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RBS/EBS/PIXE measurement of single-walled carbon nanotube modification by nitric acid purification treatment

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Abstract

Single-walled carbon nanotubes (SWCNTs) have many potential applications, including a number of promising biological applications. Nitric acid treatment solubilises CNTs by introducing functional groups, as well as removing amorphous carbon contaminants. Here, we report simultaneous RBS/EBS/PIXE measurements of nitric acid treated SWCNTs, focussing on the metal, nitrogen and oxygen content. We found that nitrogen remains constant in the samples despite washing and dialysis indicating it has either bound irreversibly via intercalation with the SWCNT and/or has been included in functional groups. We also found that the ratio between oxygen and platinum (catalyst) remains constant with treatment time (sampled at 2, 4, 6 h), indicating no more functional groups are made after 2 h exposure.

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1. Introduction

Single-walled carbon nanotubes (SWCNTs) are well known to be taken up by cancer tumours [1] and have potential in diagnostics and therapeutics. However, as-made SWCNTs are heavily contaminated with other material, and are insoluble in water. Refluxing with nitric acid is a simple and widely used treatment which addresses both of these issues by reducing the amorphous carbon contaminants and introducing a number of chemical groups including –COOH, $–CONH_2$, –CHO and COH [2–4]. However, the exact proportion of oxygen that is added to the SWCNTs is unclear, although titration experiments have shown that about 3–5% of the C atoms are oxidized (i.e. in an induced functional group) [5,6]. It is thought that nitric acid attacks the ends of the SWCNTs, as these sites have often been damaged by sonication, or by shearing forces induced by handling and so are accessible for acid modification. However, it has been noted that 3–5% is too high a proportion if just the ends of the SWCNTs were oxidized. It has been shown that amorphous carbon inherent in the production of SWCNTs also becomes oxidized, and this binds to the CNTs by hydrophobic and electrostatic interactions [7].

X-ray photoelectron spectroscopy (XPS) is also a powerful technique to investigate the oxygen content of oxidized SWCNT, and also to determine the nature of the carbon species. In fact, there is little in the literature directly on oxidized SWCNTs, perhaps because a complete assignment of all carbon species is rendered more difficult by the asymmetry of the graphitic carbon signal and the unknown peak positions of the functional groups. This

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problem has recently been overcome by Jung et al. [8] who showed that with HiPCO produced SWCNTs, refluxed in 3 M nitric acid for 48 h at 130 °C, there was 13% oxygen, 5% nitrogen and of the carbon 7.4% was in the COOH form (the N was added covalently using $NH_4 \cdot H_2O$). It must be noted that XPS studies have been performed on multi-walled CNTs (MWCNT) (for example see [9]) but these findings are not directly relevant here, as MWCNTs, although similar, have many differences to SWCNTs. There have been limited ion beam analysis studies of CNTs species mainly looking at contamination or catalyst content [10–12], with no studies looking at either nitrogen or oxygen.

Here, we report Rutherford backscattering spectrometry (RBS), elastic (non-Rutherford) backscattering spectrometry (EBS) and particle induced X-ray emission (PIXE) measurements of nitric acid treated SWCNTs, produced with Pt/Rh/Re catalyst [13]. We investigate the elemental content of SWCNTs that have been treated to different exposure times in nitric acid, with particular focus on O, N and Pt. The elemental content of solubilised SWCNTs is vital to know if SWCNTs are to be used as therapeutics or in diagnostics.

2. Material and methods

The as-made CNTs, produced with Pt/Rh/Re catalyst [13], were immersed in 16 M nitric acid, sonicated for 10 min in an ultra-sonicating water bath (60 W) and then left in a water bath at ~99 °C for various times. The nitric acid is bought (Fisher, N/2250PB17) at a 70% (equivalent to 16 M) concentration. It was used as it was because we found that with our rather more gentle procedure (i.e 99 °C in a waterbath rather than refluxing at 130 °C for 48 h in 3 M) was not strong enough to solubilise the CNTs. Samples were taken at set times (2, 4 and 6 h), passed through a Millipore 0.2 μm polycarbonate filter to wash off nitric acid, and then dialysed in 100,000 MW tubing (Spectra/Por Biotech cellulose ester membrane) against 18 MΩ water for 14 days with a change of 10 L of water every two days, to remove any unbound contaminants.

Samples were then pipetted on a 6 μm polypropylene (CH_2) thin film, and irradiated with a 2.582 MeV proton beam for about 30 min per sample. The beam size was about 4μm, obtained using Surrey's microbeam facility [14]. The RBS/EBS and the PIXE spectra were collected simultaneously, using an ion implanted Si diode for the particle spectra with a solid angle of 60 msr, a scattering angle of 155° and a resolution of 25 keV; and a Si–Li detector for the X-ray spectra with a solid angle of about 20 msr, a scattering angle of 135°, a resolution of 150 eV and a 150 μm Be filter. The RBS applies to the heavy element components of the spectra such as platinum, while the EBS applies to lighter elements whose scattering cross-sections are non-Rutherford.

The PIXE maps and spectra were analysed using OMDAQ [15] software. OMDAQ is based on the GUPIX code [16]]. OMDAQ collects data in list mode, so that thay can be re-analysed off-line and energy spectra obtained in selected energy regions and for selected areas.

The data were fitted with the DataFurnace [17,18] software using NDFv8.2L which incorporates the LibCPIXE code for PIXE analysis [19]. LibCPIXE does not take the PIXE spectrum itself as input, but the line areas, which are extracted from the spectrum using OMDAQ. DataFurnace can fit multiple spectra (including both particle and photon spectra) simultaneously and self-consistently. For the present samples it was usually adequate to obtain the heavy element ratios with PIXE and then fit the particle spectra using those ratios. In all cases we relied on the ability of DataFurnace to fit with molecular "logical elements" [20].

Non-Rutherford scattering cross-sections were used for C [21], N (unpublished), O [22], Si [23], Na [24]and Ca [25]. The C, N, O, and Si cross-sections are available on SigmaCalc [26] and the Ca cross-sections are available on IBANDL [27].

3. Results and discussion

3.1. RBS/EBS analysis of thin film samples

The main purpose of this experiment was to treat SWCNTs with nitric acid, taking samples at time intervals to compare the oxygen content, with the hypothesis that the longer they were exposed, the more O would be present on the SWCNTs. The 16 M nitric acid treatment effectively solubilised the SWCNTs for all time points (2, 4, 6 h). A 2 μl drop of these solutions was pipetted onto a polypropylene film which dried into a thin film which could be seen easily by eye.

Fig. 1 shows the "high energy" map of one of these drops from a SWCNT sample treated for 6 h in nitric acid. This map is created using all the backscattered particles which have an energy above the C edge in the RBS/EBS spectrum, and which are from all the elements in the sample heavier than C, including the metals. This figure is representative of the maps from all the samples. A uniform region of the map was then selected from which RBS/EBS/PIXE spectra were obtained. The PIXE spectrum shows a large amount of Pt and Rh which is to be expected since this was the catalyst used for growing the SWCNTs. However, there is also a large amount of other contaminants such as Cl and Fe, shown in Table 1. This probably comes both from the nitric acid which contains these elements in significant amounts, and from other preparative steps involved in the CNT production.

With the elemental ratio of the heavy elements given by the PIXE spectrum (a representative PIXE spectrum is shown in Fig. 2) an RBS/EBS/PIXE fit of the data could be obtained (Fig. 3). Using this fit, the thickness for each element could be obtained and is shown in Table 1. Note that the number of N atoms is considerably higher than the other contaminants such as Cl, Ca and Fe, which is expected as