Phase Analysis of Magnetic Inclusions in Nanomaterials Based on Multiwall Carbon Nanotubes

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Functionalized multiwall carbon nanotubes as well as nanocomposite based on that material covered by nanoparticles composed of iron oxides were the subject of investigations. In order to identify all iron-bearing phases including those reported on the base of previous X-ray diffraction measurements, the transmission Mössbauer spectroscopy was utilized. The experiments were carried out both at room temperature and also at low temperatures. It was stated that in the investigated nanotubes some impurities were present, originating from the catalyst remains, in form of Fe–C and α-Fe nanoparticles. The Mössbauer spectra collected for the nanocomposite showed a complex shape characteristic of temperature relaxations. The following subspectra related to iron-based phases were identified: sextet attributed to hematite, with hyperfine magnetic field reduced due to the temperature relaxations, sextet corresponding to iron carbide as well as two doublets linked to superparamagnetic hematite and ferrihydrites.

1. Introduction

Multiwall carbon nanotubes (MWCNTs), described as multiple rolled layers of graphene, have been intensively studied since their discovery in 1991 [1]. They are of special interest for the industry because of their excellent electrical, mechanical, thermal and chemical properties as well as many commercial — present and evolving — purposes in medicine, electronics, optics, mechanics, energy storage and other fields of material science [2–4]. Recently, the development of an innovative manufacturing process took place [5] in order to reach a supplementary incorporation of magnetic components to the surface of the nanotubes, which makes their possible applications much wider.

Two kinds of nanomaterials based on multiwall carbon nanotubes are the subject of this paper: (A) so-called functionalized MWCNTs — with COONH$_4$ groups introduced on the surface of the multiwall carbon nanotubes — as a reference sample and (B) nanocomposite containing the same material covered by iron oxide nanoparticles. The carbon nanotubes were produced by the chemical vapor deposition (CVD) using metallic iron as a catalyst and their subsequent chemical processing. This method has crucial advantages: it does not need high

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temperature; furthermore, the growth rate and dimensions of the final product can be easily controlled by a congruent choice of reaction parameters. However, some iron containing phases can arise in the course of nanotubes growth due to the use of metallic iron as a catalyst [6, 7]. The presented study is intended to identify such inclusions in both kinds of investigated materials and also to analyze phase composition of nanocomposite (B).

2. Experimental details

The raw MWCNTs (93% of purity, CNT CO., Ltd. from South Korea) were manufactured via CVD method with iron (Fe) as the catalyst. The details of the functionalization process, resulting in forming MWCNTs–COONH$_4$, have been described in Ref. [5]. Moreover, the further procedure showing how to cover the nanotubes by the nanoparticles of iron oxides is also reported there. The structure and morphology of the final material was previously studied using X-ray diffractometry (XRD) and transmission electron microscopy (TEM) [5], while in this paper, ^{57}Fe Mössbauer spectroscopy was used in order to identify the components comprising iron. The measurements were performed in the temperature range from –180 °C to 22 °C, by means of a standard Mössbauer spectrometer (POLON) and ^{57}Co/Rh source of γ-radiation of activity about 50 mCi, located on a head of a vibrator working in a constant acceleration mode. Powder samples were placed in a small container made of boron nitride. A proportional counter was employed

in order to detect the γ-radiation. Hyperfine parameters of individual subspectra: hyperfine magnetic field (HMF), isomer shift (IS, comprising both chemical and temperature shift in relation to pure metallic iron) and quadrupole splitting (QS) as well as relative intensities of the components (A) were determined by the use of NORMOS program dedicated to the Mössbauer spectra analysis.

3. Results and discussion

As reported in Ref. [5], TEM images proved that the diameter of nanotubes varied from 10 to 40 nm. Moreover, for samples A and B the traces of catalyst were visible in a form of nanoparticles located inside the nanotubes while nanoparticles composed of iron oxides were observed at the nanocomposite (sample B) surface. The average diameters of iron oxides and catalyst traces were approximately 50 nm and 12 nm, respectively. Both nanomaterials exhibited weak and somewhat different magnetic properties. XRD patterns showed, except for a component attributed to graphite which occurred in both cases, a presence of hematite in the nanocomposite. However, the results did not prove presence of internal inclusions, probably due to their very low concentrations.
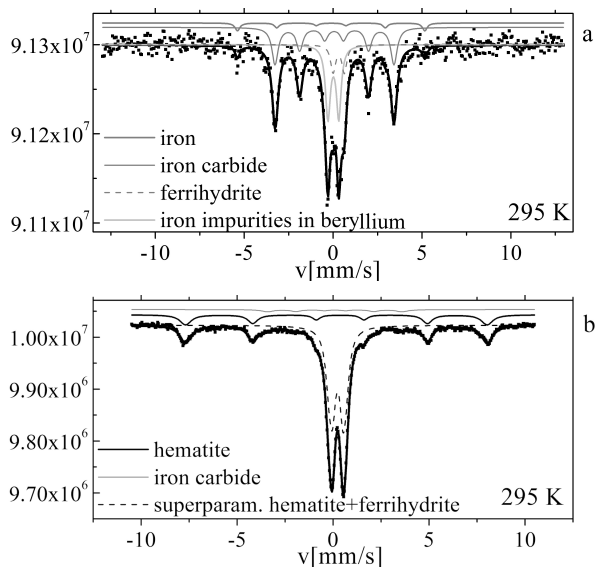

Fig. 1. RT Mössbauer spectra of the nanomaterials: MWCNTs–COONH$_4$ (a) and nanocomposite (b).

Room temperature (RT) transmission Mössbauer spectra collected for both materials are shown in Fig. 1. Due to very small amount of iron phases in MWCNTs–COONH$_4$, the quality of the spectrum is not good, in spite of the unusually long time of the experiments (several weeks). The spectrum was fitted with two sextets representing magnetic phases and two doublets reproducing the central part. The final parameters of individual components as well as their relative intensities are presented in Table I. The sextet of larger intensity with

hyperfine magnetic field (HMF) 20.7 T and isomer shift 0.17 mm/s is attributed to non-stoichiometric iron carbide Fe$_x$C while the smaller sextet, characterized itself by HMF equal to 32.8 T and IS equal to zero is ascribed to α-Fe. Both phases occurred in the form of inclusions, as a result of the application of the iron catalyst.

TABLE I

Hyperfine parameters of components of Mössbauer spectra collected for samples: (A) functionalized MWCNTs–COONH$_4$, (B) nanocomposite — the former material covered by iron oxides. Int. [%] — relative intensity, IS [mm/s] — isomer shift, QS [mm/s] — quadrupole splitting, HMF [T] — hyperfine magnetic field.

Smp. T [K]	Param.	Sxt. 1 α-Fe	Sxt. 2 Fe$_x$C	Sxt. 3 Fe$_2$O$_3$	Dbl. 1	Dbl. 2
A 293	Int.	9	64		19	8
	IS	0.00	0.17	—	0.12	0.42
	QS	0.00	0.02		0.61	0.63
	HMF	32.8	20.7		–	–
A 293	Int.corrected corrected	11	79	–	-	10
B 293	Int.		8	39		54
	IS	–	0.20	0.38	–	0.34
	QS		0.0	−0.20		0.66
	HMF		21.7	48.7		–
B 183	Int.		5	54		41
	IS	–	0.25	0.43	–	0.41
	QS		0.00	−0.23		0.71
	HMF		21.5	50.9		–
B 77	Int.		4	59		38
	IS	–	0.31	0.49	–	0.45
	QS		0.0	−0.22		0.72
	HMF		21.8	51.9		–

The doublet of smaller intensity and IS= 0.42 mm/s can be attributed to ferrihydrite. The other paramagnetic component — doublet 1, with intensity about 19%, was difficult to identify. The additional experiments which were performed without any sample in the way of γ-radiation showed that an origin of this doublet is an iron impurity in beryllium [8] present in the window of the counter. This phase, due to its vestigial amount, is negligible in usual measurements but it became manifested as a consequence of very long time of experiment caused by insignificant concentration of iron in the investigated sample. The corrected intensities of the components, made by evaluations ignoring this doublet, are shown in the next line in Table I.

The Mössbauer spectrum collected at room temperature for the nanocomposite comprised of MWCNTs–COONH$_4$ covered with iron oxides showed a more complex shape characteristic of temperature relaxation. It consists of three main subspectra: a sextet related to iron carbide, a doublet attributed to ferrihydrite — Fe$_5$HO$_8$ · 4H$_2$O (or possibly to iron linked to carboxylic groups) as well as a sextet of high hyperfine magnetic

field 48.7 T. Both isomer shift (0.38 mm/s) and quadrupole splitting (–0.20 mm/s) derived for the sextet are typical of α-Fe$_2$O$_3$. However, hyperfine magnetic field is clearly smaller than the value characteristic of bulk hematite at room temperature (51 T). Moreover, the lines are asymmetrically broadened towards the spectrum centre. All these facts can be related to temperature relaxations of magnetic moments of small α-Fe$_2$O$_3$ particles, i.e. fluctuations of the magnetization directions among the energy minima, which causes — among others — some reduction of hyperfine magnetic field [9]. Therefore, the considered sextet has been attributed to hematite which is in accordance with XRD results reported in Ref. [5].
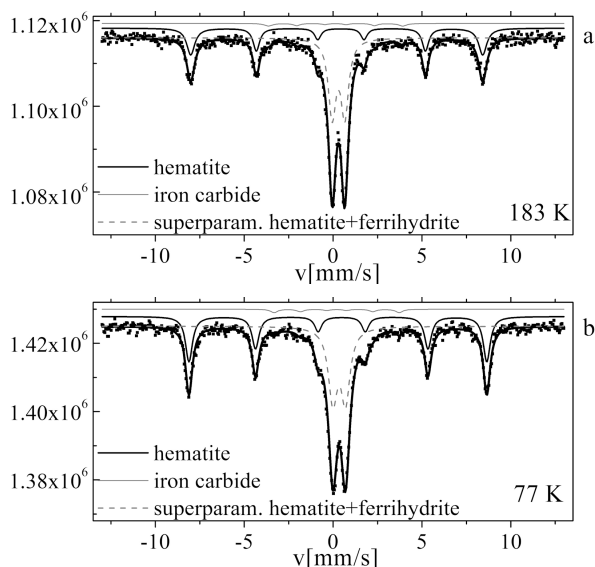

Fig. 2. Mössbauer spectra of the nanocomposite (sample B) at low temperatures.

As usually dimensions of nanoparticles exhibit some distribution, fast relaxations of the smallest particles may cause that average value of magnetization is zero, i.e. so-called superparamagnetic behavior is observed. Hence, the magnetic subspectrum is accompanied by a superparamagnetic component and proportion between their intensities depends on the temperature. In order to prove the superparamagnetic behavior, two supplementary measurements at lower temperatures (183 K and 77 K) were performed for the nanocomposite. Respective Mössbauer spectra are presented in Fig. 2 and they are similar as those collected at room temperature. As can be seen in Table I where the fitted parameters of components are shown, the lower temperature of the nanocomposite, the larger intensity of the sextet related to hematite is stated. At the same time, the intensity of the doublet decreases, but even at 77 K it persists at the level of 38%. We cannot expect such considerable contribution of superparamagnetic hematite particles — according to Ref. [10], where it has been shown that the Fe$_2$O$_3$ particles of medium diameter 16 nm exhibit the blocking temperature of 143 K. Thus, the central doublet probably consists of

two overlapping components of similar parameters: one of them originates from ferrihydrite, while the other — from superparamagnetic hematite.

4. Conclusions

The results of the Mössbauer spectroscopy investigations proved, in accordance with previous XRD and TEM outcomes, the presence of iron-bearing inclusions in novel nanomaterials based on multiwall carbon nanotubes. In MWCNTs–COONH$_4$ the impurities had the form of Fe$_x$C and α-Fe nanoparticles, originating from the catalyst remains. In the Mössbauer spectra of the nanocomposite consisted of MWCNTs–COONH$_4$ covered with iron oxides, besides of iron carbides, the hematite components were also found. Moreover, temperature relaxations of magnetic moments of the α-Fe$_2$O$_3$ nanoparticles were reflected in the spectra evolution characteristic of superparamagnetism. It has been stated that the Mössbauer spectroscopy enabled identification of iron phases occurring in a vestigial amount and thus not recognisable to other experimental methods.

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