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Iron filled carbon nanotubes for bio-applications

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One of the most interesting bio-applications of nanoparticles refers to as “magnetic fluid hyperthermia” (MFH), i.e. a controlled heating of tumor tissue. In the MFH therapy, magnetic nanoparticles are infiltrated in deep tumor tissue and inductively heated by applying alternating current magnetic fields. The biggest challenge of MFH therapy is the temperature control for which fibre-optic thermometers should be inserted into a tumor. A potential way to overcome this problem seems to be application of carbon nanotubes filled with iron which could provide *in-situ* temperature controlling. Therefore, the synthesis routes of iron filled single-walled carbon nanotubes (Fe-SWCNT) and iron filled multi-walled carbon nanotubes (Fe-MWCNT) has been presented. These two types of nanostructures were prepared *via* wet chemistry technique and by *in situ* single step chemical vapour deposition for Fe-SWCNT and Fe-MWCNT, respectively. The samples were examined by means of transmission electron microscopy, in bright and dark field images modes, and X-ray diffraction.

Key words: *carbon nanotubes; filling of carbon nanotubes; transmission electron microscopy; X-ray diffraction*

1. Introduction

Carbon nanotubes (CNT) are carbon nanostructures of a small diameter on the nanometer scale with one or more walls, and a length large in comparison to the diameter. They have mechanically and chemically stable carbon shells which can be opened, filled and closed again without losing their stability. Experiments in filling CNT date back to their identification in 1991 [1, 2]. Extensive work has been performed to synthesize CNT and to endohedrally and exohedrally functionalize them [3–18]. CNTs may be filled with metals, biomolecules, salts, organic materials, etc. The filling procedure can be done during the synthesis process or through subsequent opening and filling of the CNT. In particular, the filling can consist of ferromagnets such as Fe, Ni, and Co [17, 18]. Due to a large form anisotropy of ferromagnetically filled CNT, an

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enormously large heating efficiency compared to other nanoparticles is realized when exposing them to AC magnetic fields.

An outstanding example for the use of ferromagnetic nanoparticles is magnetic fluid hyperthermia (MHF), i.e., controlled heating of a tumor tissue. In the MFH therapy, magnetic nanoparticles are infiltrated in deep tumor tissues and inductively heated by applying AC magnetic fields. One challenge of the MFH therapy, however, is the temperature control for which fibre optic thermometers must be inserted into the tumor. A potential way to overcome this problem seems to be the use of CNT which could provide *in-situ* temperature controlling [19, 20].

2. Experimental

Pristine SWCNTs, with a mean diameter of 1.50 nm and length up to several μm, were fabricated by using a standard laser ablation technique [21]. The 'as produced' material contains amorphous carbon and catalyst particles (Pt, Rh, Re). In order to purify and open the tubes, acid treatment was performed. The laser ablated soot was placed in a diluted aqua regia solution and refluxed for 24 h at ca. 400 K. Subsequent filtration and washing for several hours with distilled water opened and purified the nanotubes which were then transferred to a beaker containing an over-saturated solution of iron(III) chloride ($FeCl_3$). The as-prepared solution was then stirred for 20 h at room temperature.

To yield pure Fe filled SWCNTs, washing out the $FeCl_3$ which is not incorporated into the tubes but remains on the walls or in the space between the bundles, was very important. This was accomplished by quick washing with concentrated HCl (several seconds) and multiple centrifugations with distilled water at which the water was removed and replaced after each centrifugation cycle. As the last step, the sample was heated in air at 593 K for 1 h in order to decompose the $FeCl_3$ to iron and chlorine.

The sample was synthesized by catalytic decomposition of ferrocene, under methane gas flow, in a quartz tube reactor inside a dual zone furnace. Ferrocene is the iron source, while methane acts as the carbon feedstock and the carrier gas. The main parameters are the sublimation temperature of ferrocene (applied in the first furnace stage), $T = 174$ °C, the deposition temperature (in the second furnace stage), $T = 950$ °C, and the methane flow rate of 200 cm^3/min. The reaction time was 0.5 h and before the process took place, the system was evacuated to ca. 10^{-3} mbar at room temperature.

The as-produced material was purified by annealing in air at 350 °C for 1 h, after which the acid treatment was performed. Afterwards, the product was filtrated and washed thoroughly with distilled water and acetone.

The chemical composition of iron filled single-walled carbon nanotubes (Fe-SWCNT) and iron filled multi-walled carbon nanotubes (Fe-MWCNT) was examined using X-ray diffraction (XRD) and the morphology of the sample was studied using high resolution transmission electron microscopy (HR-TEM).

3. Results and discussion

The high angle dark field images in scanning TEM (HAADF-STEM) show thin and long nanowires, as expected with the efficient filling of SWCNTs (Fig. 1a). A more systematic study of the nanowires indicates that most of them have lengths in the range 5–100 nm. Absolute identification of the iron filling using standard TEM was very challenging due to the diameter of the metal wires being so small that it was impossible to differentiate between individual single nanowires and nanotube walls in the bundle. Therefore, Fig. 1a presents an HAADF-STEM image of the pristine SWCNT. Here, one cannot notice any presence of lines indicating formation of iron nanowires in the cavity of the tubes.

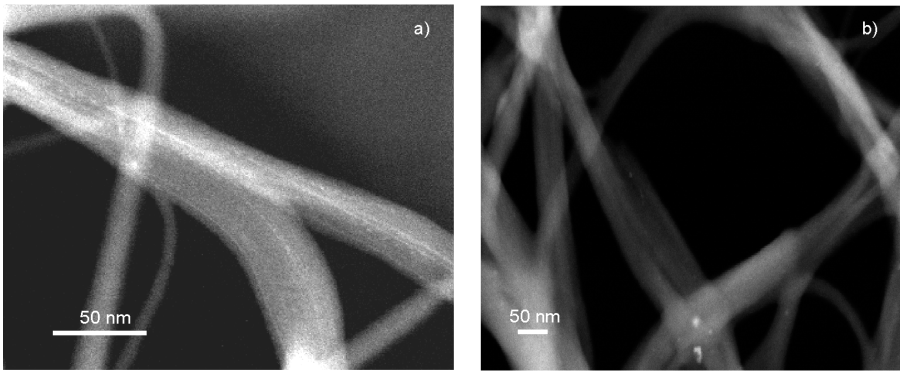

Fig. 1. HAADF-STEM images of Fe-SWCNT (a) and pristine SWCNT (b)

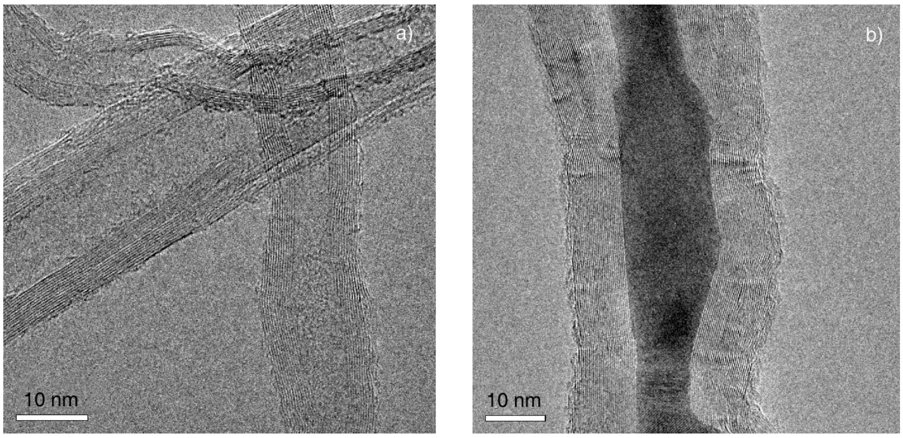

Fig. 2. TEM images of unfilled MWCNTs (a) and Fe-MWCNT (b)

The identification of multi-walled carbon nanotubes and their filled core is much easier due to much higher tube diameters. Bright field TEM was sufficient to observe the morphology of the sample. In Figure 2a, one can observe MWCNT with empty core and parallel graphitic layers forming the multiwalled structure of the tubes. Figure 2a presents an individual MWCNT with a filled iron nanowire. The analysis of TEM images enabled estimation of the mean outer diameter of the tubes (40 nm) and of the filling iron nanowires (100 nm).

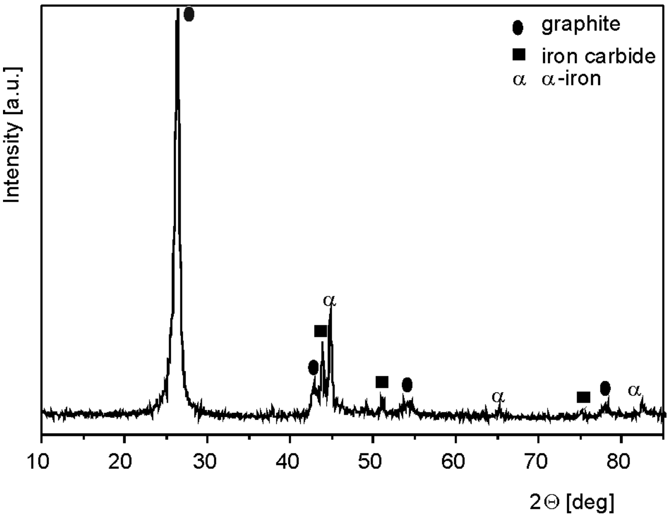

Fig. 3. XRD pattern of Fe-MWCNT

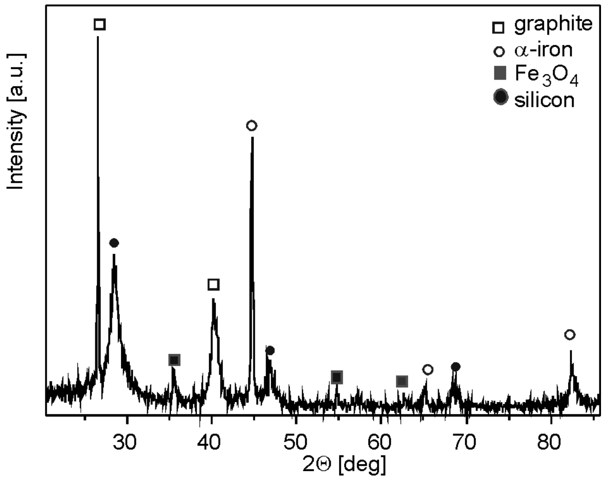

Fig. 4. XRD pattern of Fe-SWCNT

The XRD pattern presented in Fig. 3 shows only the peaks originating from carbon (MWCNT), iron carbide and α-Fe, with a body centered cubic crystal structure. The presence of only one iron structure is very unusual as normally the composition of different iron phases is produced. Here, one can observe that MWCNT are filled only with the ferromagnetic phase of iron.

The crystallographic analysis of Fe-SWCNT clearly indicates the presence of graphite, α-Fe and Fe_3O_4 in the sample (Fig. 4). The peaks associated with silicon originate from the substrate used for XRD measurements.

The presence of α-iron is not surprising as our previous investigations of the magnetic properties of Fe-SWCNT proved that SWCNTs are filled with ferromagnetic form of iron. The ferromagnetic behaviour was observed at room temperature and at liquid nitrogen temperature [18]. The Fe_3O_4 signal comes probably from the oxidized reminiscence of iron which was not incorporated into the cavities of the tubes. The carbon layers protect against the oxidation only the iron incorporated into the interior of the singlewalled tubes [18].

4. Conclusions

We have presented a study on the synthesis and structural analysis of Fe-filled single- and multi-walled CNT bulk samples which can be suitable candidates for bio-applications. Due to the fact that iron filled carbon nanotubes contain a ferromagnetic form of iron, they can be investigated in the magnetic fluid hyperthermia. The insertion of iron filled tubes into the tumor could provide *in-situ* temperature controlling. Nevertheless, further medical investigations are required for a complete understanding of the interactions involved.

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