# Characterisation of carbon microspheres using electron paramagnetic resonance spin-concentration techniques

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**Abstract**. A new technique to accurately determine the nitrogen concentration of doped carbon microspheres was developed using electron paramagnetic resonance (EPR) techniques. Samples of carbon microspheres of varying nitrogen concentrations were synthesised in a horizontal chemical vapour deposition reactor. The spin concentrations of samples of known nitrogen concentration were determined using a Bruker ESP 300E and used to calibrate the device. Samples of unknown nitrogen doping were then analysed to determine their concentration. Raman spectroscopy was also used to confirm the effect the nitrogen incorporation has on the structure of the microspheres.

#### 1. Introduction

In recent years many allotropes of carbon have been studied extensively [1,2,3] because of their many applications. One of these allotropes, the carbon microsphere (CMS), has recently been the subject of new attention due to its applicability to lubricants, electronic devices and lithium ion batteries [1,4]. The level of nitrogen doped in to the spheres can affect many of its properties hence a non-destructive technique to determine dopant levels will prove useful. With refinement, electron paramagnetic resonance (EPR) spectroscopy could determine small nitrogen concentrations, beyond what is currently possible with other elementary analysis techniques, without consuming the sample.

Samples were prepared using the popular chemical vapour deposition (CVD) technique [5,6] in a horizontal reactor. The advantage of CVD reactors is their ability to produce spheres without a catalyst. [7] Synthesis was conducted using varying reactor parameters to create spheres of with different characteristics.

EPR and Raman spectroscopy have successfully been used to study the structure of CMS [8]. These techniques can give an indication of the effect of nitrogen incorporation Each nitrogen introduced in to the graphitic lattice creates a paramagnetic centre which adds to the EPR spectrometer signal. By normalising the signal magnitude to the mass of the sample the spin concentration, and therefore the nitrogen concentration, of the samples can be determined. A calibration curve for a specific spectrometer under a specific set of conditions can be created allowing for the characterisation of samples of unknown nitrogen content. Other experiments can confirm the relative levels of nitrogen concentration, such as sample g value or Raman spectrum. Dopant introduction in to any carbon structure adds disorder which can be detected in the Raman spectra [9,10]. Similarly the presence of nitrogen changes the spin-orbit coupling of electrons in the spheres, which changes the g values [11]. While these techniques can indicate a relative difference in nitrogen concentration if absolute nitrogen concentration is needed then the number of free spins per gram of sample must be determined.

#### 2. Synthesis

Synthesis of the CMS was conducted inside a horizontal CVD reactor using acetylene as the primary reagent. The acetylene is introduced via a carrier gas, in this case argon, at a flow rate of 100ml/min. The source of nitrogen dopant was acetonitrile, introduced into the gas stream during the reaction. The flow of gas was initiated when the reactor had stabilized at the desired reaction temperature. Reactor parameters were varied to create the different samples. The temperature was set to 850°C or 900°C and the reaction ran for either 1.5 or 2 hours. The reactor has a quartz tube placed in the center where the majority of the spheres are collected however some samples were collected from the quartz boat, an excess collection area, to observe the difference in the spheres based on final location in the reactor.

Sample	Concentration	Sample	Synthesis Detail
 SDA	0%	SD1	Reaction of 1.5 hours
SDB	0.4%	SD2	Reaction of 2 hours
SDC	2.5%	SD3	From quartz tube
SDD	5%	SD4	From quartz boat

 Table 1. Samples investigated.

#### 3. Characterisation

### 3.1. Electron Paramagnetic Resonance

The EPR experiments were conducted using a Bruker ESP 300E spectrometer in continuous wave mode. Spin-concentration measurements represent a particularly challenging experiment due the number of parameters which can affect the results [11]. The spectrometer settings were kept identical throughout all the spin-concentration measurements to ensure signal magnitudes could be meaningfully compared. Further parameters which affect the results include the mass of the samples, sample geometry as well as conductive shielding therefore the samples were packed in identical quartz tubes and their masses carefully measured.

The CMS samples all display a single, strong paramagnetic resonance signal characteristic of carbon materials [12] which is slightly Dysonian in character. Dysonian lineshapes are indicative of conduction electrons [13] which we expect to see introduced with the nitrogen. The spin-concentration can be determined by double integration of signal however great care must be taken to ensure the baseline for the integration is corrected for, [11] therefore the spectrometer was set to a wide sweep of both the low-field and high-field sides of the spectrum. Figure 1 shows the results from the samples of known nitrogen concentration. The regression curve has a  $R^2$  value of 0.86 and represents the calibration curve for the spectrometer. The samples do not fit the expected straight line especially well, this may be due to errors in the determination of nitrogen concentration. The spectrometer detects only paramagnetic nitrogen bonded in to the lattice structure, other techniques, such as mass spectrometry, detect the total number of nitrogen atoms present. The unknown samples were then measured and placed along the curve to determine the concentration of paramagnetic nitrogen. Their concentrations are displayed in Table 2.



**Table 2.** Nitrogen Concentrations of unknown samplesdetermined by spin-concentration EPR experiment.

Sample	Concentration	Error
SD1	1.7%	0.5%
SD2	3.3%	0.9%
SD3	3.4%	1.0%
SD4	1.7%	0.5%

The g value of the samples was investigated using a deconvolution technique. The samples were placed in standard EPR quartz tubes with a smaller tube containing DPPH placed within the larger one. The DPPH is used as a standard marker in EPR experiments because it has a well defined resonance peak. This is then used to mark a particular magnetic field value to the well known g-value of DPPH. By measuring the difference between the peak of the DPPH signal and the peak of the microspheres a relatively accurate determination of the sample's g-value can be obtained. The results for the known samples are shown in Figure 2. It shows the g value of the spheres tends away from the free electron g-value. This implies that spin-orbit coupling increases as nitrogen is introduced in to the lattice.





**Figure 2.** Effective g value of sample with increasing nitrogen content.

The unknown sample's g values were also investigated with the same technique. SD1 and SD2 have similar nitrogen doping levels however the SD1 has a larger g value. This indicates that a longer time spent in the reactor seems to increase the coupling the free electron has with the lattice. This may be due to annealing, which appears to be confirmed by Raman spectroscopy. SD4 has a much larger g value than SD3 which indicates that depending on where in the reactor a sample is collected has a large effect on the chemistry of the bonds seen by the free electron. This may be due to the spheres collected in the boat experiencing a varying temperature on the periphery of the pyrolisis, creating a different bond structure.

#### 3.2 Raman Spectroscopy

Raman spectroscopy was used to confirm the EPR data by observing the effect of the nitrogen on the structure of the CMS. The CMS samples were studied at 514 nm and 647 nm laser wavelengths. Major peaks were observed at  $1381 \text{cm}^{-1}$  and  $1595 \text{cm}^{-1}$  with a minor peak at approximately 1200cm. The two dominant spectral lines, namely the D and G bands, indicate the presence of a graphitic carbon structure [14]. The G peak is indicative of a doubly degenerate  $E_{2g}$  phonon mode characteristic of sp2 hybridised carbon networks, while the D peak is induced by defects in the carbon structure [15]. The peaks studied are very broad which makes curve fitting difficult, and reduces the resolution for detecting the peak centres.

The intensity ratio, R, is given by

$$R = \frac{I_D}{I_G}$$

where  $I_D$  and  $I_G$  are the intensities of the D and G bands respectively.

 $I_D$  is proportional to the number of ordered rings in the sample and is reduced as the introduction of the nitrogen causes bond bending disorder in the structure. Sp3 hybridized bonds can also be formed during the introduction of the nitrogen, further reducing the intensity of the D peak [16,17]. The it is found that R of the known samples decreases for the 514 nm laser indicating the presence of bond bending disorder introduced in to the structure with the nitrogen. The 647 nm laser does not show this trend and has a relatively unchanged intensity ratio. Resonance of the D band at this laser wavelength can occur and completely overshadow the smaller effect of the increased bond disorder. An anomaly can be seen in both laser wavelengths for the SDB sample. This seems to indicate an error in the reactor conditions when this sample was produced. The anomaly is shown on the graph as a triangle.



Figure 3. Intensity ratio change with nitrogen incorporation.

The centre of the G line shifts towards a higher frequency as the nitrogen is introduced in to the sample at both laser wavelengths explored. A blue shift in the G peak is expected when a sample changes from nanocrystaline structure to a less ordered (amorphous) structure as the disorder in the sample increases [18]. A red shift in the spectra of carbon microspheres doped with boron has been associated with increases in average CMS size [6,19]. It is important to note that the red shift was not indicative of a particular sphere diameter, but rather of a trend towards larger spheres being produced on average in the presence of boron dopant [19]. It is possible in this case that the spheres have a slightly smaller diameter when nitrogen is introduced, if unlikely. Further TEM investigations are required to confirm this possibility. The G shift in either case is caused by the reduction of the characteristic length  $L_a$  of the lattice, [20] either by shrinking sphere size or introduced disorder.

		514 nm Laser Wavelength			617 nm Laser Wavelength		
Sample	Nitrogen Content	R	G band width	G band centre	R	G band width	G band centre
SDA	0%	1.104	107	1600.2	1.487	81	1590.8
SDB	0.4%	0.916	95	1599.8	1.426	78	1589.8
SDC	2.5%	0.972	96	1592.0	1.488	80	1585.6
SDD	5%	0.945	91	1592.4	1.509	84	1584.5

**Table 3.** Raman spectra data of known nitrogen concentration samples.

The ratio R and the G peak blue shift are signs that the sample is becoming increasingly amorphous as defects are introduced in to the graphitic structure. Ferrari *et al* [9,18] describe this as the second stage of their 3 stage model of carbon Raman spectra. Reduction of the G peak width for the green laser wavelength can also be observed. Previous research has detected the formation of a D' peak around  $1620 \text{cm}^{-1}$  with increasing sample disorder and, while not clearly visible in the spectra as a separate line, it is the likely contributing to thinning the G peak [20,21].

## 4. Conclusion

The CVD technique employed synthesized CMS. A rudimentary calibration curve was successfully created for the EPR spectrometer and the nitrogen content of unknown samples was determined. Measurements of the g value of the samples and the Raman spectra confirm that trends in these values are directly related to nitrogen dopant level. This confirms that spin concentration, with complementary experiments, can determine the nitrogen concentration of CMS samples.

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