IV-I Properties of Gas Adsorption on Single-Walled Carbon Nanotube Aggregates

The discovery and bulk synthesis of single-walled carbon nanotubes (SWNTs) has stimulated great interest as a material of a novel nano-scale electronic devices owing to their unique structure. On the other hand, another intrigunging property of SWNTs aggregates is gas adsorption due to the nature with particularly high surface to volume ratio and correpondingly high coverage. It is well known that actual SWNT aggregates form crystalline bundles arrenged in triangular lattices with a lattice constant of 1.7 nm. If we assume that the diameter of tube is 1.3 nm, two kinds of cylindrical micropores must be exist: one is the intra-tube pore with the diameter about 0.9 nm, and interstitial pore between the tubes (inter-tube pore) with that about 0.3 nm. However, as grown SWNTs are known to be capped at the ends. Cutting is needed to open the capped ends and to enable gas to adsorb in intra-tube pore. The properties of gas adsorption on micropores in SWNTs were studied in this project. ^{129}Xe-NMR were performed for xenon gas adsorbed SWNTs samples both before and after heat treatment. Several kinds of gas adsorption isotherm measurements were also performed for both end-closed (capped) and end-opened (uncapped) SWNTs.

IV-I-1 Properties of Micropores in Single-Walled Carbon Nanotubes Studied by N_2 Gas Adsorption Isotherm Measurements

OGATA, Hironori; KUNO, Shogo[1]; SAITO, Yahachi[1]
([1]Mie Univ.)

The effects of heat treatments on the property of micropores have been studied on SWNTs by means of the N_2 adsorption isotherm measurements. SWNT samples used in this study were synthesized by the dc arc discharge method using non-ferromagnetic Pt-Rh mixed catalyst. Amorphous carbon and nano-graphite particles contained in the raw soots obtained were removed by modified Tohji's procedure using hydrogen peroxide (H_2O_2), as follows: (1) The raw soots was heated at 100 °C for 10 hours in 20% H_2O_2 solution in a flask with reflux attachment to oxidize only the amorphous carbon uniformly. (2) The residual soots were added distilled water and was sonicated for 3 hours and collect the precipitate after leaveing it for 12 hours to separate SWNTs and nano-graphite particles. Procedures (1)–(2) were repeated several times. The purification procedure was monitered and the purity of SWNTs were checked by both Scanning Electron Microscope and Powder X-ray diffraction measurements. The heat treatments were performed at 420 °C for 20 minutes in the dried air. Figure 1 shows the adsorption isotherms of N_2 on the as-prepared (△), after H_2O_2-treated (●) and heat-treated (○) SWNTs at 77 K. The adsorption isotherms are close to type II, which include features of a type I due to micropore fillings. Most distinguished feature is the large increase of the amount of N_2 gas adsorbed at low p/p_0 region. The high resolution α_s-plot analysis revealed that the heat treatment increases the intensity of two upward swings (*f*- and *c*-swing) below $\alpha_s = 1.0$. This fact suggests that the heat treatment leads to the micropore filling and capillary-like condensation inside the tube space.

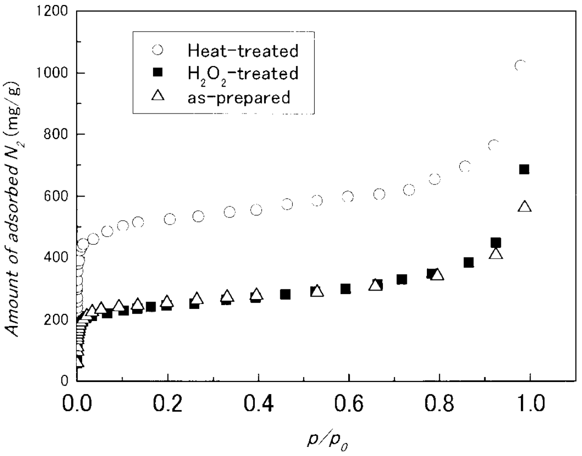

Figure 1. N_2 adsorption isotherms for SWNTs at 77 K.

IV-I-2 Direct Evidence of Xenon Gas Adsorption Inside of Snigle-Walled Carbon Nanotubes Studied by ^{129}Xe-NMR

OGATA, Hironori; KUNO, Shogo[1]; SAITO, Yahachi[1]
([1]Mie Univ.)

It is well known that ^{129}Xe-NMR of xenon gas adsorbed in confined pore is essential way to investigate the pore structure. The most distinctive advantage of this technique is to detect only xenon gas confined in uniform pore and by analyzing the value of ^{129}Xe chemical shift we can get the information about the size of the pore through the value of mean free path of xenon gas. Effects of heat treatments on the micropore structure of SWNTs were studied by ^{129}Xe-NMR for xenon gas adsorbed SWNTs samples. Figure 1 shows the ^{129}Xe-NMR spectra for the xenon gas adsorbed on SWNTs samples before and after treatments. The pressure of xenon gas adsorbed was about 15×10^4 Pa at 296 K for each samples. The reference signal for the chemical shift was set to that of xenon gas extrapolated at zero pressure. One sharp peak at about 1 ppm is contained in raw soots sample (a), which is attributed to be free xenon gas. Weak broad peak is added in soots after H_2O_2 treatment (b). This peak is strongly enhanced after heat treatment (c). Repititive heat treatment, however, decrease this peak intensity ((d): after two times' treatments, (e): after three times' treatments), which is casused by burning down the SWNTs. It was also confirmed by Raman scattering measurements. From the extrapolated value of the ^{129}Xe shift at zero pressure ($\delta(S)$ = 75 ppm) (Figure 2), we can conclude that the broad peak is attribute to the Xe gas confined inside the tube space.

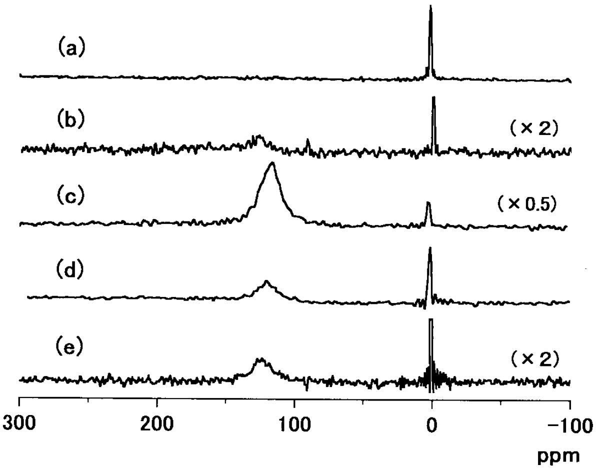

Figure 1. ^{129}Xe-NMR spectra for xenon gas adsorbed SWNTs after various treatments.

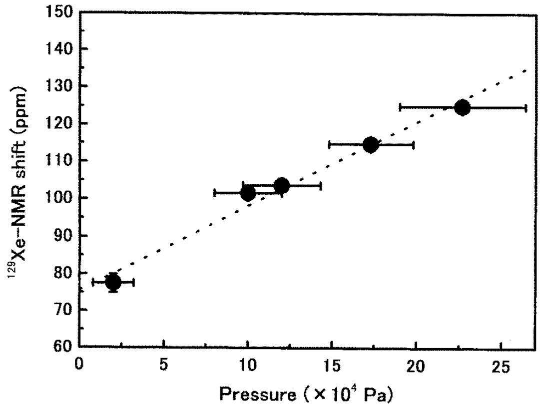

Figure 2. Pressure dependence of the xenon gas on ^{129}Xe-NMR shift for xenon gas adsorbed SWNTs.

IV-J Electronic Properties of Pristine and Doped Snigle-walled Carbon Nanotubes aggregates

^{13}C NMR and Raman scattering measurements were performed for both pristine and doped single-walled carbon nanotubes (SWNTs) aggregates to investigate the electronic structure below 100 K.

IV-J-1 Electronic States of Single-Walled Carbon Nanotube Aggregates Studied by Low Temperature ^{13}C-NMR

OGATA, Hironori; KUNO, Shogo[1]; SAITO, Yahachi[1]
([1]Mie Univ.)

^{13}C-NMR experiments have been carried out for single-walled carbon nanotubes aggregates (SWNTs), which were produced by using non-ferromagnetic Rh-Pt mixed catalysts. Hydrogen peroxide was used to remove amorphous carbon particles in the raw soot almost perfectly. Figure 1 shows the ^{13}C NMR spectrum measured at 10 K. From the line shape analysis, the ^{13}C spectrum is considered to be composed of two components with the shift tensors (δ_{11},δ_{22},δ_{33}) = (194,182,194) ppm and (203,180,52) ppm. To obtain more detailed information about the electronic state of SWNTs, we performed ^{13}C spin lattice relaxation time (T_1) measurement by the saturation-recovery method. The obtained saturation recovery curves could be fit with a double-exponential function: approximately one-third of the ^{13}C-nuclear spins relaxes much faster than the other two-thirds. Temperature dependence of ^{13}C-T_1 found that both components follow a Korringa-like behavior ($T_1 \times T$ = 3100 ± 500 (sec.K) and $T_1 \times T \fallingdotseq$ 12000 (sec.K)) in the temperature region between 4.2 K and 100 K. The fast-relaxing and slow relaxing components are thought to be associated with metallic and semiconducting SWNTs, respectively.

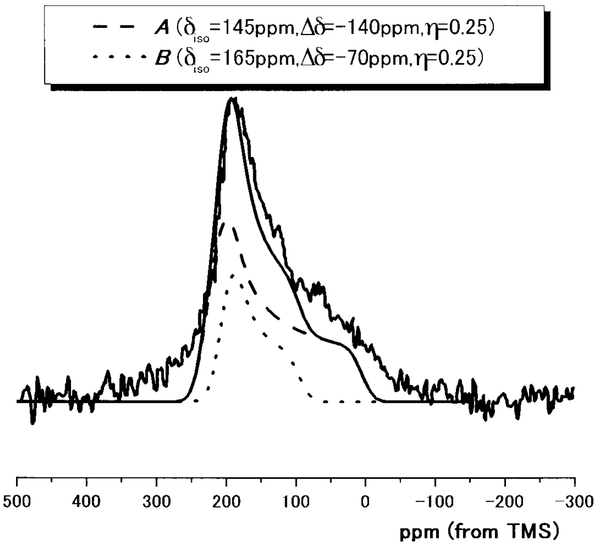

Figure 1. ^{13}C NMR spectrum of SWNTs at 10 K.

IV-J-2 Electronic States of Alkali-Metal Doped Single-Walled Carbon Nanotube Aggregates

OGATA, Hironori; YAKUSHI, Kyuya; KUNO, Shogo[1]; SAITO, Yahachi[1]
(1Mie Univ.)

Electronic states of alkali-metal doped single-walled carbon nanotube aggregates (SWNTs) were studied by both ^{13}C-NMR and Raman spectroscopy. The effects of opening the ends of SWNTs on the intercalation level and the evolution of electronic states were also studied. Dopings of alkali metals were performed for both pristine (capped) and open-ended (uncapped) SWNTs samples by two-bulb method. Raman scattering spectra of the tangentia (E_{2g}) modes of SWNTs showed more downshift by using the SWNTs (uncapped) as a host sample. This result suggests that opening the ends lead to dope inside the tube and achieve higher doping level. Recovery of ^{13}C-magnetization for pristine SWNTs was found to be able to fit with a double-exponential function. On the other hand, single exponential-like curve fitting can be reproduced the data points of ^{13}C-magnetization curve for both K-doped SWNTs samples (Figure 1). Furthermore, The values of spin-lattice relaxation time (T_1) become shorter by K-dopings. Temperature dependence of ^{13}C-T_1 found that both K-doped samples follow a Korringa-like behaviors ($T_1 \times T = 400 \pm 50$ (sec.K) for capped sample and $T_1 \times T = 170 \pm 50$ (sec.K) for uncapped) in the temperature region between 4.2 K and 100 K. This result suggests that cap-opening enables to achieve higher intercalation level. The value of density of states at Fermi level increases three times as much as that of metallic tube for capped sample and four times for uncapped sample by K-doping.

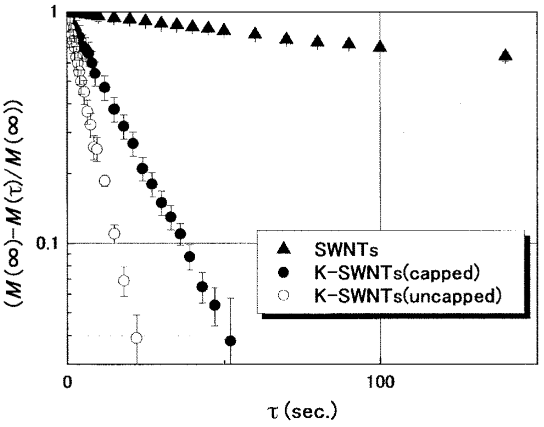

Figure 1. Recovery curve of ^{13}C-NMR for pristine SWNTs (▲), K-doped SWNTs (capped) (●) and K-doped SWNTs (uncapped) (○) measured at 25 K.

IV-J-3 Electronic States of Br_2 Doped Single-Walled Carbon Nanotube Aggregates

OGATA, Hironori; YAKUSHI, Kyuya; KUNO, Shogo[1]; SAITO, Yahachi[1]

([1]Mie Univ.)

Electronic states of Br_2 doped single-walled carbon nanotube aggregates (SWNTs) were studied by both ^{13}C-NMR and Raman spectroscopy. The effects of opening the ends of SWNTs on the intercalation level and the evolution of electronic states were also studied. Doping of Br_2 was performed for both pristine (capped) and open-ended (uncapped) SWNTs samples by measureing the adsorption isotherm of Br_2 *in-situ* in order to controll the doping level and obtain the information on the composition of the doped samples. For both samples, dopings of Br_2 were stopped when the micropore-fillings were completed. The compositions of the samples were evaluated to be (Br/C =) 0.09 for capped sample and 0.2 for uncapped sample. Raman scattering spectra of the tangential (E_{2g}) modes of SWNTs showed more upshift by using the SWNTs (uncapped) as a host sample. This result suggests that opening the ends lead to dope inside the tube and achieve higher doping level. Recovery of ^{13}C-magnetization for both Br_2-doped SWNTs was found to be able to fit with a single exponential-like function (Figure 1). Temperature dependence of ^{13}C-nuclear spins relaxation found that both Br_2-doped samples follow a Korringa-like behaviors ($T_1 \times T = 950 \pm 200$ (sec.K) for capped sample and $T_1 \times T = 1550 \pm 250$ (sec.K) for uncapped) in the temperature region between 4.2 K and 100 K. This result suggests that cap-opening enables to achieve higher intercalation level. The value of density of states at Fermi level increases about 1.8 times as much as that of metallic tube for capped sample and 1.4 times for uncapped sample by Br_2-doping. Decrease in density of states by increase in the doping level is a characteristic nature of the electronic states of SWNTs.

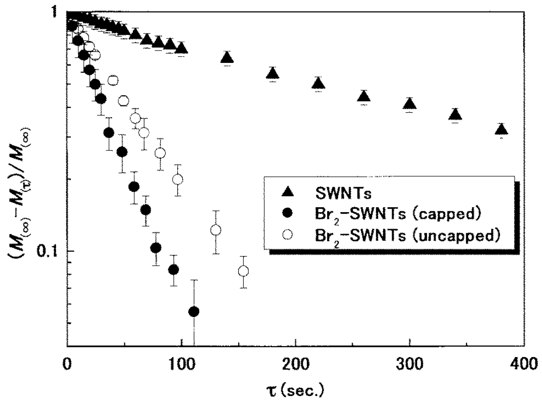

Figure 1. Recovery curve of ^{13}C-NMR for pristine SWNTs (▲), Br_2-doped SWNTs (capped) (●) and Br_2-doped SWNTs (uncapped) (○) measured at 25 K.

IV-K Structural and Electronic Properties of Fullerene-based Compounds

Structural and electronic properties were studied for several types of fullerene-based compounds in this project. Recently, Oszlanyi *et al.* found that Na_4C_{60} forms two-dimensional polymeric phase of body-centered monoclinic (bcm: *I2/m*) at room temperature. The structure and electronic states of Na_4C_{60} polymer phase were investigated by

X-ray powder diffraction, ESR, electric resistivity and solid state ^{13}C-NMR measurements.

IV-K-1 Study on the Physical Properties of Na_4C_{60}

TAKABAYASHI, Yasuhiro[1]; KUBOZONO, Yoshihiro[1]; FUJIKI, Satoshi[1]; KASHINO, Setsuo[1]; ISHII, Kenji[2]; SUEMATSU, Hiroyoshi[2]; OGATA, Hironori
([1]Okayama Univ.; [2]Univ. Tokyo)

The structure and electronic states of Na_4C_{60} polymer phase were investigated by X-ray powder diffraction, ESR, electric resistivity and solid state ^{13}C-NMR measurements. The spin susceptibility determined from ESR showed a rapid increase with a decrease in temperature from 100 to 50 K and a rapid decrease below 50 K. Further, the slope of plots of the peak-to-peak line width, ΔH_{pp}, *versus* temperature changes at 100 K. These results suggest the transformation of a Pauli paramagnetic state around 100 K. The lattice constants, *a* and *b*, determined from temperature dependent X-ray powder diffraction showed a discontinuous change around 50 K, while the *c* shows a continuous variation. The results suggest the structural transition around 50 K which may be associated with the transformation found by ESR. This transition can be attributed to the dimerization due to CDW or Spin-Peierls as in the case of CsC_{60}, because the ESR and the X-ray diffraction suggest the nonmagnetic ground state and the structural transition, respectively. New Bragg diffractions were not found below 100 K as in CsC_{60}. The registivity at 300 K was 6.9×10^3 Ωcm, which is larger than those of K_3C_{60} and Rb_3C_{60}. The temperature dependence of the registivity showed a semiconducting behavior from 300 to 190 K. The band gap energy, E_g, estimated from the registivity was 0.8 eV, which is in agreement with those of K_4C_{60} and Rb_4C_{60}. Figure 1 shows the temperature dependence of ^{13}C-NMR spectrum for Na_4C_{60}. Appearance of a new peak at 70 ppm at low temperature suggests that existence of sp^3-like carbon in this compound. Temperature dependence of ^{13}C-nuclear spin-lattice relaxation time didn't follow a Korringa-like behavior in the temperature region between 300 K and 4.2 K, which suggests a non-metallic behavior for Na_4C_{60} polymer.

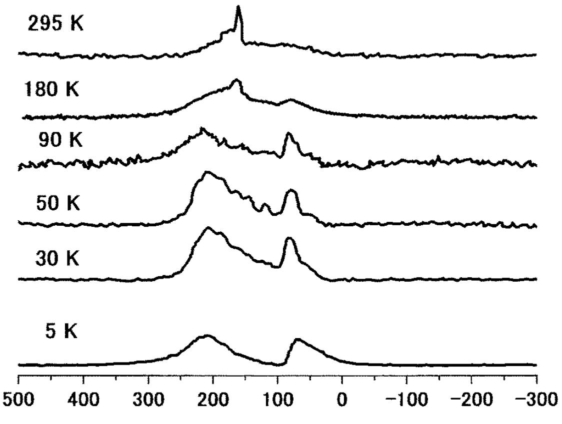

Figure 1. Temperature dependence of ^{13}C-NMR spectrum for Na_4C_{60} polymer.