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K-doping into the aggregate of single-wall carbon nanohorns (SWNHs) and into the bundle of single-wall carbon nanotubes (SWNTs) are introduced in this study. Electron spin resonance (ESR) of the pristine SWNHs and SWNTs show that the pristine SWNHs are ESR active and the linewidth (ΔH) is susceptive to the partial pressure of O_2, while the pristine SWNTs are ESR silent. ΔH of K-doped SWNHs becomes wider by a factor of ~2 than that of the pristine one. For K-doped SWNTs, the Dysonian type ESR comes to be observed. Details of the ESR features are discussed.

Keywords: electron spin resonance; single wall carbon nanohorns; single wall carbon nanotubes; magnetic susceptibility

INTRODUCTION

The single-wall carbon nanotubes (SWNTs)[1-3] or recently discovered single-wall carbon nanohorns (SWNHs)[4] can be classified into low density materials due to their tubular structures. Especially the SWNHs have unique structural feature represented by

a typical diameter of ~2 nm with a length of ~30 - 50 nm, and an edge region is encapsulated like horn with an average corn angle of 20 degrees[4]. The SWNTs form a bundle structure with a typical bundle diameter of several tens nm and a length of greater than one micrometer. On the other hand, the SWNHs have a tendency to aggregate and to form a *dahlia* like structure. In this paper, the magnetic properties of pristine SWNHs and SWNTs, and also of K-doped SWNHs and SWNTs studied by electron spin resonance (ESR) are introduced.

Single Wall Carbon Nano-Horns (SWNHs)

The SWNHs were prepared by a CO_2 laser vaporization of a carbon target in an atmospheric pressure of Ar gas. The powder x-ray diffraction (XRD) profile of as-prepared SWNHs is shown in Fig. 1,

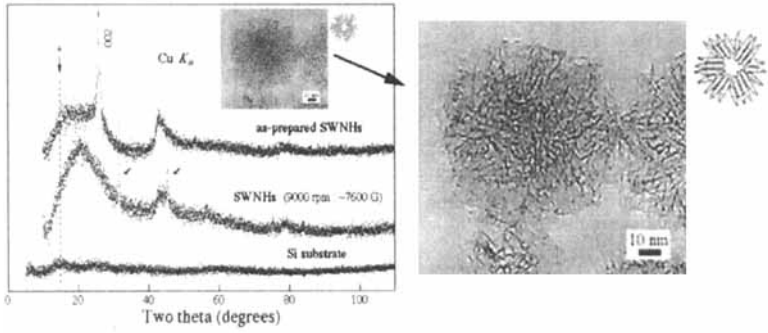

FIGURE 1 X-ray diffraction profiles taken for as-prepared SWNHs and centrifugally separated SWNHs. The samples were put on the Si substrate. No 002 diffraction of graphite is detected in the centrifugally separated SWNHs. Sharp diffraction peaks (indicated by arrows) detected in the SWNHs are unknown. A weak peak indicated by * is from the Si substrate.

which shows 002 ordinary graphite diffraction peak, indicating the existence of impurity carbons in the sample. Removal of these impurity carbons can be achieved by the centrifugal separation using

a colloidal suspension of soot: Briefly, ~1 mg of as-prepared SWNHs was suspended in a 30 ml of ethanol by sonication, and the liquid thus prepared was spun at 9000 rpm (~7600 g, where g is the gravity) for 30 min. Then the suspension liquid above sediment was decanted and dried. The XRD profile from thus purified SWNHs is in Fig. 1 which shows no 002 diffraction peak, but showing a huge broad peak at $2\theta \sim 21$ degrees. This broad peak should originate from the double layer diffraction associated with the nearest C-C distance between SWNHs. The electron micrograph(s) and schematic illustration in Fig. 1 indicate typical SWNH aggregate(s).

The pristine SWNHs were ESR active and the lineshape was changed by changing the O_2 pressure as indicated in Fig. 2. At 1

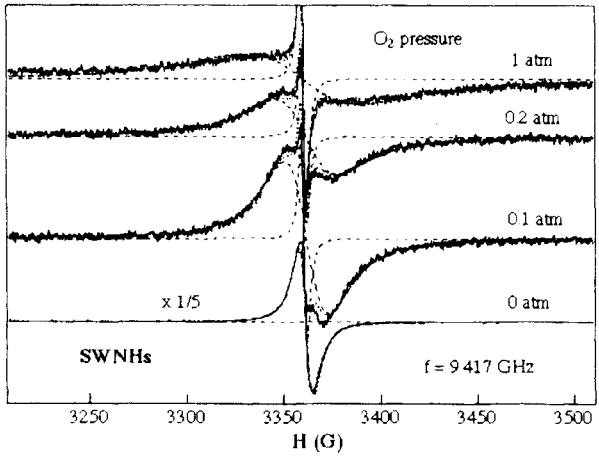

FIGURE 2 ESR spectra taken at various pressures of O_2.

atmospheric pressure of O_2, two ESR lines can be observed. The linewidth (ΔH) of broader ESR depended on the O_2 pressure, while ΔH of narrower one did not depend on the O_2 pressure. The pressure dependence of ΔH was neither observed in N_2 nor in He gas. Furthermore, in air, the magnitude of ΔH was almost the same as that

in 0.2 atm of O_2, which suggests that ΔH can be represented by a function of the O_2 pressure. The integrated ESR intensity, *i.e.*, spin magnetic susceptibility χ, of the broad ESR did not depend on the O_2 pressure, indicating that the ESR does not originate from spurious adsorbent materials.

Temperature dependences of ΔH, g-value and χ were measured in the temperature range between 100 and 560 K (see Fig. 3). Although ΔH of pristine SWNHs decreased with decreasing temperature (T), a small terrace was observed in the temperature range between ~200 and 250 K (see the closed circle in Fig. 3 (a)). Physical meaning of this terrace is not clear. The g-value was almost constant with g = 2.0019 ± 0.0001 (see the open circle in Fig.3 (a)). The χ behaved like Curie when T < ~400 K (see the closed circle in Fig. 3 (b)). However, the χ became almost constant when T > ~400 K. Such a temperature dependence of χ may be explained by the thermal excitation of the electrons from the localized spin state to the conduction state at high temperatures. The origin of such a localized spin state is not clear, but it probably stems from the electronic state of pentagons at the tip of the SWNH since 5 pentagons are necessary at the edge region of SWNH to explain the 20 degrees corn angle [4].

K-doping into SWNH aggregates was carried out by the hot vapor method using a 5 mm in diameter ESR tube; 1.88 mg of purified SWNHs was set at one end of the ESR tube and K vapor was transferred in vacuum in order to condense at the other end of the ESR tube (~20 cm apart from the SWNHs). In prior to seal the ESR tube, the sample was evacuated for 5 hours by the diffusion pump. The sample tube thus prepared was set into the double furnace. The temperatures of SWNHs and K were elevated, respectively, to 513 K and 473 K and kept for 660 hours. By the doping, the g-value at 300 K was increased from 2.0019 to 2.0026 (see the circle with cross in Fig. 3 (a)). Temperature dependence of ΔH (indicated by the closed diamond in Fig. 3 (a)) showed slightly steeper slope than that of

pristine one, and no terrace-like structure was detected. The Curie constant decreased by ~26 % after the doping (see Fig. 3 (b)). This decrease of Curie constant should be a result of the interaction between the electron spin of SWNH and of K.

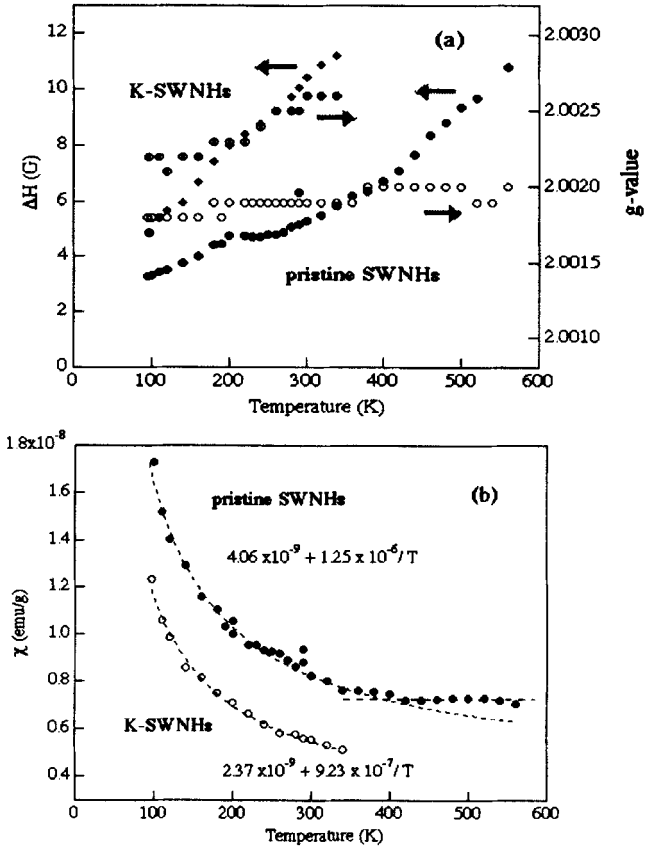

FIGURE 3 Temperature dependences of ESR features taken for pristine and K-doped SWNHs. Spin susceptibility derived from the integrated ESR intensity is represented by χ.

Single Wall Carbon Nano-Tubes (SWNTs)

The SWNTs were prepared by a pulsed Nd: YAG (yttrium aluminum

garnet) laser vaporization[3] of a Co-Ni containing (1.2-1.2 at %) carbon target at 1473 K in a 100 sccm flow of Ar gas (500 Torr). As-prepared soot was immediately introduced to the second furnace set at 773 K by the Ar flux mixed with a 20 % of O_2 gas. In the second furnace, the amorphous carbons and carbon polyhedral nanoparticles are selectively burnt out. The soot passing through the second furnace was almost the SWNTs and metal nanoparticles, latter of which can be removed by soaking in HCl. 0.97 mg of SWNTs thus purified were used for the present study.

The pristine SWNTs was basically the ESR silent, excepting a weak ESR signal with $\Delta H \sim 2.7$ G at $g \sim 2.0026$ (see the top spectrum in Fig. 4), whose spin concentration is estimated at the order of 10^{15} to 10^{16} spins/g. This weak ESR signal might originate from the electronic state of the pentagons at the tip region of the SWNT, which is the same as considered in the SWNH.

Regarding to the conduction electron spin resonance (CESR) of the pristine SWNTs, we could not detect any signal at X-band (9.419 GHz). Here, we try to explain this experimental fact. The magnitude of the local molecular field interacting with the conduction electron spins on the SWNTs will change due to the motion of the electrons winding around the tube, when the magnetic field applied perpendicular to the tube axis[6]. This change of the local molecular field will disturb the Larmor motion of the electron spins. The scattering time of the electron spin (τ_{int}) due to the change of the local molecular field can be estimated by a relation $\tau_{int} \sim l_{int}/v_F$, where l_{int} is the mean free path of the electron, which can be substituted by $\sim \pi d/4$ (d is tube diameter), and v_F is the Fermi velocity. Using d = 1.36 nm and v_F = 1 x 10^6 m/s (from graphite)[7], τ_{int} can be estimated at the order of 10^{-15} s. Therefore, ΔH from τ_{int} is estimated at the range of 10^2 to 10^3 G by using the relation $\Delta H \sim (\Delta g)^2 \hbar/(2\sqrt{3}\, g\, \mu_B\, \tau_{int})$[8], where Δg is the g shift from the free

electron value and is estimated at 10^{-2} order since g value of the in-plane conduction for graphite is 2.049, $\hbar$ the Planck's constant divided by 2π and μ_B the Bohr magneton. Therefore, it is reasonable to consider that such a broad ESR is difficult to detect due to the weak magnetism of conduction electrons and the sensitivity limit of instrument.

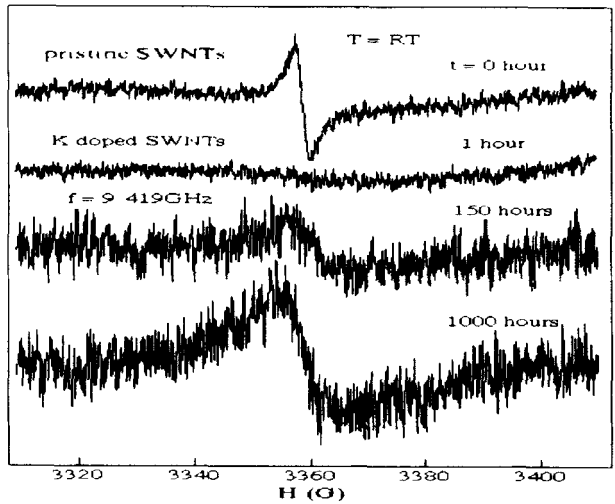

FIGURE 4 ESR spectra taken at various doping times. In pristine SWNTs (t = 0), a narrow ESR signal at g = 2.0026 with ΔH = 2.7 G was detected, which was disappeared after 1 hour doing, and a weak Dysonian type ESR was started to observe after ~50 hours.

Above consideration is for the conduction electrons in a single SWNT, not for those in the bundles. However, even if the individual SWNTs crystallize into triangular lattice and form bundle, the electrons in the tubule have to wind around each tube and thus feel the change of the local molecular field before making the inter-tubular transport. Hence τ_{int} will be the same order of magnitude with that of a single SWNT; ΔH of CESR from the SWNT bundles will also be a very broad one and thus difficult to detect.

The K-doping was carried out by the same method as described in the doping procedure of SWNHs. The weak ESR observed in the pristine SWNTs ($t = 0$) disappeared after 1 hour doping (see Fig. 4). After 50 hours doping, a weak Dysonian type ESR spectrum, which is typical lineshape for CESR, came to be observed. The CESR spectra taken at the doping times of 150 and 1000 hours are indicated in Fig. 4. The intensity of CESR was saturated at the doping time longer than ~400 hours.

No temperature dependence was observed both for ΔH_{pp} (peak-to-peak ΔH of CESR, 12 ± 2 G) and for g-value (2.0022 ± 0.0002) within the experimental error. However, χ increased slightly when the temperature decreased, whose dependence is somewhat different from the usual temperature independent Pauli paramagnetism. The magnitude of χ for K-doped SWNTs was about one order of magnitude smaller than that of the ordinary graphite (~2 x 10^{-8} emu/g at ~300 K)[9]. This small magnitude of χ is possibly based on the nature of the electronic structure for the pristine SWNTs: since two third of the SWNTs are semiconducting under the assumption of random distribution of the tube chirality[10], the decrease of the magnitude of χ is reasonable.

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