

Ferrocene encapsulation in carbon nanotubes: Various methods of filling and investigation

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One of the most exciting properties of carbon nanotubes is their ability to encapsulate molecular species in their quasi-one dimensional channels. We present results on single-walled carbon nanotubes filled with ferrocene, the most stable and commercially available metallocene. For encapsulation of the ferrocene molecules we attempted two types of filling: a high temperature vapor-phase method and nano-extraction from ethanol. To confirm the encapsulation, double-walled carbon nanotubes were created from the samples by annealing. The

inner tubes could be detected by Raman scattering via their radial breathing mode. These experiments confirmed that only the high-temperature annealing method was successful. The product was characterized by infrared attenuated total reflection (IR-ATR), Raman, ultraviolet–visible (UV–VIS) and Mössbauer spectroscopy. By the latter method other iron-containing phases were observed. Mössbauer spectra proved that no charge transfer occurs between the nanotube and the ferrocene molecules.

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1 Introduction One of the most interesting and unconventional properties of carbon nanotubes is their ability to encapsulate molecular species in their quasi-one dimensional cavity. In this way they can be used as nanochambers for catalytic reactions and molecular separation, transporters for drugs and other materials and electronic nanodevices.

There are several examples of molecules successfully encapsulated into nanotubes, to mention a few: fullerenes and their derivatives, bio-macromolecules and ionic compounds such as metal halides. Organometallic, particularly iron-containing molecules are especially interesting in this regard, because of the electronic, magnetic, and catalytic properties of iron [1].

Nanotubes have already been filled with metallocenes such as $M(C_5H_5)_2$ ($M = Fe, Co, Ru, V$). Ferrocene ($M = Fe$), the most stable metallocene, contains ^{57}Fe , a Mössbauer nucleus, and can therefore be investigated by Mössbauer spectroscopy, a method sensitive to the molecular environment of iron inside the nanotubes. These molecules – equally to fullerenes – can be converted to an inner tube inside the nanotube by annealing, thus we can also create double-walled carbon nanotubes from the filled samples.

In this paper we present a study of ferrocene encapsulation into single-walled carbon nanotubes, including a complex cleaning process with investigation methods in every step. We present evidence by Mössbauer spectroscopy for a lack of charge transfer between nanotubes and ferrocene molecules.

2 Experimental

2.1 Samples Single-walled nanotubes were purchased from Carbon Solutions Inc. (type P2) prepared by arc discharge, with an average diameter of 1.4 nm [2], while the size of ferrocene molecules is 0.33 nm [3] (Fig. 1).

We tried two methods to insert ferrocene molecules into the nanotubes: by vapor [4] and liquid-phase method [5–7], respectively. In both cases the first step was the opening of the tubes by annealing in air at 570 °C for 20 min. By the vapor-phase method 100 mg nanotube and 100 mg ferrocene were loaded into an evacuated quartz tube, which was heated in a furnace according to a temperature program shown in Fig. 2. In the case of the liquid-phase method 20 mg of nanotubes and 25 mg ferrocene were sonicated in 20 ml ethanol for 30 min in an ultrasonic bath, then the mixture was

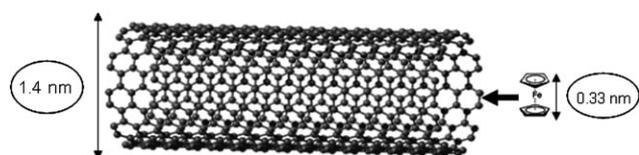


Figure 1 Structural diagram of the nanotube and the ferrocene molecule.

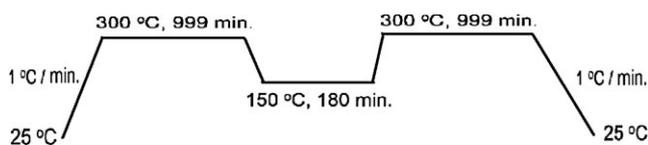


Figure 2 Temperature program of the vapor-phase method.

left to stand for one day. Subsequently, the dispersion was filtered through a nylon filter.

The next step in both methods was the removal of adsorbed ferrocene molecules from the surface of the nanotubes. This procedure will be discussed thoroughly in the next section. Finally we filtered the samples through a polytetrafluoroethylene filter, and investigated them in the form of buckypapers.

In order to determine the efficiency of the encapsulation, the filled tubes were converted to double-walled nanotubes by annealing at 800 °C for 2 h [8, 9].

2.2 Characterization The samples were investigated by Raman, UV–VIS, infrared attenuated total reflectance (IR-ATR), and Mössbauer spectroscopy.

Raman spectra were taken by a Renishaw 1000 MB spectrometer at room temperature, using 785 nm excitation wavelength, UV–VIS spectra by a Jasco v550 spectrometer, ATR spectra by a Bruker Tensor 37 spectrometer, combined with a Helios ATR Microsampler using a germanium crystal. ^{57}Fe Mössbauer spectra were recorded by a constant acceleration spectrometer with a source activity of 0.70 GBq at 12 K. The amount of the sample used in the latter case was about 90 mg.

3 Results and discussion Raman spectra of the samples after annealing (Fig. 3) proved that double-walled carbon nanotubes formed only from the material filled by the vapor-phase method; the liquid-phase method was unsuccessful. Below, we will discuss the results on the vapor-phase sample.

To achieve reliable characterization results, it is very important to remove the ferrocene molecules adsorbed on the nanotube surface after encapsulation. For this purpose we applied a complex cleaning process with different organic solvents and control measurements at every step. At first we washed our sample with ethanol and acetone, then analyzed it by Raman and IR-ATR spectroscopy [10]. In addition, the UV spectrum of the filtrate was examined and compared to ferrocene solutions with known concentration [11]. Figure 4

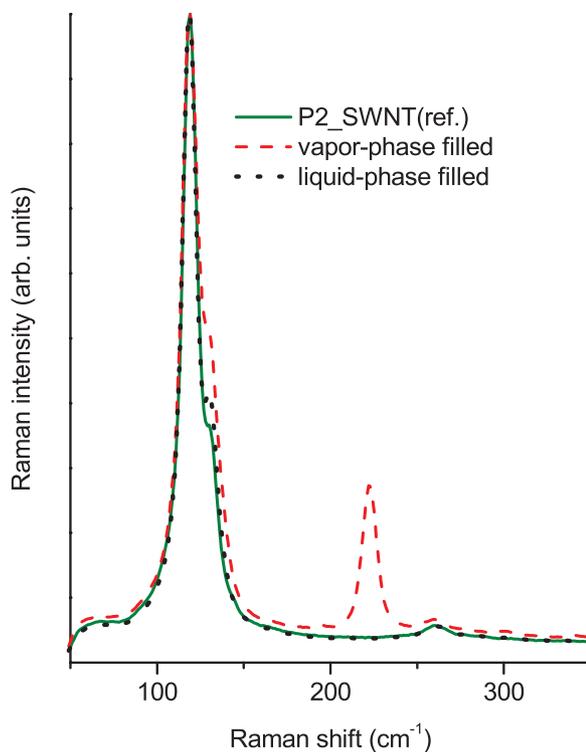


Figure 3 (online color at: www.pss-b.com) Raman spectra of the samples after annealing. The high-frequency RBM mode of the inner tube appears only in the vapor-phase filled sample.

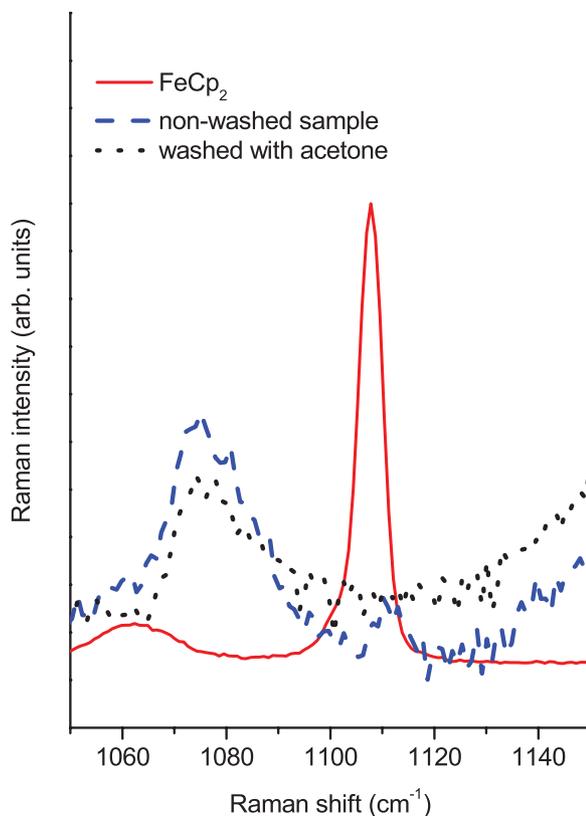


Figure 4 (online color at: www.pss-b.com) Raman spectra of the washed and non-washed samples.

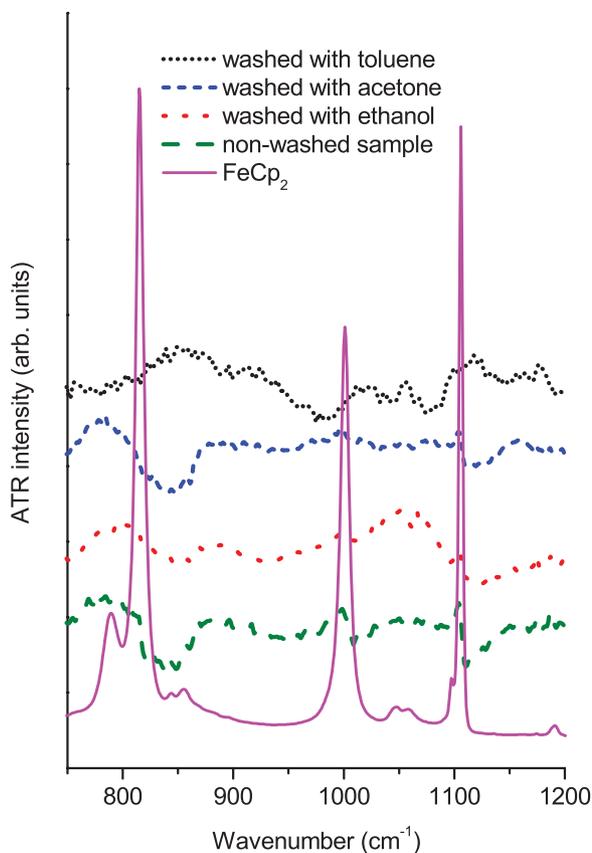


Figure 5 (online color at: www.pss-b.com) ATR spectra collected after each step of the cleaning process.

shows Raman spectra of the washed and non-washed sample compared to that of the pure ferrocene focused on a very intense peak at about 1105 cm^{-1} , which is attributable to the breathing mode of the cyclopentadienyl ring in ferrocene [12]. Figure 5 shows IR-ATR spectra in the same frequency range. Here, ferrocene shows three strong peaks, at 816 , 1000 , and 1106 cm^{-1} , respectively.

As it can be seen in Figs. 4 and 5, the ferrocene peaks disappeared from the Raman spectra but remained in the ATR spectra after washing the sample with ethanol and acetone. (The UV peak of ferrocene at 430 nm was not seen in the last filtrate after washing, either.) This means on the one hand that ATR is a more sensitive method to follow the cleaning process than the others, on the other hand that some adsorbed ferrocene still remained on the surface. After changing the solvent to toluene, we investigated the sample only by IR-ATR after washing. According to Fig. 5 this change resulted in the peaks disappearing from the spectra, thus toluene proved to be the most suitable solvent to remove the excess of ferrocene.

After removing the ferrocene molecules from the surface of the sample, we analyzed it by Mössbauer spectroscopy. The measurements were carried out at 12 K , and the reference nanotube and ferrocene (annealed according to the same temperature program as the filled sample) were

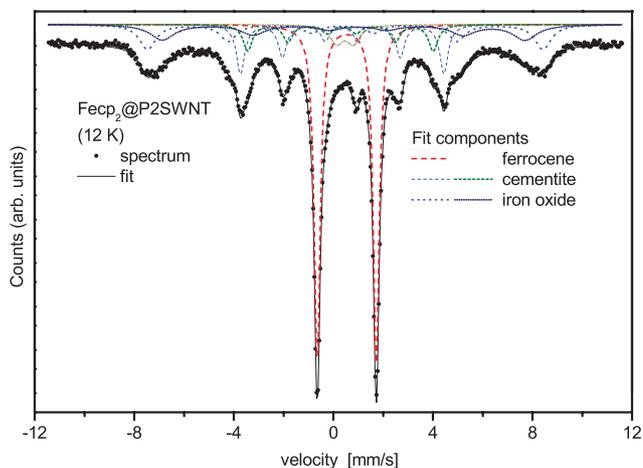


Figure 6 (online color at: www.pss-b.com) Mössbauer spectrum of $\text{FeCp}_2@P2\text{SWNT}$ at 12 K and the components of the fit: ferrocene, cementite, and iron oxide phases.

investigated as well. In the reference nanotube no Mössbauer effect was observed, which is expected since the catalyst used for nanotube production does not contain iron [2].

Figure 6 shows the Mössbauer spectrum of the filled sample at 12 K , along with a result of a fit using the previously determined ferrocene spectrum and other known iron-containing phases. It can be observed that the iron content of the sample is in the form of ferrocene, besides other iron-containing phases like iron carbide (cementite, Fe_3C) and a mixture of iron oxides and hydroxides. The two typical Mössbauer parameters, the isomer shift and the quadrupole splitting do not differ appreciably from that of ferrocene, indicating that no charge transfer occurs which involves the guest molecules. The isomer shift would change with the charge on the iron nucleus, and the quadrupole splitting would be characteristic of variations in the symmetry of the charge distribution in the cyclopentadienyl rings. We obtain an isomer shift of $0.539(1)\text{ mm/s}$ for the filled nanotube and $0.540(1)$ for pure ferrocene, way within the estimated measurement precision of 0.01 mm/s .

From carbon photoelectron spectra in laser-ablated nanotubes, Shiozawa et al. [8, 9] came to different conclusions. Theoretical calculations, however, did not agree with the simple charge transfer model; instead, they had to evoke some type of covalent bonding involving the ferrocene molecules. In view of the above results, this scenario is even more unlikely. Since more than one type of carbon is present in the sample, the carbon photoelectron spectroscopy seems less reliable than Mössbauer spectroscopy, where ferrocene can be unambiguously assigned.

4 Conclusions In this work, we demonstrated a complex analysis to follow the cleaning process of ferrocene-filled nanotubes. This characterization included IR-ATR, UV-VIS, Raman, and Mössbauer spectroscopy. Out of ethanol, acetone, and toluene, the latter proved to be

the most suitable solvent to remove the adsorbed ferrocene molecules from the nanotube surface, while IR-ATR was found the most sensitive method to detect residual adsorbed material. We were able to detect the ferrocene molecules inside the nanotubes by Mössbauer spectroscopy, but also observed other iron-containing phases. This observation calls for designing alternative low-temperature filling methods. The Mössbauer spectra also proved that no charge transfer occurs to or from ferrocene molecules.

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