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EELS Study of Deformed Carbon Nanotube

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EELS Study of Deformed Carbon Nanotube

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Electron energy loss spectrum (EELS) of deformed carbon nanotube was acquired and compared with the density of states calculation to see the influence of the deformation to the electronic structure of the tube. Deformation caused by the external stress was found to change the electronic structure of the tube compared to the straight tube, and it is suggested that EELS could be an interesting tool for characterizing nanoscale structure of carbon nanotubes.

Keywords: Carbon nanotube; EELS; ELNES; Deformation

INTRODUCTION

It is well known that carbon nanotubes have different structural aspects such as various helical pitches, radius, and so on. These structural characteristics determine the interesting and specific physical properties of carbon nanotubes. Studies on the electronic properties of nanotubes, mainly focused on the relation between the helical pitch and the band gap, have proved the potential use of nanotubes as an electronic device material. In using nanotubes as a functional material, we will need some way to control the energy gap. It could be done by controlling the helical pitch while producing the tube which is unrealistic, and another way, which is easier, is to deform the tube to a certain amount to obtain the electronic structure you want.

In this study, EELS observation was carried out to observe the electronic structure of the deformed part of the tube. To relate the structure observed under the electron microscope and the structural model built for different parts of the tube, we have performed the ab-initio molecular orbital calculations, and checked the characteristics appearing in the observed spectra.

EXPERIMENTS

Carbon nanotube was prepared by the common arc discharge method. Graphite electrodes were put in a chamber that was kept under 60 Torr pressure with constant flow of helium gas. Electric current and voltage was 300 A and 25 V, respectively. Nanotubes separated from the core of the rod-like cathodic

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deposit were suspended in ethanol and sonicated to purify as much as possible. The skim was extracted and dried to obtain the nanotubes as a specimen for the TEM observation and EELS acquisition. This experiment was performed on JEM 2010E transmission electron microscope equipped with Gatan PEELS model 666. The energy resolution of the spectrometer was 1.5 eV. We have focused on the energy loss near edge structure (ELNES), which appears at the higher energy loss range of the EELS. ELNES is sensitive to the electronic structure of the atom.

The spectrum of the corrugated part of the tube was obtained from the deeply set part of the corrugation as shown in Fig. 1. To compare with the corrugated part, we also acquired the spectra from the straight part of the tube. The magnification for acquiring the spectrum was chosen so that the area of the entrance aperture of the spectrometer is totally covered by the targeted part, which was a circle of 4 nm diameter at 400k magnification. All the spectra were acquired placing the objective part, deeply set part of the corrugation for example, within the size of the aperture, taking care not to include unnecessary part like the other side of the tube. To avoid the irradiation damage during the acquisition of the spectrum, the beam was not completely converged. By doing so, the acquisition will take about 60 seconds, and the drift of the specimen may occur. Thus, we made sure that the region has not moved before and after the acquisition. We also made sure that the tubes were not damaged by checking before and after the acquisition of the spectra.

RESULTS AND DISCUSSION

The ELNES obtained for the corrugated part, the straight part, inside of the knee-like part of a bent tube are shown in Fig. 2. The diameters of the tubes that we have acquired the spectra were within the range of 15 to 20 nm, with about 20 layers.

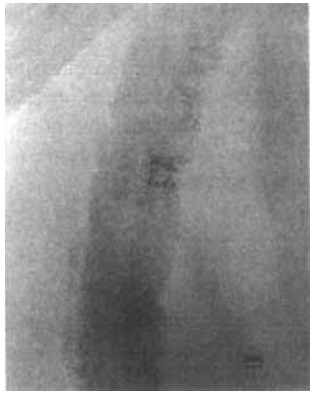

Fig. 1
TEM image of the deformed tube

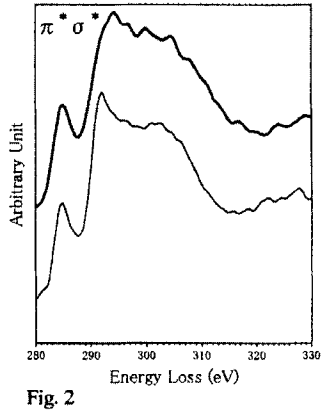

Fig. 2
ELNES of deformed tube (top) and straight tube

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The spectrum of the straight part is very similar to that of graphite, and is consistent with the results reported by other group [1]. The features that can be observed are the peak at 285 eV and the peak of 292 eV, 296 eV, and 303 eV. The 285 eV and 296 eV features comes from π^* symmetry, the 292 eV feature comes from the σ^* symmetry, and the 303 eV feature are assigned to $\sigma^* + \pi^*$ symmetry.

Looking at the spectrum of the corrugated part of the tube, we can find the features different from the straight part at about 300 eV and 305 eV. Looking into the assignment, we can say that the 300 eV feature may be coming from σ^* symmetry and the 305 eV from $\sigma^* + \pi^*$ symmetry.

The dependence of the spectra to the incident angle of the electron/ X-ray beam is especially well known in graphite. Since carbon nanotubes consist of cylindrical form of graphene layers, it is also dependent on the incident angle. But as found in the spectra in the literature [1], we can see that no drastic change, such as strong enhancement of the π^* peak, occurs in the spectra of the nanotubes in the valid region where the main features are apparent. In nanotubes, the ratio of the π^*/σ^* peak is subject to change by the incident angles. In our experiment, the spectra were acquired from larger region (4nm diameter area) compared with other study that uses STEM (sub-nm order area)[1], which results in including various angular regions of the tube. Thus, considering the already small angular dependence of the nanotube and the wide acquisition area, the angular dependence of the specimen in the present study can be considered to be small.

Molecular orbital calculations were performed using 6-31G* basis set. Due to the limited computational resources, we were unable to perform the calculation using the multi-layered model. Instead, we performed the calculations for the single layered tube units taken out from the model shown in Fig. 3. All the ends were terminated with H atoms to reduce the end effects. Since we obtain the *p*-orbital projected density of unoccupied states (*p*-DOS) in a discrete form, to make it comparable to the actual spectra, we have broadened to several extents wider than the energy resolution of the spectrometer.

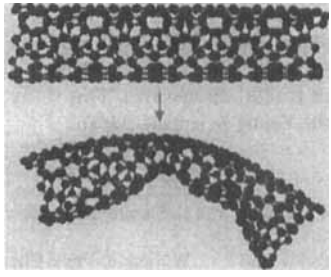

Fig. 3
Model of the (8,2) corrugated tube

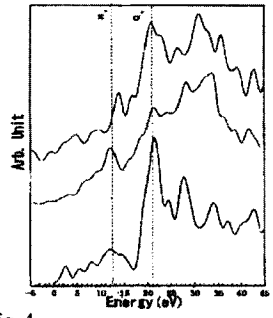

Fig. 4
p-DOS of the corrugated part of the tube (top), H atoms added (middle), and the straight part

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In Fig.4, we show the *p*-DOS obtained from the MO calculations. Obtained result for the straight part was in good agreement with the result obtained by other group [1]. *p*-DOS of straight unit was in very good agreement with that of the flat graphene sheet, and they are consistent with the observed spectrum of the straight part which is reported to have no major difference from the spectrum of graphite. In the calculation, when the corrugation occurs, the ratio of the σ^* peaks becomes different from the straight part. The peak at higher σ^* region became one of the major feature. This is presumably caused by the change of the bonding angle of the carbon atoms. When we explicitly change the bonding state of the atoms at the corrugated region from sp^2 to sp^3 by adding the H atoms, the higher energy σ^* region that was just relatively higher than the lower σ^* region in the non-H added model is much more enhanced. From these results, we can say that the bonding angle and the bonding state of the carbon atoms are the key factor for the enhancement of the higher σ^* region. When we look at the acquired spectrum of the corrugated part, we can find some extra features at the higher energy σ^* region not appearing in the straight part. Considering the *p*-DOS calculations, it is suggested that the strained structure which makes bonding angle change is causing the difference which appears in the higher σ^* region of the spectrum of the corrugated part. From this result, whether explicit change of the bonding state has occurred at the corrugated part or not was unclear possibly due to the limited spatial resolution and energy resolution.

CONCLUSIONS

The difference of the structural aspects of the tube appeared in the σ^* region of the spectra rather than in the π^* region. Whether the specimen is straight or corrugated was recognizable from the spectra.

The evidence of the change of the bonding state of the deeply set part of the corrugated tube was not clear, but according to Botton et.al. [2], the reduction of the intensity of the σ^* feature compared with the straight part might support our model that the bonding state has changed from sp^2 to sp^3 at the corrugated part.

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