Characterization of nitrogen- doped carbon nanospheres using electron spin resonance

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EMR Spectrometer

Figure 1 Bruker ESP 300 E X-band spectrometer used to characterize the carbon nanospheres in this investigation.

Where is the nitrogen?

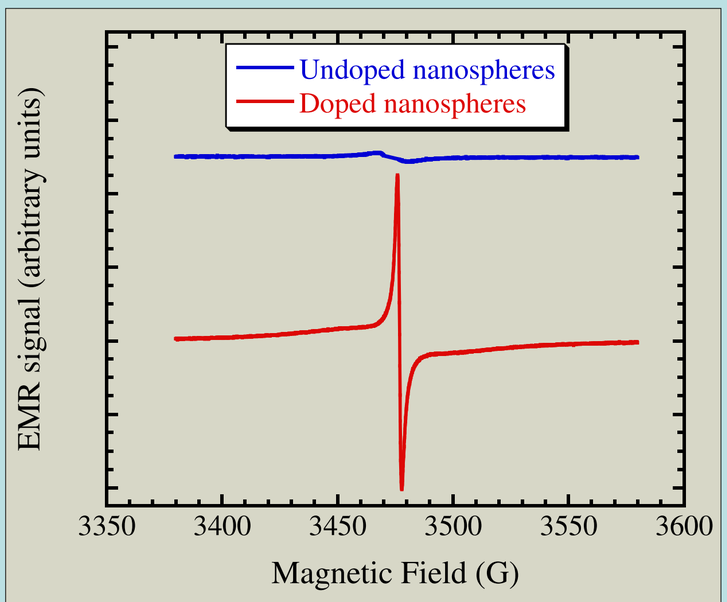


Figure 2 EMR derivative curves for undoped and nitrogen doped CNS. The spectra were obtained using comparable spectrometer settings, and using a similar quantity of sample. The appearance of the strong paramagnetic peak supports our conclusion that the nitrogen occupies substitutional sites in the carbon matrix.

What is the best nitrogen source?

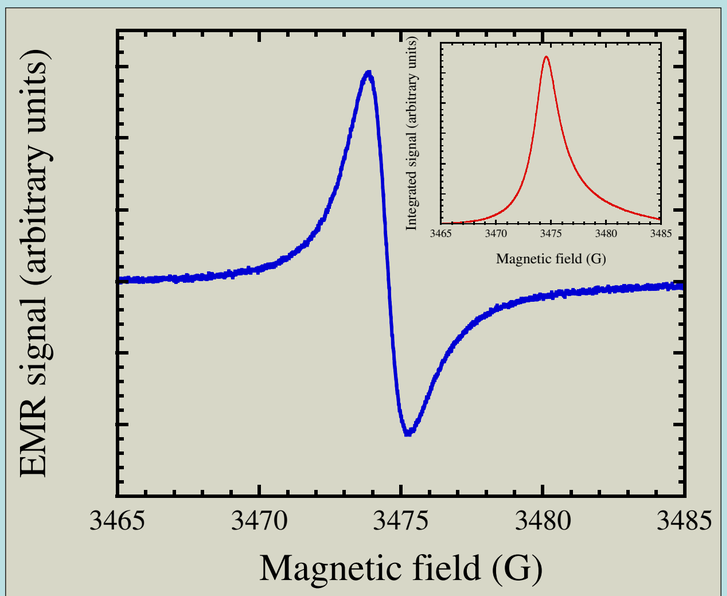


Figure 3 EMR derivative curve for CNS doped with pyridine as the nitrogen source. The inset shows the integral of the experimental curve, and highlights the asymmetric (Dysonian) nature of the signal. Pyridine provides the most effective source of nitrogen for the CNS – the signal here is at least two orders of magnitude bigger than the signal obtained for the sample prepared using ammonia.

Summary

Carbon nanospheres (CNS) were synthesized using Chemical Vapour Deposition (CVD) methods (for details see the panel below). The samples were presented for Electron Magnetic Resonance (EMR) characterization in three stages. A Bruker ESP 300 E X-band spectrometer (see Fig. 1) was used.

Stage 1

The first attempt to dope the CNS with nitrogen utilised ammonia as a nitrogen source. Thermogravimetric Analysis indicated the presence of nitrogen in the spheres. EMR spectra of the undoped and nitrogen-doped spheres are shown in Fig. 2. The appearance of a large paramagnetic component provides evidence that the nitrogen is incorporated in the carbon matrix, and we suggest that this is probably in substitutional sites.

Stage 2

The search for the best nitrogen source was then started. In Fig. 3 we present the EMR spectrum for a sample doped using pyridine as the nitrogen source. The peak is at least two orders of magnitude larger than that for the doped sample shown in Fig. 2. The spectrum is asymmetric (Dysonian) leading to speculation that the sample has an appreciable conductivity. Analysis of the characteristics of the EMR lines show that there is a small *g*-factor shift for the Sample 6 (pyridine used as the nitrogen source), and that relaxation rates may be expected to be rapid (see Fig, 4). There is evidence that the relaxation rates for Sample 6 are longer than those for Sample 3 (ammonia the nitrogen source).

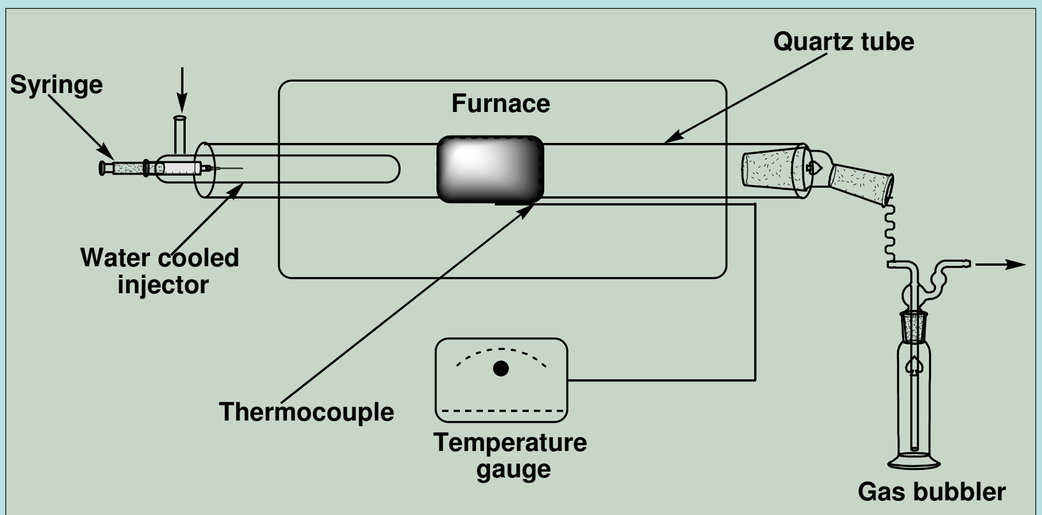
Stage 3

In an attempt to control the nitrogen concentration the pyridine was mixed with toluene in different molar ratios (from 0% toluene to 100% toluene). The sample with 100% toluene was indistinguishable from the undoped sample as expected. Fig. 5 shows the results of EMR analysis of the 10%, 90% and 100% pyridine mixtures. The integral of the obtained derivative line was normalized to the mass of each of the samples and plotted as a function of the nominal concentration. An inset shows the EMR derivative curves for each of the three samples. It is clear that we are able to change the concentration of nitrogen in the CNS using this method, but more work is necessary if we are to quantify the nitrogen concentrations. Further sample synthesis is in progress.

Future work

We plan to extend the CW-EPR measurements to low temperatures, and to use Fourier Transform EMR to investigate relaxation times, if this becomes feasible. In addition, broad-line pulsed Nuclear Magnetic Resonance (NMR) measurements and solid-state NMR measurements are planned. If necessary samples will be prepared using sources with enriched concentrations of the NMR active nuclei.

Sample Synthesis



A schematic diagram of the horizontal reactor employed in the synthesis of the CNS is shown above. The reactor is placed in a furnace, and the operation is controlled as far as temperature and gas flow rates are concerned. Mixtures of toluene and the relevant nitrogen source are injected into the assembly via a syringe, through the water cooled injector. The furnace is maintained at 1000 °C, and a carrier gas mixture of 5 % H_2:Ar at a flow rate of 100 mL/min is injected into the reactor. Most of the synthesized hydrocarbon product formed in the middle of the reactor tube. The procedure was time consuming; it took approximately 2 h to run the reaction. The product is left to cool for 15-20 minutes, which in some cases results in secondary reactions occurring on the sphere perimeter.

A Transmission Electron Microscope image of one of the samples is shown on the right.

Resonance line characteristics?

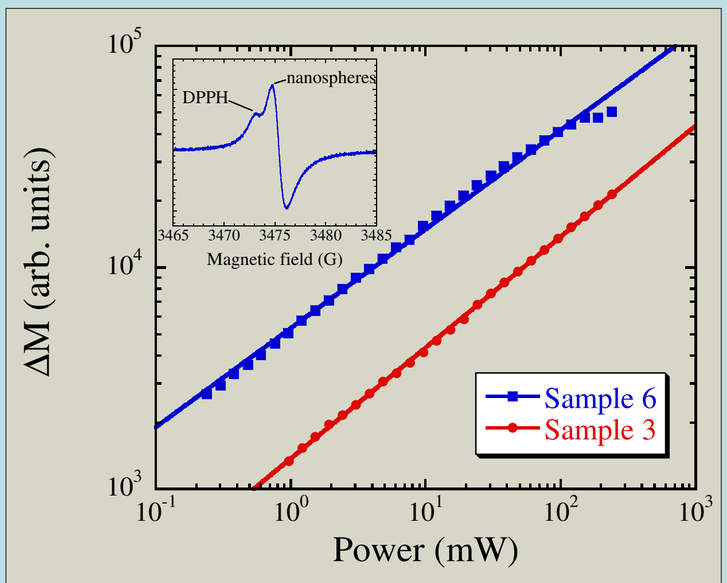


Figure 4 CW-EMR power saturation curves for ammonia (Sample 3) and pyridine (Sample 6) nitrogen-doped CNS. There is a hint of saturation at the highest power values for Sample 6, but the data is not reliable enough to estimate relaxation times. The inset shows the EMR derivative curve for a composite sample of DPPH and Sample 6, showing that there is a small *g*-shift in this sample (– 0.05 ± 0.01 %).

Controlling the concentration?

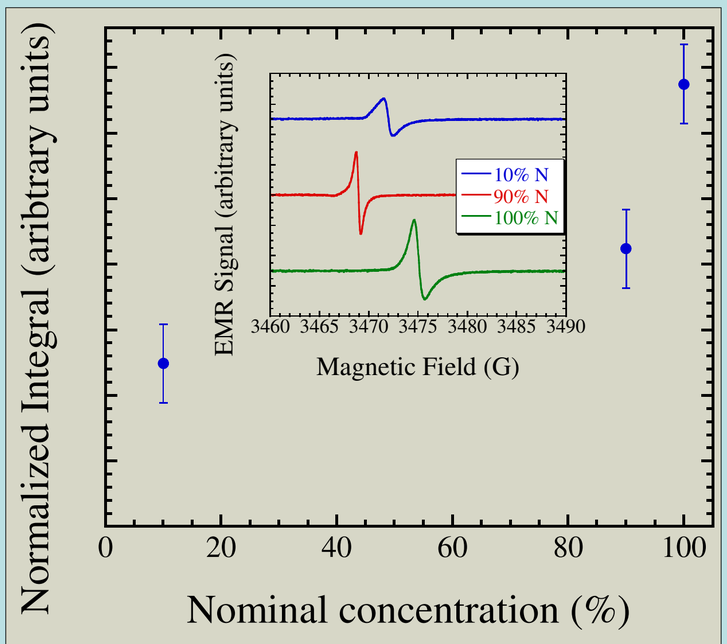


Figure 4 The integral of the EMR derivative curves normalized to the mass of the sample as a function of the nominal concentration. It may be expected that this gives an indication of the concentration of paramagnetic spins in each of the samples. However, there is a broad background signal intrinsic to the CNS that may be a source of a significant systematic error. The inset shows the EMR derivative curves for each of the samples. The shifts evident are not evidence of relative *g*-factor shifts – they arise from the different resonant frequencies of the microwave cavity as the samples are changed.

Sphere Morphology