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Chemical Physics Letters 452 (2008) 152–155
CHEMICAL PHYSICS LETTERS
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Electron spin resonance studies of hydrogen adsorption on single-walled carbon nanotubes

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Received 16 November 2007; in final form 14 December 2007
Available online 23 December 2007

Abstract

Temperature and pressure dependent electron spin resonance (ESR) studies were conducted on two oxidatively purified single-walled carbon nanotube samples. For both samples, the ESR signal is composed of two components. The narrower component is ascribed to localized spins due to defects, the broader one to conduction electrons. Hydrogen predominantly interacts with defects. Below the condensation point, addition of hydrogen is suggested to cause diamagnetic dilution of the conducting sample, which leads to increased signal intensity.

The 1997 report [1] of a hydrogen storage capacity of single-walled carbon nanotubes (SWCNTs) on the order of 5–10 wt% resulted in thousands of publications over the last ten years. Despite a decade of research, the dispute on the suitability of carbon nanotubes as hydrogen storage materials is ongoing. Recent theoretical work suggests that despite the fact that smaller diameter tubes result in higher storage capacities, SWCNTs cannot meet the department of energy's target for an economically viable hydrogen storage medium [2,3]. We hypothesized earlier [4,5] that the wide range of storage capacities reported by different authors was due to the large number of preparation and purification methods, resulting in vastly dissimilar samples available to different researchers. In previous work [4], we found that hydrogen adsorption causes the electron spin resonance (ESR) signal of SWCNTs to be quenched, suggesting adsorption on localized defects. In this work, we investigate this effect in more detail through temperature and pressure dependent ESR studies of two oxidatively acid-purified SWCNT samples ('CNI' and 'MRSW') in the absence and presence of hydrogen. The unpurified SWCNTs gave rise either to a ferromagnetic resonance (CNI) or to only a very weak signal (MRSW) [4], and these samples were not further considered.

Commercially available SWCNT samples ('MRSW' from MER Corporation, Tucson, AZ, and 'CNI' from Carbon Nanotechnologies, Inc., Houston, TX) were previously [6] characterized using high resolution transmission electron microscopy (TEM), inductively coupled plasma analysis with mass spectrometry detection (ICP/MS), and resonant Raman microscopy. Samples were characterized before and after an oxidative, acid-based purification procedure [7]. Acid purification greatly reduced the number of residual metallic catalyst particles [6]. For ESR experiments, the acid treated samples were weighed into melting point capillaries (9.39 mg MRSW, 6.25 mg CNI) that were then inserted into low-defect synthetic quartz J.-Young type ESR sample tubes ('Suprasil', Wilmad, Buena, NJ). The sample tubes were placed into the ESR cavity, with their stopcocks connected to tubing providing a link to the vacuum rack and hydrogen tank. This setup allowed us to evacuate the samples and to adjust the hydrogen pressure without affecting the sample tube position in the cavity. Reproducibility of the line shapes was tested by evacuating the samples after hydrogen exposure, which resulted in the originally observed line shapes. Temperature was controlled using an Oxford 900 cryostat. ESR spectra

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doi:10.1016/j.cplett.2007.12.043

were recorded with a Bruker EMX spectrometer, equipped with a 10 kG magnet, and operating in the X-band (9.4 GHz). The microwave power was set to 0.2 mW, the modulation amplitude to 5 G, and conversion time and time constant were 20.48 ms.

In the absence of hydrogen and for both samples, the signal intensity increases with decreasing temperature, reaching a maximum around 25 K. The signal intensity for MRSW is larger by about an order of magnitude than that of CNI (Fig. 1). This is most pronounced at higher temperatures. While the signal intensity is slightly decreasing for MRSW below 10 K, it remains constant for CNI. As evident from Fig. 1, the temperature dependence of the MRSW sample deviates strongly from the Curie law. The weak temperature dependence is indicative of a Pauli contribution to the signal intensity [8], consistent with the lower defect density found for MRSW using Raman spectroscopy [6]. For CNI, the Pauli contribution dominates only below 25 K. Above this temperature, the signal intensity drops faster than predicted by the Curie law, similar to the results by Salvetat et al. [9]. They discussed thermal deactivation or superparamagnetism as possible origins for this behavior.

To correlate ESR signal intensity and amplitude, we also conducted a detailed analysis of the observed line shapes, using the line fitting software 'Grace'. At all temperatures and pressures, a narrow (1) and broad (2) component was necessary to obtain good fits. Some of these data are provided in Fig. 2 and Table 1. They show that for CNI, component 1 contributes about twice as strongly to the total signal intensity, explaining the dominance of the Curie contribution. This is consistent with our Raman results [6] that show a lower defect density for MRSW than

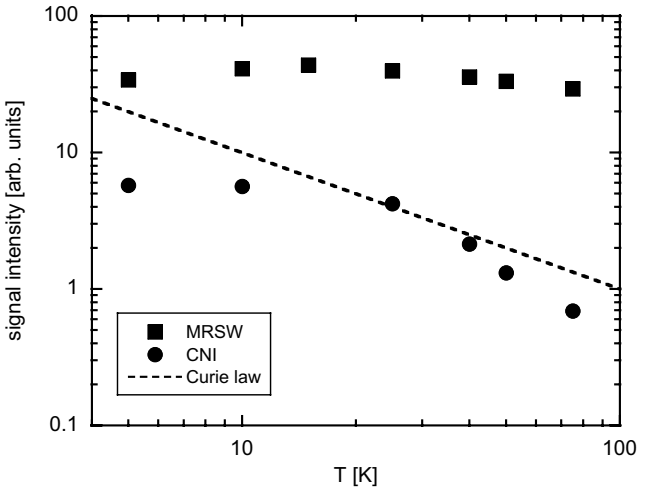

Fig. 1. Double-logarithmic plot of the ESR peak-to-peak amplitude as a function of temperature for two SWCNT samples (squares-MRSW, circles-CNI). The dashed line represents the Curie law dependence. Note that the peak-to-peak amplitude is directly proportional to integrated signal intensity at constant line width. Data have been corrected for different sample weights. Error bars are approximately the size of the symbols.

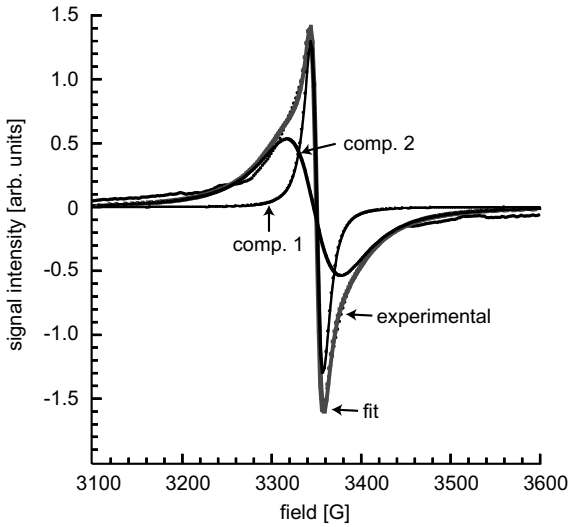

Fig. 2. Results from spectral decomposition of ESR signals (data from Fig. 3) into two components using Grace software, as reported in Table 1, for MRSW at 5 K and 106 kPa. The gray line represents the fit, the black dots are experimental points. The black lines marked components 1 and 2 result from the decomposition into two signal components.

for CNI. Indeed, in MRSW component 2 contributes about twice as strongly to the total signal intensity. This confirms our tentative assignment of this component to conduction electrons, with the exception of the point at 0 kPa and 5 K. Here, the two contributions are about equal in magnitude. Hence, addition of hydrogen significantly aids ESR observation of the Pauli component. The line width and g-factor is, within error, constant with temperature for the narrow component for both samples. The line width decreases slightly for the broad component. Such a temperature dependence is expected for conduction electrons [10].

The temperature dependence of the ESR signal intensity changes markedly upon addition of hydrogen (Fig. 3). For MRSW at ambient temperature, the signal intensity is weak and not affected by hydrogen, while that of CNI gradually decreases as hydrogen is added. The initial drop is steep and saturation is reached at about 53 kPa. This suggests that the decrease in signal intensity arises from quenching of localized defects. Once all defects are saturated, there is no further decrease in signal intensity. With decreasing temperature, the temperature dependence of the CNI signal intensity first disappears (50 K) and then inverts (5 K). The sudden increase in signal intensity upon addition of hydrogen at 25 K for CNI is most likely due to improved temperature equilibration in the presence of hydrogen. At 5 K, however, the increase in CNI signal intensity prevails over a range of pressures, until it reaches an equilibrium value. Note that at 5 K the Pauli contribution dominates the ESR signal.

These data are in agreement with previous work [4] where we showed that for multi-walled carbon nanotubes (MWCNTs) the ESR signal intensity increases upon addition of hydrogen while it decreases for SWCNTs. In this