Characterization of nitrogen-doped carbon nanospheres using electron magnetic resonance

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Abstract. Carbon nanospheres (CNS) were produced using two different sets of chemical vapour deposition (CVD) apparatus - a vertical and a horizontal reactor. Nitrogen was introduced into the samples using a several sources of nitrogen, including pyridine. Electron magnetic resonance (EMR) was used to characterize a range of samples of varying concentrations of nitrogen at room temperature. The spheres doped with nitrogen show a strong paramagnetic peak at $g \simeq 2$, indicating that the nitrogen takes up substitutional sites in the carbon matrix. Careful analysis enables us to determine the nitrogen content in each of the samples by integration of the resonance peak, and normalising to the mass of the sample. Comparison with a reference sample allows us to extract g for each sample. Power saturation experiments show the the relaxation rates of the nitrogen ions are high in all the samples studied. This paper reports on the synthesis and the EMR results of the nitrogen-doped nanospheres.

1. Introduction

Since the studies on carbon nanotubes by Iijima [1] nanomaterials have received considerable attention from scientists and engineers. Carbon nanomaterials exhibit many remarkable physicochemical properties [2]. In addition, carbon nanomaterials are produced in a large range of morphologies, including tubes, spheres and horns. Carbon spheres come in a range of sizes, from the fulleride family and graphitic carbon onions (2 - 20 nm), to the less graphitic carbon spheres (50 nm - 1 μm), to carbon beads (1 μm upwards)[3]. In this paper we focus on the second category - carbon nanospheres (CNS) that consist of graphene flakes. In particular we are interested in the properties of CNS that contain nitrogen.

Synthesis of CNS may be accomplished using a number of techniques, including chemical vapour deposition (CVD). The recent review by Nieto-Márquez *et al* [2] provides a current summary of these techniques. In addition, Nieto-Márquez *et al* [2] provide a comprehensive summary of the broad current and potential applications of these materials. The study of undoped and doped CNS is consequently of considerable scientific and technological significance. A recent paper by Mondal *et al* [4] has reported on the synthesis and characterization of CNS that contain boron. Carbon materials containing substitutional boron or nitrogen occur naturally (in diamond, for example) as these two elements are adjacent to carbon in the periodic table.

Electron magnetic resonance (EMR), which is also known as electron paramagnetic resonance (EPR) or electron spin resonance (ESR), may be used to characterize materials that have unpaired electrons. In the past these investigations have included a studies of the properties of nitrogen centres in diamond. EMR has recently been used to successfully characterize boron-doped multi-walled carbon nanotubes [5], and has also been used in the characterization of other nanomaterials (see for example Corzilius *et al* [6]). Nitrogen containing CNS should be sensitive to EMR, particularly if the nitrogen is incorporated into the carbon matrix providing a paramagnetic centre. In this paper we report on the EMR characterization of nitrogen-doped CNS, and show that the nitrogen is present in substitutional sites. EMR is also used to determine the properties of the impurity sites, and to estimate the concentration of the paramagnetic centres.

2. Sample synthesis

Two CVD reactors were used to produce doped and undoped CNS samples using a variety of carbon and nitrogen sources, No catalyst was required to produce CNS samples using either reactor.

2.1. Vertical CVD Reactor (v-CVDR)

This apparatus was designed and fabricated in the Nanotechnology Laboratory of the School of Chemical and Metallurgical Engineering, University of the Witwatersrand [7]. It consists of a vertical silica plug flow reactor, immersed in a furnace with a sensitive temperature regulator. A system of rotameters, pressure controllers and valves control the flow of gases into the reactor. The upper end of the reactor is connected to a condenser, which leads to the two delivery cyclones, where the carbon structures produced are collected. Full details of the synthesis procedure are given elsewhere [8]. Doping was achieved using a range of nitrogen sources - the details are given in Table 1.

2.2. Horizontal CVD reactor (h-CVDR)

Carbon spheres were synthesized in a horizontal reactor. The reactor was placed horizontally in an electronically controlled furnace, allowing production of the carbon material.A syringe is used to inject the carbon and nitrogen sources into the quartz reactor. The heating rate, the reaction temperature and the gas flow rates may be maintained accurately as required. Full details of the synthesis procedure and a schematic diagram of the reactor are given elsewhere [8]. Doping was achieved by injecting a mixture of pyridine and toluene into the reactor (see Table 1) with all the other reactor parameters kept at constant values.

2.3. Sample details

Nine samples in total were presented for EMR analysis. Four of these were synthesized using the v-CVDR, and the rest were synthesized using the h-CVDR. The samples were expected to have varying concentrations of nitrogen, including possibly nitrogen at substitutional sites in the carbon matrix.

3. Experimental considerations

The reactor products were characterized using a suite of analytical tools including elemental analysis (see Table 1), Transmission Electron Microscopy (TEM), Thermogravimetric Analysis (TGA), Powder X-ray diffractometry and Raman Spectroscopy. No catalyst was required for the synthesis of the CNSs, and hence no purification was required.

EMR measurements were done at room temperature using a Bruker ESP 300E X-band spectrometer operating in the frequency range 9.4 - 9.9 GHz. All of the EMR experiments were performed using standard continuous wave (CW) techniques. Polycrystalline DPPH reference

Table 1. Details of the samples presented for EMR analysis. Acetylene was used as a carbon source in the v-CVDR. Sample NK5 was synthesized at 850 °C. Samples NK6, NK7, NK8 and NK9 were synthesized at 1000 °C. The nitrogen content was obtained from elemental analysis.

Sample	Nitrogen Source	Reactor	Nitrogen %
NK1	Undoped	Vertical	< 0.02
NK2	NH_3	Vertical	0.19
NK3	NH_4^+ ions	Vertical	-
NK4	Pyridine	Vertical	0.15
NK5	100:0 Pyridine:Toluene	Horizontal	-
NK6	100:0 Pyridine:Toluene	Horizontal	5.00
NK7	10:90 Pyridine:Toluene	Horizontal	1.48
NK8	0:100 Pyridine:Toluene	Horizontal	0.13
NK9	90:10 Pyridine:Toluene	Horizontal	3.52

samples were employed to determine the g-factors and the spin concentrations of nitrogen in the samples. The size of the DPPH sample used varied depending on the size of the EMR signal produced by the CNS sample. All of the data were obtained using phase-sensitive detection, and the EMR spectra shown later are the first derivative of the absorption spectrum.

4. Results and Discussion

Full details of the results of other characterization techniques employed in the analysis of these samples are provided elsewhere [8]. This paper will concentrate on the results obtained using CW EMR.

4.1. CW EMR characterization

A summary of the EMR results is provided in Table 2. All of the samples showed evidence of unpaired electrons, with $g \simeq 2$ (corresponding to a resonance field of approximate 3470 G) in all cases. No additional EMR features were seen over a wide field scan (6000 G) in any of the samples. The linewidth and estimates of the g-shift are given for all samples. More detailed discussion of the results for samples produced by the two reactors is provided below. As will be seen the CNS products produced from the two reactors are significantly different.

A comparison between an undoped (NK1) and a nitrogen-doped (NK2) sample is provided in Fig. 1. The appearance of a narrow paramagnetic line with a linewidth of 5.0 G in the spectrum for NK2 indicates that the nitrogen has been incorporated into the carbon matrix. This feature is a characteristic of localized spins [9]. The relatively broad features in both samples may be ascribed to delocalized spins and are probably due to conduction electrons [9]. The delocalized spins in NK1 have a smaller linewidth than the broad background in NK2. This may be evidence that the delocalized spins have been affected by the paramagnetic impurities. Conductivity measurements in boron-doped CNS [4] indicate that the conductivity decreases on boron doping, and the broadening of the line for the delocalized spins may be related to this observation. Fig. 2 compares the spectra for NK2, NK3 and NK4. The spectra have been normalized to the background signal provided by the delocalized spins. NK3 exhibits a much larger paramagnetic signal, indicating that these spheres have a larger paramagnetic nitrogen component.

Table 2. Summary of the EMR characterization results of the linewidth (ΔB) and the relative g-shift Δg for all samples.

	NK1	NK2	NK3	NK4	NK5
ΔB (G)	9.5 ± 0.5	5.0 ± 0.2	3.2 ± 0.1	1.8 ± 0.1	2.4 ± 0.2
Δg (%)	1.5 ± 0.5	- 3.4 ± 0.1	- 1.4 ± 0.1	- 1.4 ± 0.1	- 1.1 ± 0.1
	NK6	NK7	NK8	NK9	
ΔB (G)	1.36 ± 0.01	0.57 ± 0.01	12.5 ± 0.5	1.14 ± 0.01	
Δg (%)	- 5.09 ± 0.02	- 1.5 ± 0.02	- 8 ± 1	- 5.24 ± 0.02	

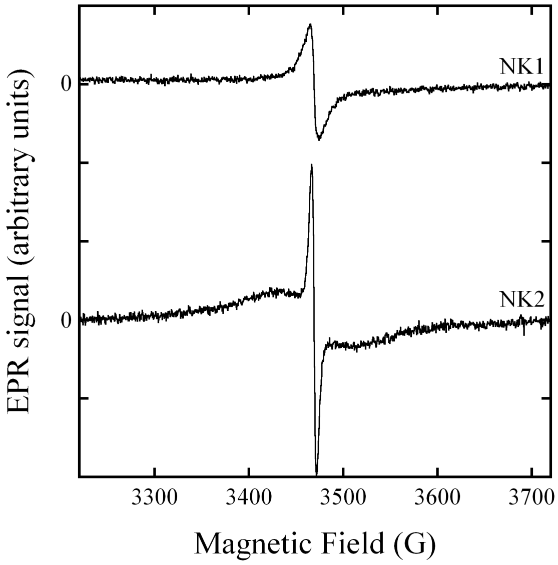

Figure 1. A comparison of the EMR spectra for undoped (NK1) and nitrogen-doped (NK2) CNS produced in the v-CVDR. Note the presence of a strong paramagnetic peak (indicating localized spins) in the spectrum for NK2, as well as the broadening of the signal due to delocalized spins.

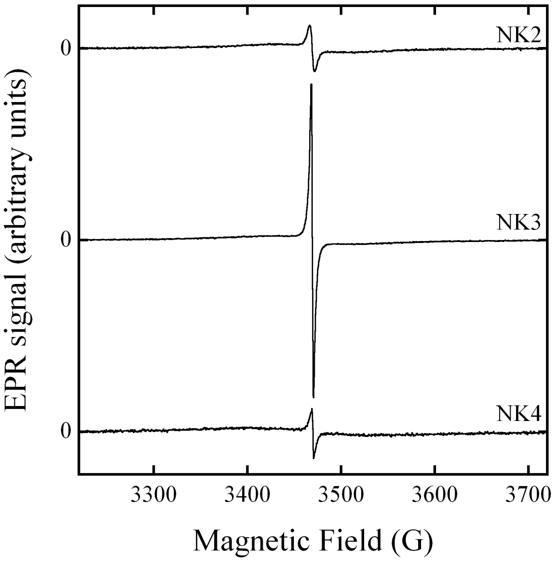

Figure 2. A comparison of the EMR spectra for the three nitrogen-doped samples produced in the v-CVDR. As expected from the results of the elemental analysis (see Table 1) the sample doped with NH_4^+ ions (NK3) has the largest paramagnetic component in the spectrum.

Three of the samples produced using the h-CVDR are qualitatively and quantitatively very different from those produced using the v-CVDR. The other two have some similarities. Sample NK8 (0% pyridine) has features that are comparable with NK1 (the undoped sample produced using the v-CVDR). The EMR signal for NK8 may therefore be assumed to originate from delocalized spins (conduction electrons). The spectrum for NK5 (produced using the h-CVDR at 850 °C) has features similar in character to NK3, but the broad background signal in this sample is relatively much smaller than the paramagnetic peak. From the evidence it would appear that the concentration of nitrogen in this sample is of the same order of magnitude as the nitrogen-doped CNS produced using the v-CVDR.

The other nitrogen-doped CNS samples prepared using the v-CVDR (at 1000 °C) showed a much larger (approximately two orders of magnitude) paramagnetic peak. Fig. 3 compares the spectra obtained for NK6, NK7 and NK9. Several features are of note. As the concentration of pyridine in the source increases the EMR spectrum becomes progressively broader, and the spectrum becomes more asymmetric (or more Dysonian in character). In common with NK5, the broad background observed in samples produced using the v-CVDR is less significant, in these samples completely swamped by paramagnetic nitrogen, indicating that the concentration of delocalized spins is smaller. This may well have an effect on the electrical properties, leading to a decrease in the conductivity in common with the effect seen previously in boron-doped CNS [4] In Fig. 4 spectra containing the reference sample DPPH are shown. These spectra show clearly the g-shift of the paramagnetic ions. The results of deconvoluting these composite spectra for all samples are provided in Table 2.

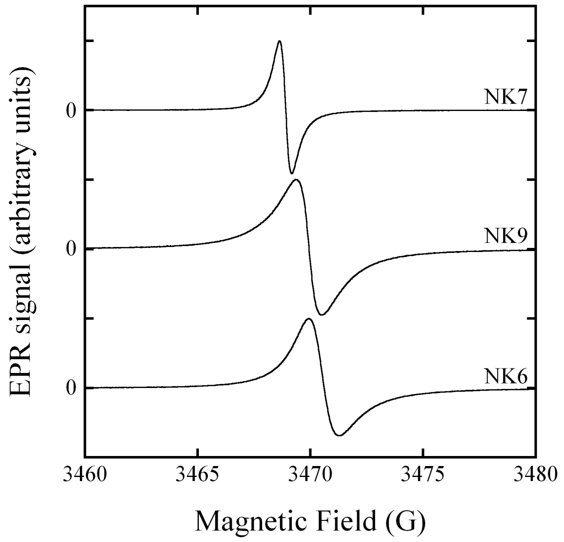

Figure 3. A comparison of the EMR spectra for nitrogen-doped CNS produced in the h-CVDR. As the nitrogen content of the spheres increases the spectrum becomes broader and progressively more Dysonian in character.

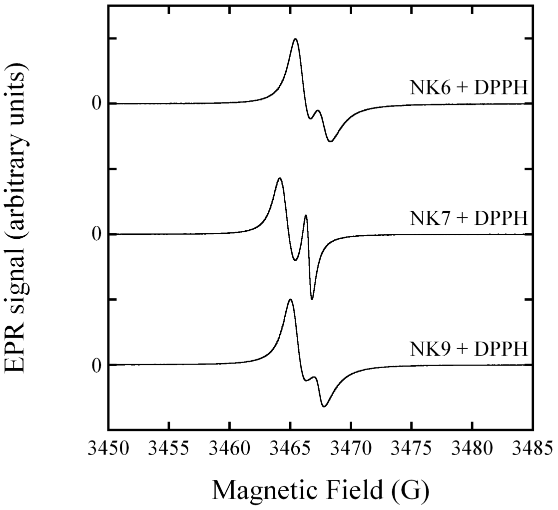

Figure 4. A comparison of the EMR spectra for the composite samples of the DPPH reference and the three nitrogen-doped samples produced in the v-CVDR. The g-shifts given in Table 2 was obtained from composite spectra such as these.

Power saturation measurements were performed for all samples. This involves progressively increasing the microwave power applied to the sample. No evidence was found for power saturation in any of the samples, indicating that relaxation rates are high, and the spin-spin and spin-lattice relaxation times are therefore of the order of ns. Relaxation times may be accurately determined using pulsed EMR techniques, but these are not available at present.

Finally, an attempt was made to determine the relative nitrogen concentration, and the spin concentration relative to a reference sample (DPPH) for NK6 NK7 and NK9. Careful measurements of the mass of each of NK6, NK7 and NK9 were made. Due to the small masses involved (< 10 mg), the mass determination has large inherent errors. The double integral of the spectrum obtained for each sample was determined, normalized to the mass and compared. The results are tabulated in Table 3, together with the results of elemental analysis for these samples. The results show that the concentration may be controlled by the mixture of different amounts of pyridine and toluene in the source, but these do not correspond to the initial concentrations. Comparison with DPPH shows that the paramagnetic spin concentration is of the order of 3% of DPPH in the highest concentration sample (NK6). It is suggested that the concentration of substitutional nitrogen is of the order of a few percent, at most, in the h-CVDR samples and at least an order of magnitude lower in the samples produced using the v-CVDR.

Table 3. Concentration of paramagnetic nitrogen centres. The relative concentration is calculated with respect to NK6, while the absolute concentration is found by comparing the sample to a polycrystalline DPPH sample. Error estimates are not provided, but these are expected to be large due to the error in the determination of the mass of the samples.

Sample	Elemental analysis (%)	Relative concentration (%)	Absolute concentration(%)
NK6	5.00	100	3.2
NK9	3.52	16.2	0.55
NK7	1.48	8.4	0.3

5. Conclusions

CNS have been prepared using two CVD methods, and characterized using a suite of techniques, including EMR. The EMR results indicate that nitrogen is present in substitutional sites in the CNS to concentrations not exceeding a few percent. The concentration of substitutional nitrogen in the CNS prepared using the h-CVDR is much higher, in general, than those produced using the v-CVDR method. Different sources change the nitrogen concentration in the product, but it would appear that this cannot be done in a controlled fashion. Increasing the nitrogen concentration changes the character of the EMR spectrum, the spectrum becoming more Dysonian in character as the concentration increases. It is suggested that the addition of nitrogen in relatively large quantities may affect the conductivity of the pristine CNS. Power saturation measurements show that the spin relaxation rates of all samples are high at room temperature. It is also of interest to those who may find further uses for these materials that the paramagnetic signals have remained stable since the start of this investigation over two years ago, indicating that the nitrogen remains incorporated in the carbon matrix for at least this length of time.

Acknowledgments

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