

Iron-containing microphases in multiwalled carbon nanotubes

Alexey V. Sobolev · Nikolai B. Cherkasov ·
Igor A. Presniakov · Serguei V. Savilov

© Springer Science+Business Media B.V. 2011

Abstract The phase composition of carbon nanotubes (CNTs) with encapsulated iron atoms was examined by ^{57}Fe Mössbauer spectroscopy. It was shown that iron atoms were stabilized in thermodynamically stable iron carbide and oxide phases and phases that are not usual under synthesis conditions ($\gamma\text{-Fe}$ and $\gamma\text{-Fe}_2\text{O}_3$).

Keywords Multiwalled carbon nanotubes · Mössbauer spectroscopy

1 Introduction

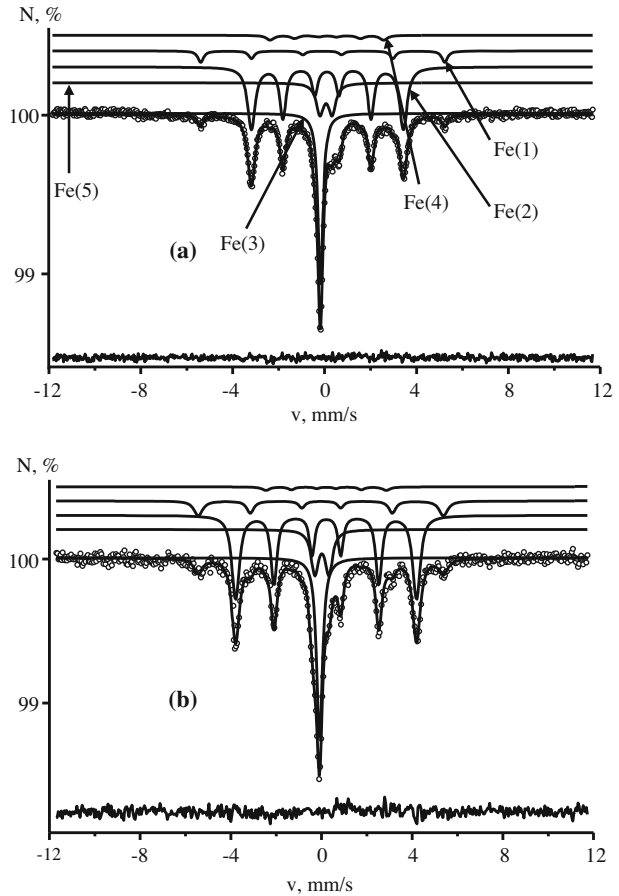
The interest of researchers specializing in various areas of material sciences in carbon nanotubes (CNT) has increased in recent years primarily because of a wide range of their application in different technologies. A fairly high surface area of these materials and their thermal stability allow nanotubes to be used as carriers of various catalysts, and the possibility of chemical modification of their surfaces enables to create new hybrid materials [1].

2 Experimental

The synthesis of iron-containing multiwalled carbon nanotubes was performed on an injection unit following the procedure described in [2].

A. V. Sobolev (✉) · N. B. Cherkasov · I. A. Presniakov · S. V. Savilov
Chemistry Department, Lomonosov Moscow State University, Moscow, 119991, Russia
e-mail: salex12@rambler.ru
URL: <http://www.chem.msu.ru/rus/radio/03.html>

Fig. 1 ^{57}Fe Mössbauer spectra of the Fe-CNT sample at 293 K (a) and 77 K (b)



3 Results and discussion

The ^{57}Fe Mössbauer spectrum of CNT measured at $T = 293\text{ K}$ was best fitted as a superposition of three magnetic subspectra Fe(1), Fe(2), and Fe(4) one paramagnetic quadruple doublet Fe(5) and singlet line Fe(3) (Fig. 1a). The hyperfine parameters of subspectra and its composition are listed in Table 1. The situation with two paramagnetic subspectra Fe(3) and Fe(5) is unambiguous. The isomer shift ($\delta(5)$) and quadrupole splitting ($\Delta(5)$) of the Fe(5) doublet can correspond either to $\text{Fe}_{1-x}\text{C}_x$ superparamagnetic particles [3] or to the iron-graphite complex already mentioned above [4]. The high quadruple splitting value for Fe(5) component is evidence of a substantial distortion of the local environment of iron atoms, and broadened linewidth ($\Gamma(5) \approx 0.40\text{ mm/s}$) shows that its nearest environment is nonuniform. The isomer shift of the Fe(3) subspectrum can be assigned either to the face-centered γ -Fe polymorph, which becomes magnetically ordered only at low temperatures [3], or to small α -Fe phase particles in the superparamagnetic state ($d \sim 60\text{ \AA}$) [5]. To solve the problem of the origin of the Fe(3) singlet component, we measured the Mössbauer spectrum at 77 K. The model interpretation of the spectrum (Fig. 1b)

Table 1 Hyperfine parameters of the ^{57}Fe Mössbauer spectra of the Fe-CNT sample

T, K	Component	$\delta, \text{mm/s}$	$\varepsilon, \text{mm/s}$	H, kOe	$\Gamma, \text{mm/s}$	$S, \%$	Phase
293	Fe(1)	0.00(1)	0.01(1)	332(1)	0.29(2)	7.1(4)	$\alpha\text{-Fe}$
	Fe(2)	0.20(1)	0.01(1)	207(1)	0.40(1)	52.8(5)	Fe_3C
	Fe(3)	-0.09(1)	0	0	0.26(1)	23.7(1)	$\gamma\text{-Fe}$
	Fe(4)	0.20(1)	-0.01(2)	155(2)	0.40(1)	4.2(4)	$\text{Fe}_3\text{C}_{1+x}$
	Fe(5)	0.15(1)	0.27(1)	0	0.39(1)	12.3(6)	Fe-gr.
77	Fe(1)	0.08(1)	-0.01	338(1)	0.46(1)	10.5(9)	$\alpha\text{-Fe}$
	Fe(2)	0.31(1)	-0.01(1)	250(1)	0.40(1)	52.0(8)	Fe_3C
	Fe(3)	0.01(1)	0	0	0.32(1)	22.1(9)	$\gamma\text{-Fe}$
	Fe(4)	0.34(2)	-0.1(1)	166(5)	0.40(1)	2.1(6)	$\text{Fe}_3\text{C}_{1+x}$
	Fe(5)	0.20(2)	0.31(1)	0	0.40(1)	13.3(8)	Fe-gr.

showed that the relative contributions ($S(i)$) of all the partial components including the Fe(3) singlet line remained almost unchanged within the temperature dependence accuracy to the λ -Mössbauer factors (Table 1). This result allows us to exclude the possibility of the formation of small α -Fe particles, i.e. the Fe(3) singlet component should be assigned to γ -Fe particles. This conclusion is favored by Fe(5) singlet line broadening observed in the low temperature spectrum ($\Gamma_3(300 \text{ K}) = 0.26 \text{ mm/s} \rightarrow \Gamma_3(77 \text{ K}) = 0.32 \text{ mm/s}$), which can be caused by the beginning of magnetic ordering of γ -Fe particles [3]. The temperature of the appearance of the line broadening at $T \approx 85 \pm 5 \text{ K}$, obtained from recent temperature dependence of Γ_3 ($77 \div 300 \text{ K}$), is very close to the Neel temperature ($T_N = 90 \text{ K}$) of polycrystalline γ -Fe particles [3], which shows that γ -iron particles are not amorphous or superparamagnetic. Unexpectedly, the γ -Fe phase, which is thermodynamically unstable at $T < 1011 \text{ K}$ [6], is characterized by a substantial relative contribution of $S_3 \approx 24\%$ (Table 1). Conversely, the relative contribution of the Fe(1) component corresponding to the thermodynamically stable α -Fe phase comprises only several percent ($S_1 = 7\text{--}10\%$). There can be several reasons for the stabilization of a significant amount of the γ -Fe phase unstable at low temperatures in Fe-CNT samples. The kinetic factor is a high rate of cooling of the products of CNT-Fe synthesis, which can cause “freezing” of the γ -iron phase formed at high temperatures. A similar explanation was suggested in a study of multiwalled CNTs grown on an inert oxidized silicon substrate preliminarily covered by an iron-containing catalyst performed using conversion electron Mössbauer spectroscopy [7, 8]. It was shown that metastable γ -Fe particles with Fe_3C carbide coating were largely localized at nanotube tails, where the rate of product cooling was maximum. The thermodynamic factor is related to different specific volumes of two iron polymorphs, $V_{\gamma\text{-Fe}} < V_{\alpha\text{-Fe}}$ [9]. According to this inequality, the $\gamma\text{-Fe} \rightarrow \alpha\text{-Fe}$ low temperature phase transition should be accompanied by an increase in the specific volume of the system. It follows that, when iron particles are closely packed in a small volume inside nanotubes, reversible $\gamma\text{-Fe} \leftrightarrow \alpha\text{-Fe}$ transition equilibrium remains strongly shifted to the left even at low temperatures.

4 Conclusions

In the Fe-CNT samples obtained, iron-containing particles are stabilized in the form of three phases magnetically ordered and two paramagnetic at $T = 293 \text{ K}$ phases.

Over the whole temperature range studied, magnetically ordered α -Fe and Fe_3C particles do not exhibit superparamagnetic behavior. The temperature dependence of Γ_1 of α -Fe component amounting to its area (S_1) reveals a small part of α -Fe to be the only phase in amorphous or nanoscaled.

Acknowledgement This work was financially supported by the Russian Foundation for Basic Research (project no. 09-03-00840a).

References

1. Serp, P., Corrias, M., Kalck, P.: Appl. Catal. A: Gen. **253**, 337 (2003)
2. Savilov, S.V., Zosimov, G.A., Lunin, V.V.: RF Patent No. 2310601 (2007)
3. Prados, C., Crespo, P., Conzalez, J.M., et al.: Phys. Rev. B **65**, 113405 (2002)
4. Novakova, A.A., Yu, T., Kiseleva, Il'ina, Yu.V., et al.: Al'tern. Energ. Ekol. **3**, 37 (2004)
5. Morup, S., Knudsen, J.E.: J. Phys. C **18**, 2943 (1985)
6. Bodker, F., Morup, S., Linderroth, S.: Phys. Rev. Lett. **72**, 282 (1994)
7. Ruskov, T., Asenov, S., Spirov, I., et al.: J. Appl. Phys. **96**, 7514 (2004)
8. Ruskov, T., Spirov, I., Ritschel, M., et al.: J. Appl. Phys. **100**, 084326 (2006)
9. Matter, P.H., Wang, E., Millet, J.-M.M., et al.: J. Phys. Chem. **111**, 1444 (2007)