EXAFS investigations of Iron in Multi-Walled Carbon Nanotubes

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Carbon nanotubes (CNTs) are formed as one or more seamlessly joined cylindrical graphene layers (i.e. "single-walled" or "multi-walled" CNTs). They exhibit exceptional mechanical and electronic properties, such as high flexibility and stress resistance, and good conductivity. Thus CNTs are attractive for a range of applications, including strong light-weight composites and field emission flat-panel displays [1-3]. Carbon nanotubes can be synthesized using chemical vapour deposition (CVD) methods. Commonly, vapours based on ferrocene (C₅H₅-Fe-C₅H₅) are used. The iron (Fe) acts as a growth catalyst [4], remaining predominately inside the nanotubes. The controlled formation of Fe in CNTs is of particular interest. Such a process would enable the production of nanoscaled metal wires encapsulated in high-strength nanotubes, providing a class of materials with large application potential in nano-electronics and composites development.

In this report, EXAFS investigations of Fe in CVD deposited multi-walled carbon nanotube materials are discussed. Samples were pressed to free standing solid disks (13 mm diameter) using cellulose powder (Sigma-Aldrich; 30 µm particle size) as the binding agent. EXAFS data up to k = 17.5 Å⁻¹ were acquired at beamline C using a Si(111) double crystal monochromator. The beam intensity was controlled using a digital monochromator stabiliser (D-MoStab). Higher harmonics were rejected by detuning the MoStab to 55% of the peak intensity of the monochromator rocking curve. The ionisation chambers at the beamline were filled with: 850 mbar N₂ (I₁), 800 mbar N₂ + 50 mbar Ar (I₂), and 500 mbar Ar + 500 mbar Kr (I₃). An Fe reference spectrum was recorded simultaneously for each CNT sample. The data were processed using the freeware VIPER [5].

Figure 1 shows EXAFS data of one of the CNTs materials (black) and of the Fe reference foil (blue). It can be observed that the amplitude of the oscillations of the nanotube sample are considerably weaker than the signals of metallic iron. X-ray Photoelectron Spectroscopy data (not presented here) show that Fe species are only present in traces on the surface of the multi-walled nanotubes; the majority of the Fe is located inside the tubes. Given that the inner diameter of the nanotubes is in the order of 1-2 nm, any Fe species inside the tubes can be considered a nanoparticle or nanostructure. In EXAFS, nanoparticles typically exhibit diminished χ(k) amplitudes, which is consistent with the data shown in Figure 1. It can also be seen, that the frequency and shapes

![Figure 1: EXAFS data of Fe in carbon nanotubes (black) and of an Fe metal reference foil (blue)](image-url)
of the \( z(k) \) curves are very similar for both, CNTs and metallic Fe. The Fourier Transform of the EXAFS data (see Figure 2) underlines these observations.

In the literature, various Fe species inside CNTs have been discussed, in particular metallic iron phases (bcc and fcc) and iron carbides \((\text{Fe}_x\text{C}_y)\) [6-9]. The data shown in Figure 1 indicate that in our case nano-size bcc iron was stabilised inside the nanotubes. This result needs confirmation via, e.g., modelling of the EXAFS data. If it can be confirmed, then the CVD process employed to form the nanotubes may be attractive to produce metallic nanowires in high-strength nanotube materials.

EXAFS data of differently CVD prepared carbon nanotubes (data not presented here) also show a prominent first shell around \( R = 2 \, \text{Å} \) but lack signals from higher shells. Interestingly, the first shell signal is almost as intense as the first shell peak in Figure 2 (CNTs, black curve). The structure of Fe in those cases is still subject to discussion. Several possibilities are to be considered, including: (a) Fe is present as very small nanoparticles with very large surface-to-bulk ratios, (b) Fe is present as iron with a high degree of disorder, (c) Fe is no longer pure iron but a carbide or a mixture of carbides.

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References