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Solution-phase EPR studies of single-walled carbon nanotubes

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Abstract

We report EPR studies on pristine, purified, shortened and soluble SWNTs in various solution phases. Some of these samples give rise to strong, sharp EPR signals, and this technique is useful for monitoring the presence of SWNTs in aqueous and organic solvents. The soluble SWNTs carry about 1 unpaired electron per 10000 carbon atoms and give a free electron *g*-value.

1. Introduction

With unique electronic [1,2] and mechanical [3,4] properties combined with chemical stability, single-walled carbon nanotubes (SWNTs) are receiving a great deal of attention due to their many possible applications — such as reinforced composite materials [5] and nano-scale electronic/optical devices [6]. In order to realize fully the potential of SWNTs, it will be necessary to develop solution-processing techniques and to achieve a full understanding of their solution properties. Virtually all of the previous reports on the properties of SWNTs refer to solid state materials, and this has hindered the development of the chemistry [7].

Electron paramagnetic resonance spectroscopy (EPR), is a very sensitive probe of electronic structure and can provide information on the chemical environment of the unpaired electrons. In the present work we report EPR studies on pristine, purified, shortened and soluble SWNTs in various solution phases.

2. Experimental

2.1. Preparation of SWNTs samples for EPR

The SWNT material (obtained from CarboLex), was synthesized by use of a modified arcing technique for mass production developed at the University of Kentucky [8]. The pristine sample was analyzed using SEM, TEM and Raman and the purity was in the range of 50–70%. The purified SWNTs and shortened SWNTs were prepared using the methods reported by Smalley and co-workers [9], and are terminated with carboxylic acid groups. The shortened SWNTs were reacted with thionyl chloride and then octadecylamine to generate the soluble nanotubes (s-SWNTs), which are terminated with amide functionalities (SWNT-CONH$(CH_2)_{17}CH_3$) [10]. The iodine-doped SWNTs were generated directly in solution from the reaction of I_2 with s-SWNT-CONH$(CH_2)_{17}CH_3$ in benzene.

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2.2. EPR spectroscopy

The EPR spectroscopy was carried out on Varian E-Line and Bruker EMX EPR spectrometers. Unless noted otherwise, all of the EPR spectra were recorded at a concentration of ~ 1 mg/1 ml. The samples were contained in melting point tubes inserted into standard EPR tubes. The solvents were tested for EPR signals before the SWNT samples were prepared.

For the as-prepared pristine sample, an unstable suspension was generated by sonication in either ethanol or water. The samples of purified SWNTs and shortened SWNTs were prepared as stable basic suspensions in water by use of a surfactant (Triton X-100). The samples of soluble SWNTs (SWNT-CONH$(CH_2)_{17}CH_3$) [10], were prepared in benzene or carbon disulfide solution. All of the EPR spectra were recorded at room temperature. In order to measure the g-value and the concentration of unpaired electrons in the s-SWNTs, the free radical TEMPO was used as an internal and external reference, respectively.

3. Results and discussions

3.1. Pristine SWNTs

The pristine as-prepared SWNT suspension was EPR silent. In the initial report on the preparation of this material, the observation of the EPR signal was complicated by the presence of ferromagnetic catalyst residues which produce an intense line, of width $\Delta H \approx 400$ G at 300 K [11]. In our studies, the poor dispersion of the SWNTs may also contribute to the absence of an EPR signal.

3.2. Chemically purified SWNTs

The chemically purified SWNT sample gave a weak signal with a linewidth, $\Delta H = 2.0$ G and g-value of ~ 2.00. The purification [9] removes most of the catalytic metals used in the synthesis of the SWNTs. This has been confirmed using energy-dispersive X-ray analysis (EDS) [7]. Furthermore the purified samples gave rise to stable aqueous suspensions.

3.3. Shortened SWNTs

The aqueous suspension of shortened SWNTs, gave a strong and symmetrical EPR signal (Fig. 1), with a linewidth, $\Delta H = 1.0$ G and $g \approx 2.00$. Thus the linewidth of the purified SWNTs narrowed on shortening.

3.4. Soluble SWNTs

The benzene solution of s-SWNT-CONH $(CH_2)_{17}CH_3$ [10] gave a strong EPR signal (Fig. 2), with $g = 2.003 \pm 0.001$ and $\Delta H = 2.1$ G. Thus, within the error of our experiment, s-SWNTs give a free electron g-value.

Vacuum-annealed (1500°C) SWNTs gave an EPR signal of line width $\Delta H \approx 30$ G and a Dysonian line shape, with $g = 2.001 \pm 0.001$ [11]. For multi-walled carbon nanotubes (MWNTs), g-values of 2.012 [12] and 2.000 [13] have been reported; for graphite, values of 2.018 [12] and 2.004 [13] were found.

For the soluble SWNT sample, we were able to measure the approximate spin susceptibility (χ_s) of the sample, by using TEMPO as an external refer-

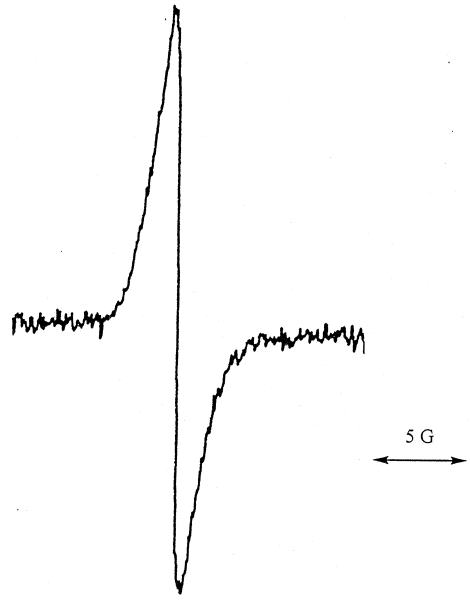

Fig. 1. The EPR spectrum (9.4 GHz) of shortened SWNTs as an aqueous suspension at room temperature.

ence. Neglecting the SWNT end groups, we obtain $\chi_s = 1.6 \times 10^{-7}$ emu/mol C, or $\chi_s = 1.4 \times 10^{-8}$ emu/g. Previous solid state EPR measurements on MWNTs obtained $\chi_s = 7 \times 10^{-9}$ emu/g, and for graphite $\chi_s = 2 \times 10^{-8}$ emu/g [12]. Temperature-independent Pauli behavior was found in the high-temperature regime of the spin susceptibility of the MWNTs [12].

If we assume that the unpaired electrons in our sample originate from the metallic tubes (Pauli susceptibility), then we can follow the previous analysis [12] and obtain the density of states at the Fermi level, $N(E_F) = 5 \times 10^{-3}$ states/eV-atom, and the carrier concentration, $n = 8 \times 10^{18}$ cm^{-3} or $n = 8 \times 10^{-5}$ spins/C atom. A first-principles band structure calculation reported a value of $N(E_F) = 1.5 \times 10^{-2}$ states/eV-atom for the metallic (10, 10) SWNT [14].

On the other hand, if we treat the unpaired electrons as Curie spins, the concentration of localized electrons, $n = 1.3 \times 10^{-4}$/C atom.

In either case, the sample of s-SWNTs carries about 1 unpaired electron per 10000 carbon atoms, although the spins are not expected to be uniformly distributed over the different types of SWNTs (which is known to be a mixture of metallic and semiconducting nanotubes [10]).

With regard to these calculations, it should be noted that considerable variations have been found in the SWNT types (metallic and semiconducting), present in samples of the s-SWNTs [10].

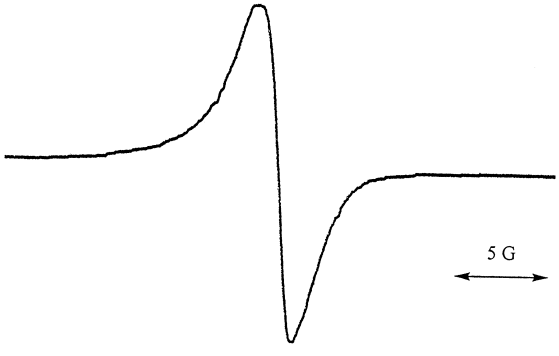

Fig. 2. The EPR spectrum (9.4 GHz) of SWNT-CONH $(CH_2)_{17}CH_3$ in benzene solution at room temperature.

Fig. 3. The EPR spectrum (9.4 GHz) of SWNT-CONH $(CH_2)_{17}CH_3$ in benzene solution at room temperature after doping with iodine.

3.5. Doped SWNTs

We measured the EPR spectra of suspensions of shortened SWNTs and solutions of s-SWNT-$CONH(CH_2)_{17}CH_3$ [10] after iodine doping (Fig. 3). The EPR signals of both samples widened but the *g*-values were essentially unchanged. The line width of the EPR signal from shortened SWNTs changed from $\Delta H = 1.0$ to 1.6 G after reaction with I_2, while the soluble SWNTs underwent a line width change from $\Delta H = 2.1$ to 4.7 G.

3.6. EPR line shapes

All of the EPR line shapes show asymmetry on close inspection. This may originate from incomplete rotational averaging of the asymmetric *g*-tensor [12].

4. Conclusions

We have measured the EPR spectra of various forms of SWNTs as suspensions and solutions. The purified SWNTs gave a weak EPR signal, whereas both the shortened and the s-SWNTs gave a strong EPR signal. The sensitivity of the EPR technique makes it useful for monitoring the presence of SWNTs in solvents, both as suspensions and solutions. The s-SWNTs [10] carry about 1 unpaired electron per 10000 carbon atoms and give a free electron *g*-value.

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