GAS ADSORPTION-SENSITIVE ELECTRICAL CONDUCTIVITY OF DEFECTIVE SINGLE WALL CARBON NANOHORNS

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Abstract

We show here electrical responses of the structurally controlled defective single wall carbon nanohorns (SWCNHs) by oxidation or compression treatment on CO_2 and O_2 adsorption. The morphological and porosity changes of defective SWCNHs were measured by high resolution-transmission electron microscopy (HR-TEM), N_2 adsorption at 77 K and Raman spectroscopy. The SWCNH and ox-SWCNH induced a semiconducting behavior and exhibited *n*- and *p-type* like conductivity responses on adsorption of CO_2 and O_2 at 303 K, respectively. Similarly, n-type response of SWCNH was transformed into p-type one with the compression treatment. The dramatic changes of electrical responses from *n-ytpe* to *p-type* nature of SWCNH by compression treatment were ascribed to both an effect of the annihilation of pentagons of a quasi-free electron and reconstruction of individual horn structures.

Introduction

The physical and chemical properties of single wall carbon nanotubes (SWCNTs) have gathered a great attention with the relevance to the nano-structures rolled up a graphen sheet. In particular, elucidation of the physical properties of SWCNT with defective structures has been requested from the viewpoint of designing better catalysts and electronic sensors. As representative defects of SWCNTs are pentagons and heptagons which donate competitive electronic behaviors, it is quite important to investigate the effects caused by structural defects on electrical conductivity upon gas adsorption. Although there have ever been many experimental and theoretical studies about the effect of exposure to gases on the electrical conductivity of SWCNTs, the study of the quantitative relationship between the electrical conductivity and the adsorption amount was far from adequate. Because SWCNTs are produced with metal catalysts, those catalysts must be removed for the study of the electrical conductivity response on gas adsorption. However, it is quite difficult to obtain metal impurity-free SWCNTs to measure the amount of adsorption. Therefore, we focused on SWCNHs without metal catalysts to determine the electrical conductivity responses of impurity-free carbon nanotubilities. SWCNH colloids produced with high purity at a high yield (>90%) have been synthesized by laser ablation of graphite without any catalyst by Iijima et al. A primary SWCNH particle is a tubule with a cone cap like a horn. The average angle of cone cap is 20° and the diameter of the tubular part is 2-4 nm with a length of 30-50 nm. They aggregate with each other to form a colloidal assembly with an 80- nm diameter. In this study, we investigated the electrical responses of the defective SWCNHs structurally controlled by compression treatment on gas adsorption. Also, the structural changes of compressed SWCNH and ox-SWCNH were studied by use of porosity measurements, Raman spectroscopy, and HR-TEM.

Experimental section

We used dahlia-flower-type SWCNH assemblies and ox-SWCNH prepared in oxygen atmosphere at 823 K. The oxidation of SWCNH can provide nano-scale windows (nanowindows) to induce adsorption of gases in the interparticle spaces. A detailed discussion on the procedure for the ox-SWCNH is found in our previous report (Utsumi et al, 2005). Each SWCNH sonicated for 30min in ethanol, dried at 343 K, and then compressed in vacuo under 500 $kgcm^{-2}$ for 10 min. The compression-treating number of SWCNH and ox-SWCNH are denoted by SWCNH/*n* and ox-SWCNH/*n* in this article, respectively. These morphological changes of SWCNH/*n* and ox-SWCNH/*n* caused by the oxidation and compression treatment were observed by a field emission high-resolution transmission electron microscope (HR-TEM: JEOL-4000EX) operated at 400 kV and Raman spectroscopy with the excitation laser wavelength of 488nm (JASCO; NRS-1000). Nitrogen adsorption isotherms at 77 K of the SWCNH/*n* and ox-SWCNH/*n* were measured to evaluate their nanoporosity with gravimetric apparatus. The dc electrical conductivity responses of samples were measured by using van der Pauw method on adsorption of CO_2 and O_2 at 303K.

Results and discussion

We directly observed the structure of SWCNH/*n* and ox-SWCNH/*n* by HR-TEM. The non-compressed SWCNH and ox-SWCNH particles form colloidal assemblies about 80 nm in diameter and the individual units maintain the horn structure. The carbon wall of an SWCNH particle is completely closed. On the other hand, ox-SWCNH particle has a nanowindow in the carbon wall, because there are some pentagons, which should be removed by the oxidation treatment. At the same time, we must note that there are many topological defects, such as kinks, in the wall of SWCNHs compared with SWCNTs. These topological defects should induce the nanowindows. Additionally, these morphological changes make progress by compression treatment. The horn structures in both samples disappeared by increasing the compression-treating number. HR-TEM images indicate ox-SWCNH with nanowindoows caused by oxidation treatment break down easier than SWCNH. Nanopore structure changes of SWCNH without compression treatment, the SWCNH/*n*, and the ox-SWCNH/*n* were examined by N_2 adsorption isotherm at 77 K. The isotherm of the SWCNHs is clearly shown that the compression treatment increased in the nanoporosities of SWCNH/*n.* The high nanoporosities of SWCNH/*n* stem from the mutually packed state of SWCNH assemblies to produce nanopores. However, the nanoporosities of ox-SWCNH/*n* decreased, indicating that the compression treatment induces disappearance of colloidal morphology and reconstruction between nanowindow and the other one. These structural changes were also confirmed by Raman spectroscopy. Raman spectroscopy *provided us important information concerned with the mechanism of the development of defective SWCNHs. Intensity ratios of G-band over D-band in Raman spectra of SWCNH/n were higher than one of ox-SWCNH/n, because the horn structures of ox-SWCNH/n with many nanowindows and defective site break down easily.* The electrical conductivity responses of SWCNH/*2* and ox-SWCNH/*2* on CO_2 and O_2 adsorption were shown in figure 1 and figure 2, respectively. They indicate the electrical conductivity increase and decrease for CO_2 and O_2 adsorption, respectively, were observed for SWCNH/*2*, whereas ox-SWCNH/*2* showed a marked electrical conductivity drop on CO_2 adsorption and almost no change on O_2 adsorption. The dramatically different electrical conductivity response between SWCNH/*2* and ox-SWCNH/*2* should stem from the annihilation of pentagons by oxidation. In compressed samples, we can reveal quite important changes of the electrical conductivity behaviors on CO_2 adsorption. The remarkable changes of electrical responses in both compressed samples are most obvious in low relative pressure. Gas adsorption in inner spaces of SWCNHs may provide the unique electrical conductivity change.

Conclusion

The present study clearly showed morphological changes SWCNH and ox-SWCNH by compression treatment. The changes of electrical sensing property of defective samples for gases suggest the importance of both existence of pentagon and adsorption site. In addition, SWCNHs should be quite helpful to elucidate the role of defective site to electrical behavior in the surface physics in single wall nanocarbons.

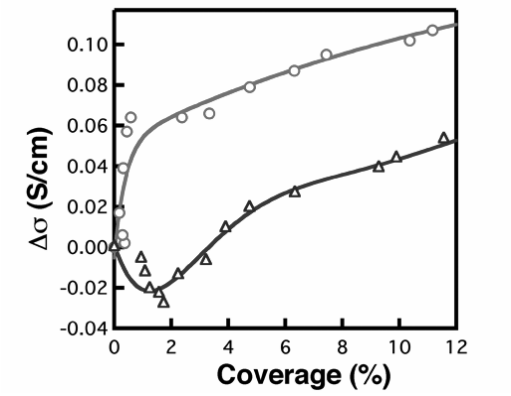

Figure 1. Electrical conductivity changes of SWCNH/*2* (open circle) and ox-SWCNH/*2* (open triangle) on CO_2 adsorption at 303K.

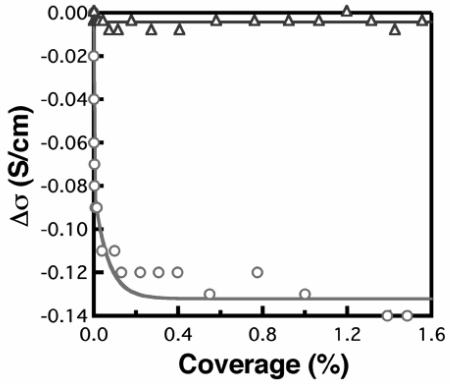

Figure 2. Electrical conductivity changes of SWCNH/*2* (open circle) and ox-SWCNH/*2* (open triangle) on O_2 adsorption at 303K.

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