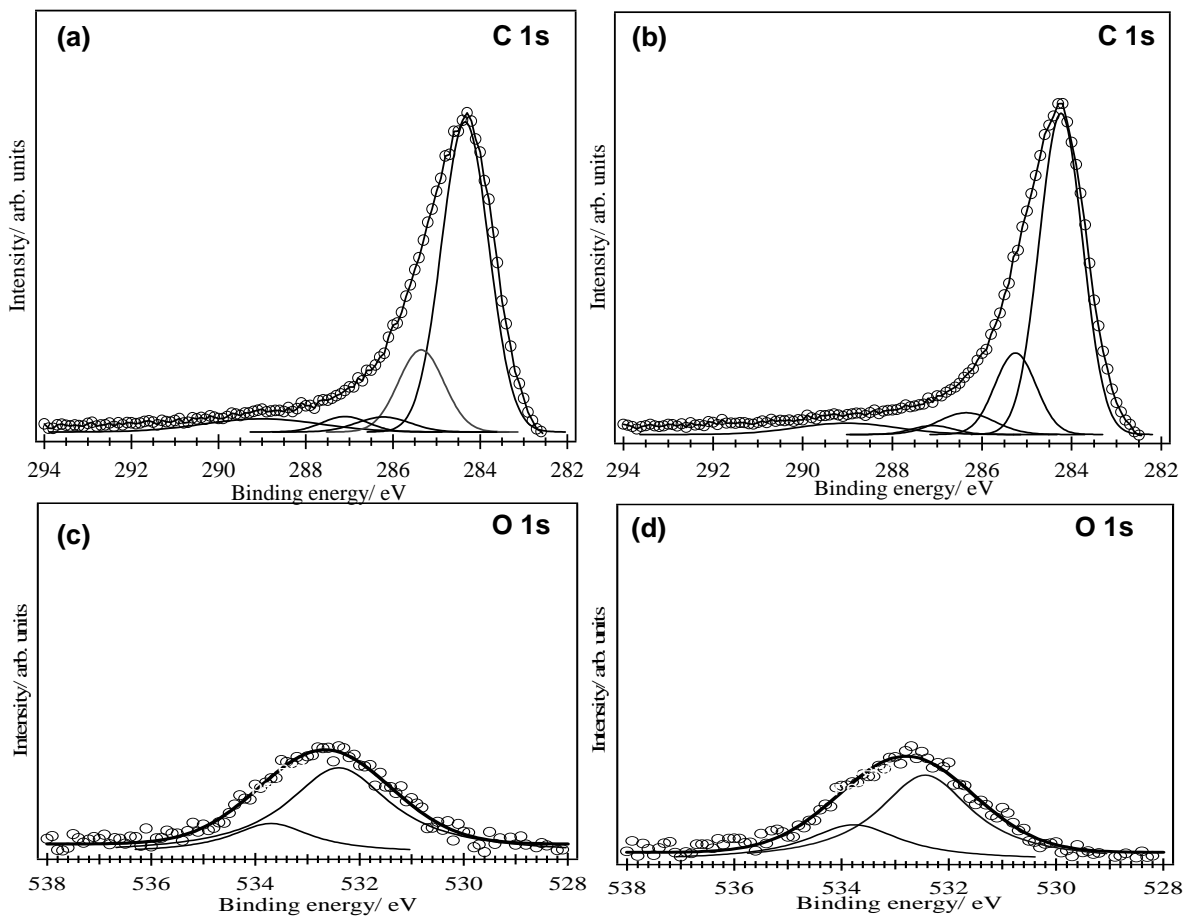


Table 1. Specific surface area and nanopores volume

Sample	S_{BET} [m ² g ⁻¹]	S_{α_s} [m ² g ⁻¹]	V_{α_s} [cm ³ g ⁻¹]
SWCNH	1300	1470	0.47
Iodine adsorbed SWCNH	1050	1090	0.37

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

Table 2. The peak shifts of Raman spectra of SWCNH with various iodine coverages

Iodine coverage	D band (cm ⁻¹)	G- band (cm ⁻¹)	D' band (cm ⁻¹)
0	1329	1575	1604
0.05	1336	1582	1612
0.10	1340	1591	1619
0.14	1342	1592	1620
0.18	1342	1594	1622

Table 3. Peak intensity ratio of sp² carbon/sp³ carbon and C/O ratios determined from XPS

Sample	Atomic ratio	
	sp ² carbon/sp ³ carbon	C/O
SWCNH	3.8	2.8
Iodine-adsorbed SWCNH	4.1	3.0

Supporting information

Pore width distribution calculated by DFT method

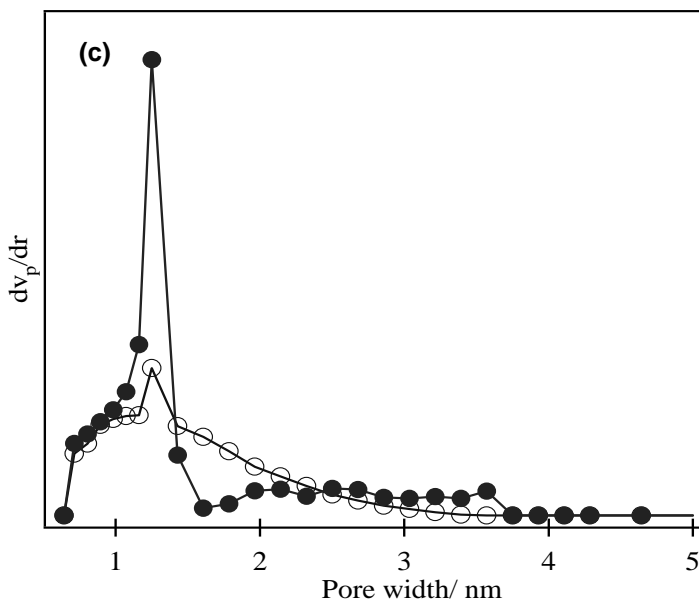


Figure 3.(c) Pore width distribution of SWCNH (●) and iodine-adsorbed SWCNH (○)