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Direct visualization of electrical transport-induced alloy formation and composition changes in filled multi-wall carbon nanotubes by *in situ* scanning transmission electron microscopy

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ABSTRACT

In order to evaluate the applicability of metal-filled carbon nanotubes, it is crucial to understand their behaviour in the presence of electric currents. In this work we exploit the significant advantages of combining *in situ* experiments with scanning transmission electron microscopy in annular dark-field mode and related analytical techniques to gain further insights into the electrical transport induced transformations in Fe-filled P,N-doped multi-wall carbon nanotubes. With these synergistic analysis techniques, we could monitor in real time the dynamical effects that take place in the carbon nanotubes and their Fe filling as a consequence of the passing of an electric current and subsequent Joule heating. A detailed analysis of the formation, evolution and composition of intermediate phases has been possible employing *in situ* experiments with transmission electron microscopy, scanning-transmission electron microscopy and analysis techniques. We show that a multistage process occurs in which the Fe filling reacts with nitrogen to form an intermediate alloy phase, which then decomposes. The presence of high concentrations of nitrogen within the inner channel of the tube is found to be crucial to this process.

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1. Introduction

Iron-filled carbon nanotubes (CNTs) have been proposed as perfect candidates for a large and varied number of applications, ranging from the biological (such as controlled heating through induction of tumour tissue or as a drug delivery carrier for diagnosis) to optoelectronics or memory storage devices [1–4]. Whichever application we consider, it is vital to be able to monitor the possible phase changes and reactions that can take place, either in the filling material or between this material and the CNT, as a consequence of temperature gradients or current flow through the filled tubes; as well as the direction and preferential paths of any migration of the filling material.

CNTs protect encapsulated material from oxidation by preventing environmental exposure and additionally their reduced dimensionality makes them behave as perfect reaction vessels to image nano-phenomena in the transmission electron microscope (TEM) at elevated pressures and temperatures while confined in two dimensions. Dynamical effects that take place when CNTs are exposed to *in situ* high electrical currents and Joule heating have been observed using conventional bright-field transmission electron microscopy (BF-TEM) [5–15] and scanning TEM-annular dark field (ADF-STEM) imaging *ex-situ* [16–18]. But due to the complexity of the doped system, additional investigations are necessary.

Intentional doping of multi-wall CNTs (MWCNTs) with foreign atoms may change their physical properties and morphology [19–23] but it results in an uneven distribution of elements inside/along the MWCNTs [24], which can have a significant impact on their functionality. Phase changes or reactions resulting from temperature gradients or current flow through the filled tubes,

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either in the filling materials or between these materials and the MWCNT also need to be monitored and understood in order to predict the behaviour of the Fe-filled doped-MWCNTs for their intended applications. While the effect of this irregular distribution of dopants is unknown at a larger scale, in our case it represents a significant advantage, as it will induce different levels of contrast in the STEM images and will facilitate analytical measurements.

Here we have performed *in situ* tests on Fe-filled phosphorous and nitrogen (P,N) co-doped MWCNTs to monitor the dynamical effects that take place as a consequence of the passing of an electric current. The *in situ* study of the behaviour of these special nanomaterials and the boundary conditions in which their properties remain constant are crucial to understand their applicability and possible routes to their exploitation in real life applications.

2. Materials and methods

The P,N-MWCNTs were synthesised using an aerosol-chemical vapour deposition (CVD) method [25] where 2.5 wt% triphenylphosphine and 7.5 wt% ferrocene in benzylamine were decomposed at 780 °C in Ar with the MWCNTs deposited on the inside of the quartz tube. Powders consisting of flakes of straight, aligned P,N-doped MWCNTs were produced with an average length of 15 μm and an average inner and outer diameters of 8 nm and 18 nm respectively [25].

The MWCNTs were mounted onto a 0.25 mm Au wire by dipping into the loose powder. The Au wire with the MWCNTs attached was then mounted into the Nanofactory® STM/TEM holder and a 0.25 mm Au wire was used as the moveable electrode which can be moved in x,y,z directions to make contact with a CNT inside the TEM. The *in situ* STEM imaging, EDX analysis and part of the EELS experiments were carried out using a JEOL ARM200F and a JEOL 3000FEG (scanning)-transmission electron microscopes operated at 200 kV and 300 kV, respectively, in bright-field TEM mode and STEM mode. The best micrographs were taken using a convergence semi-angle of 22 mrad and collection angles 54–276 mrad. The size of each image is 256 × 256 pixels and the images were acquired with a dwell time of 18 microseconds/pixel (1.2 s/image). Part of the EELS experiments were carried out on a Nion UltraSTEM 100 dedicated scanning-transmission electron microscope operated at 60 kV and equipped with a Gatan Enfina energy loss spectrometer at the SuperSTEM facilities in Daresbury, UK.

3. Results and discussion

An example of a P,N-MWCNT is shown in Fig. 1(a) (BF-TEM) and Fig. 1(b) (STEM-ADF). In the samples studied here, P is detected only in the Fe filling and not in the walls of the nanotube, while N is found trapped in the inner channel of the MWCNT [24].

A bias was applied to the as-fabricated MWCNTs mounted on a Nanofactory® STM/TEM holder and possible reactions/changes in the MWCNTs or the Fe filling as a consequence of the passing of an electrical current and subsequent Joule heating were monitored. Briefly, once a bias is applied, as will be described later, three main stages in the evolution of the Fe filled P,N-MWCNTs can be defined (summarised in Fig. 2 (Multimedia view), also see supplemental material at [URL] for the corresponding video (video S1) and further examples, videos S2 and S3). During stage 1, no significant changes are observed as the current increases. During stage 2, an amorphous transitional alloy is formed at one end of the Fe filling, which steadily grows until it detaches and forms a separate particle. During stage 3, the transitional alloy particle shrinks and transforms into several smaller particles with the same ADF contrast as the Fe filling. BF-TEM and STEM-ADF modes were employed to monitor these three stages *in situ*.

In the case of the Fe-filled MWCNT shown in Fig. 2 (Multimedia view), stage 1 starts with the individual MWCNT being contacted, and subsequently the current is increased by stepping up the applied bias. This results in Joule heating of the filling and the MWCNT, but the composition of the filling and the MWCNT remains as described above. The first significant changes (start of stage 2) are observed after a certain threshold current is applied (e.g. 21 μA in the case of the MWCNT shown in Fig. 2 (Multimedia view)). An amorphous deposit appears next to the filling in the inside of the nanotube, as imaged in BF-TEM mode (Fig. 3 (a)) and ADF-STEM mode (Fig. 4(b) and (d)) for other nanotubes. In STEM-ADF mode, the contrast of this deposit appears lower than the Fe filling but higher than the surrounding C (seen more clearly in Fig. 3(b)) indicating the formation of an alloy with an average atomic number that lies between that of the walls of the MWCNT and the pure Fe particles. Additionally, a very thin layer coating the walls of the inner channel is seen in STEM-ADF, showing a brighter contrast (see Fig. 3(b) for a clearer image at higher resolution).

EELS and EDX were used to understand how the chemical composition evolves as the current-induced structural changes described previously take place during stage 2. The transitional alloy formed and the thin coating layer along the inner channel both contain Fe, as can be seen in Fig. 3(c). In order to carry out more detailed electron microscopy analysis of the coating layer and the intermediate contrast particle, a bulk Fe-filled P,N-MWCNT sample was treated by passing a current through the sample *ex situ* (outlined in Section 1 of the Supplementary Information) and the sample investigated using aberration corrected STEM and EELS. This approach allowed us to look at snapshots of different stages of the transitional alloy formation, two of which are displayed in Fig. 4(b) and d. From the areal density of the various components (Fig. 4(a)) it can be seen quite clearly that the transitional alloy formed from the Fe filling in the MWCNT displayed in Fig. 4(b) is a Fe-C-N alloy. This is in agreement with its intermediate contrast observed in STEM-ADF.

Fig. 4(c and d) shows intermediate alloy from another heat treated Fe filled P,N-MWCNT. In this case, there is an increased Fe:N ratio in the transitional alloy compared to the one in Fig. 4(b) (see the Fe profile in the areal density). EEL spectra taken from the Fe particle and the intermediate alloy (Fig. 4(e)) show differences in the N_K edge fine structure. The Fe particle spectrum has a more pronounced π^* peak and is indicative of N in solution in Fe[24]. N was not detected in any of the particles before current-treatment of the

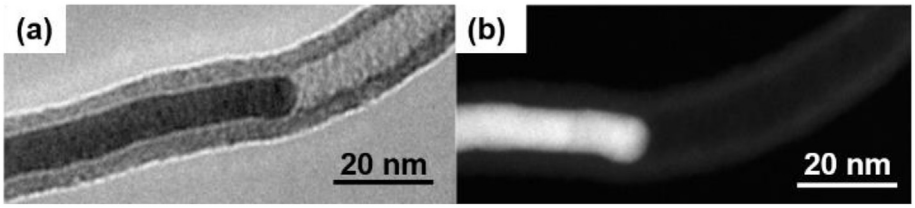

Fig. 1. An as-grown P,N-MWCNT with Fe filling imaged using (a) BF-TEM and (b) ADF-STEM.

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