materials

Supplementary Materials

Effect of Grinding and the Mill Type on Magnetic Properties of Carboxylated Multiwall Carbon Nanotubes

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Table 1. Hyperfine parameters fitted to the Mössbauer spectra measured at 85 K (*IS* – isomer shift related to the metallic Fe, *QS* – quadrupole splitting, H_{hf} – hyperfine magnetic field, ΔQ - quadrupole splitting distribution, ΔH – magnetic field distribution, *C* – relative contribution, Γ – line width).

Types of MWCNTs	**MWCNTs *as prepared***					**MWCNTs-COOH**				**MWCNTs-COONH$_4$**					
Component	**Fe_3C**	**α - Fe**	**Fe^{2+} in Fe_xO**	Fe oxides/ hydroxides/ ferrihydrates	Par **Fe^{2+}/Fe^{3+}**	**Fe_3C**	**α - Fe**	Fe oxides/ hydroxides/ ferrihydrates	Par **Fe^{2+}/Fe^{3+}**	**Fe_3C**	**α - Fe**	**Fe_xC_y**	**Fe^{2+} in Fe_xO**	Fe oxides/ hydroxides/ ferrihydrates	Par **Fe^{2+}/Fe^{3+}**
control															
C[%]	82.2±2.2	3.8±1.2	9.4±1.2	-	4.6±0.8	65.7±3.1	7.0±2/4	13.5±2.7	14.0±2.5	41.6±3.2	2.3±2.0	3.7±2.0	2.84±1.9	-	49.6±5
H_{hf} [T]	24.8 ΔH=0.6 p=0.8 24,5 ΔH=3.5 p=0.2 <H>=24.7	33.6 ΔH=0.7	8.9 ΔH=1.1	-	-	25,1 ΔH=0.54 p=0.78 25.2 ΔH=3.0 p=0.22 <H>=22.4	34.3 ΔH=1.1	8.5 ΔH=3.8	-	24.9 ΔH=0.46	33.8±1.5	13.6 ΔH=0.05	26.8 ΔH=0.1	-	-
ε /QS [mm/s]	< ε >=-0.005	0	0.02±0.04	-	0.73 ΔQ=0.37	< ε >=-0.009	0	-0.09±0.10	0.60 ΔQ=0.28	< ε >=-0.004	0	0.04±0.10	0.12±0.17	-	Q_1=0.69 ΔQ_1=0.22 (37.6%) Q_2=1.20

															ΔQ_2=0.5 (12%)
IS [mm/s]	<IS>=0.20	-0.01±0.05	0.89±0.04	-	0.12±0.06	<IS>=0.21	0.06±0.05	0.39±0.11	0.40±0.03	<IS>=0.21	0.06±0.11	0.19±0.15	0.99±0.18	-	IS_1=0.38±0.02 IS_2=0.30±0.08
agate mill															
C[%]	82.1±2.1	6.1±1.0	3.4±1.1	8.6±0.6	-	82.6±5.8	6.7±3.0	-	10.6±1.9	48.5±2.1	3.1±1.6	-	4.8±1.8	9.0±2.3	34.5±2.5
H_{hf} [T]	25.1 ΔH=0.77 p=0.8 25.1 ΔH=6.8 p=0.2 <H>=25.1	34,2 ΔH=0.78	17.2 ΔH=1.0	4.8 ΔH=1.6	-	25.1 ΔH=0.46 p=0.76 23.7 ΔH=3.3 p=0.24 <H>=24.7	32.8 ΔH=0.03	-	-	24.9 ΔH=0.29	34.7 ΔH=0.76	-	23.7 ΔH=1.0	8.6 ΔH=1.7	-
ε /QS [mm/s]	< ε >=0.001	0	0.13±0.06	0.17±0.04	-	< ε >=0.001	0	-	0.57 ΔQS=0.25	< ε >=-0.011	0	-	0.23±0.11	0.09±0.10	0.71 ΔQS=0.30
IS [mm/s]	<IS>=0.20	-0.03±0.03	0.74±0.07	0.34±0.04	-	<IS>=0.21	0.12±0.10	-	0.27±0.08	<IS>=0.20	0.06±0.10	-	1.26±0.13	0.56±0.12	0.40±0.01
steel mill															
C[%]	83.9±2.2	6.4±1.0	3.3±0.7	-	6.4±0.7	15.6±1.4	12.8±1.7	42.3±3.5	29.2±2.8	44.3±2.7	5.8±1.9	-	5.2±1.6	12.1±2.1	32.6±3.7
H_{hf} [T]	24.8 ΔH=0.62 p=0.8	34.0 ΔH=0.73	9.4±0.4 ΔH=0.008	-	-	25.04 ΔH=0.67	32.2 ΔH=2.3	55.2 ΔH=3.2 (p=0.196)	-	24.8 ΔH=0.28	34.5 ΔH=0.5	-	24.1±0.7	8.3 ΔH=1.9	-

	23.2 $\Delta H=9.6$ $p=0.2$ <H>=24.5							45.0 $\Delta H=3.0$ ($p=0.047$) 40.0 $\Delta H=3.0$ ($p=0.103$) 35.0 $\Delta H=3.0$ ($p=0.041$) 30.0 $\Delta H=3.0$ ($p=0.136$) 20.0 $\Delta H=3.0$ ($p=0.155$) 15.0 $\Delta H=3.0$ ($p=0.033$) 10.0 $\Delta H=3.0$							

								(p=0.289) <H>=29.0							
ε /QS [mm/s]	< ε >=-0.007	0	-0.03±0.05	-	0.81 ΔQS=0.28	0.006±0.010	0	0.03±0.04	QS_1=0.70 ΔQS_1=0.34 (22.3%) QS_2=0.8 ΔQS_2=0.2 (7.1%)	< ε >=-0.019	0	-	0.18±0.11	0.18±0.15	0.71 ΔQS=0.25
IS [mm/s]	<IS>=0.19	- 0.002±0.03	0.94±0.06	-	0.30±0.02	0.20±0.01	-0.01±0.04	0.52±0.04	IS_1=0.34±0.03 IS_2=0.58±0.04	<IS>=0.21	0.08±0.10	-	0.97±0.11	0.66±0.12	0.40±0.02

Figure 1. Mössbauer spectra for (**a**) as prepared MWCNTs, (**b**) MWCNTs-COOH, and (**c**) MWCNTs-COONH4: left column – the control group, middle column – after using the agate mill, right column – after using the steel mill, measured at 220 K.

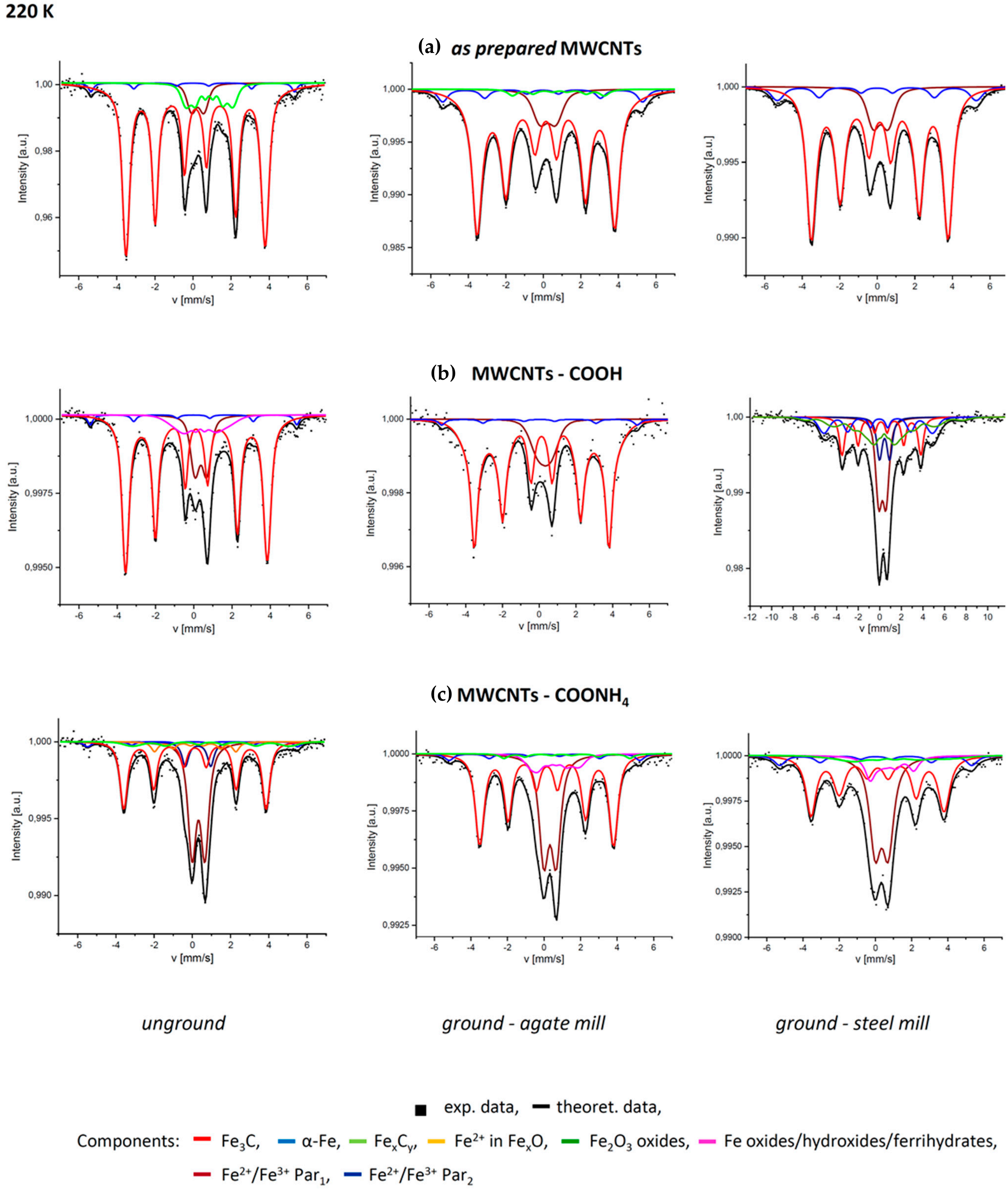


Table 2. Hyperfine parameters fitted to the Mössbauer spectra measured at 220 K (*IS* – isomer shift related to the metallic Fe, *QS* – quadrupole splitting, H_{hf} – hyperfine magnetic field, ΔQ - quadrupole splitting distribution, ΔH – magnetic field distribution, *C* – relative contribution, Γ – line width).

Types of MWCNTs	**MWCNTs *as prepared***				**MWCNTs-COOH**				**MWCNTs-$COONH_4$**					
Component	**Fe_3C**	**α - Fe**	**Fe^{2+} in Fe_xO**	Par **Fe^{2+}/Fe^{3+}**	**Fe_3C**	**α - Fe**	Fe oxides/ hydroxides/ ferrihydrates	Par **Fe^{2+}/Fe^{3+}**	**Fe_3C**	**α - Fe**	**Fe_xC_y**	**Fe^{2+} in Fe_xO**	Fe oxides/ hydroxides/ ferrihydrates	Par **Fe^{2+}/Fe^{3+}**
control														
C[%]	80.6±2.6	2.8±0.4	10.3±0.5	6.4±0.6	72.9±2.6	3.3±1.5	9.9±3.1	13.9±2.0	42.1±3.5	3.2±2.0	5.6±1.7	5.4±3.5	-	44.4±4.0
H_{hf} [T]	22.7 ΔH=0.66 p=0.77 19.5 ΔH=10.7 p=0.23	33.1 ΔH=0.07	7.6 ΔH=1.0	-	23.0 ΔH=0.60 p=0.82 19.9 ΔH=5.3 p=0.18	33.4 ΔH=0.007	7.7±2.0 ΔH=3.0	-	23.1 ΔH=0.39	Q=34.0 ΔQ=0.38	13.2±0.5	25.4 ΔQ=2.33	-	-

	<H>=22.0				<H>=22.4									
ε /QS [mm/s]	< ε >=0.002	0	0.01±0.01	Q=0.64 ΔQ=0.32	< ε >=-0.001	0	0.14±0.14	0.63 ΔQ=0.29	0.00±0.03	0	-0.05±0.14	0.007±0.175	-	Q_1=1.33±0.16 (7.8%) Q_2=0.67 ΔQ_1=0.18 (36.6%)
IS [mm/s]	<IS>=0.13	-0.01±0.02	0.85±0.02	0.25±0.04	<IS>=0.13	-0.02±0.07	0.37±0.17	0.38±0.03	0.14±0.01	0.01±0.11	0.20±0.14	0.97±0.19	-	IS_1=0.30±0.04 IS_2=0.32±0.01
agate mill														
C[%]	80.6±2.6	6.3±1.0	3.0±1.7	10.1±1.0	82.8±5.9	2.6±2.2	-	14.6±2.6	53.2±2.8	3.8±1.7	-	2.4±1.9	9.3±2.5	31.2±3.5
H_{hf} [T]	22.7	33.0	15.2	-	22.7	33.0	-	-	22.71	32.4	-	21.4	8.1±1.3	-

	ΔH=0.46 p=0.79 20.7 ΔH=7.1 p=0.21 <H>=22..3	ΔH=0.5	ΔH=0.37		ΔH=0.001 p=0.57 22.7 ΔH=3.7 p=0.43 <H>=22.7	ΔH=0.2			ΔH=0.55	ΔH=0.5		ΔH=0.007	ΔH=1.4	
ε /QS [mm/s]	< ε >=-0.004	0	-0.04±0.12	0.84 ΔQS=0.46	< ε >=0.002	0	-	0.71 ΔQS=0.66	< ε >=-0.007	0	-	0.14±0.28	0.07±0.12	0.67 ΔQS=0.21
IS [mm/s]	<IS>=0.13	-0.04±0.04	0.83±0.10	0.24±0.03	0.14±0.02	0.02±0.07	-	0.38±0.03	<IS>=0.15	0.03±0.10	-	1.1±0.3	0.53±0.14	0.33±0.02
steel mill														
C[%]	81.6±1.9	7.8±11	-	10.7±1.2	20.2±2.5	15.0±2.1	29.6±5.0	35.7±3.2	42.3±2.8	7.3±2.0	-	6.3±2.5	10.0±3.6	34.2±2.2
H_{hf} [T]	22.6±0.32 ΔH=0.59±0.11	32.9±0.4 ΔH=1.2±0.4	-	-	22.6 ΔH=0.66	31.1 ΔH=2.4	45 ΔH=3.0	-	22.8 ΔH=0.44	32.9 ΔH=0.5	-	17.6 ΔH=5.3	7.5 ΔH=0.01	-

	p=0.84 15.5±2.5 ΔH=6.2±2.4 p=0.16						(p=0.11) 35.0 ΔH=3.0 (p=0.039) 30.0 ΔH=3.0 (p=0.273) 20.0 ΔH=3.0 (p=0.076) 15.0 ΔH=3.0 (p=0.047)							

	<H>=21,5						10.0 ΔH=3.0 (p=0.455) <H>=21.3							
ε /QS [mm/s]	< ε >=-0.03	0	-	Q=0.79 ΔQ=0.38	-0.02±0.02	0	0.0	QS_1=0.67 ΔQS_1=0.3 (24.5%) QS_2=0.94 ΔQS_2=0.24 (11.2%)	< ε >=-0.003	0	-	0.25 ± 0.33	0.23 ± 0.19	0.72 ΔQS = 0.2
IS [mm/s]	<IS> = 0.15	-0.03±0.05	-	0.18±0.04	0.13±0.03	-0.10±0.11	0.41±0.13	IS_1=0.25±0.4 IS_2=0.45±0.22	<IS>=0.13	0.02±0.1	-	0.87±0.15	0.68±0.15	0.35±0.02

Figure 2. Mössbauer spectra for (**a**) as prepared MWCNTs, (**b**) MWCNTs-COOH, and (**c**) MWCNTs-COONH4: left column – the control group, middle column – after using the agate mill, right column – after using the steel mill, measured at 295 K.

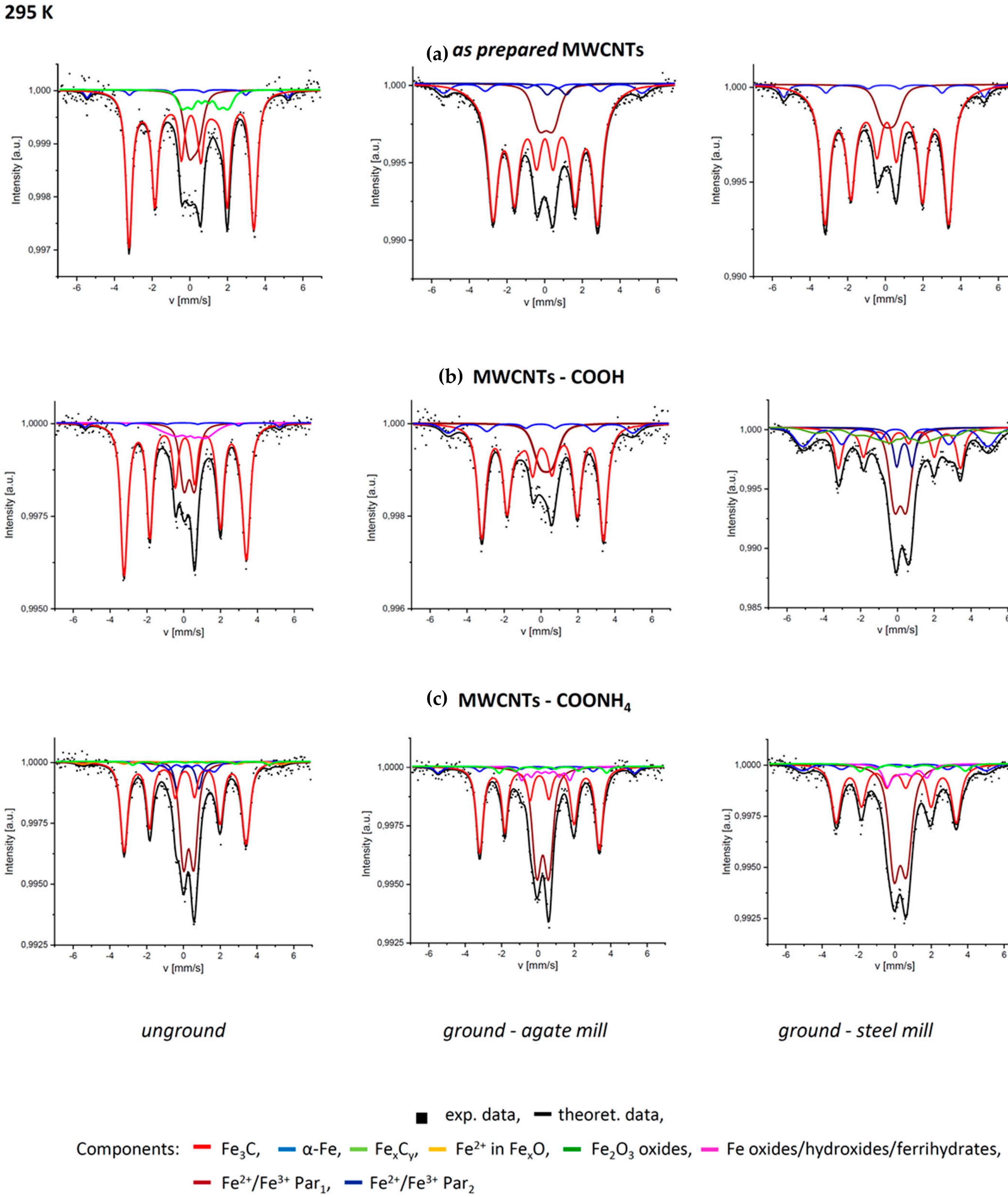


Table 3. Hyperfine parameters fitted to the Mössbauer spectra measured at 295 K (*IS* – isomer shift related to the metallic Fe, *QS* – quadrupole splitting, *H*hf – hyperfine magnetic field, *ΔQ* - quadrupole splitting distribution, *ΔH* – magnetic field distribution, *C* – relative contribution, *Γ* – line width).

Component	**Fe_3C**	**α - Fe**	**Fe^{2+} in Fe_xO**	Par **Fe^{2+}/Fe^{3+}**	**Fe_3C**	**α - Fe**	Fe oxides/ hydroxides/ ferrihydrates	Par **Fe^{2+}/Fe^{3+}**	**Fe_3C**	**α - Fe**	**Fe_xC_y**	**Fe^{2+} in Fe_xO**	Fe oxides/ hydroxides/ ferrihydrates	Par **Fe^{2+}/Fe^{3+}**
control														
C[%]	73.5±3.5	2.9±0.8	9.4±1.3	14.2±3.5	72.5±3.1	1.8±1.0	9.1±3.0	16.8±2.6	52.3±3.3	2.4±2.0	6.3±2.5	1.8±1.5	-	37.4±3.7
H_{hf} [T]	20.5 ΔH=0.41 p=0.78 13.7 ΔH=5.0 p=0.22 <H>=19.0	33.0 ΔH=0.03	H=7.5 ΔH=1.05	-	20.7 ΔH=0.49 p=0.77 19.6 ΔH=1.08 p=0.23 <H>=20.4	32.7 ΔH=0.002	7.4 ΔH=3.0	-	20.6 ΔH=0.61	H=33.4 ΔH=1.3	H=10.5 ΔH=0.9	22.3 ΔH=0.05	-	-
ε /QS [mm/s]	< ε >=-0.029	0	0.00±0.12	Q=0.48 ΔQ=0.36	< ε >=0.001		-0.07±0.17	0.57 ΔQ=0.26	< ε >=0.006	0	-0.10±0.10	0.13±0.26	-	QS_1= 0.56 $ΔQS_1$=0.22 (30.5%) QS_2=1.2 $ΔQS_2$=0.004 (6.9%)
IS [mm/s]	<IS>=0.04	-0.12±0.22	0.82±0.16	<IS>=0.18	<IS>=0.07	-0.05±0.20	0.31±0.15	0.30±0.03	<IS> =0.09	-0.10±0.11		0.82±0.26	-	IS_1=0.29±0.01

											0.09±0.13			IS_2=0.25±0.05
agate mill														
C[%]	80.4±1.5	5.3±1.3	-	14.3±3.0	76.3±1.1	8.0±3.5	-	15.7±2.9	49.7±3.0	4.2±1.5	-	3.4±.1.6	6.8±2.1	35.9±2.0
H_{hf} [T]	17.23 ΔH=0.53 p=0.63 15.1 ΔH=6.1 p=0.37 <H>=16.4	32.7±0.6 ΔH=1.2	-	-	20.51 ΔH=0.41 p=0.90 10.5 ΔH=1.2 p=0.10 <H>=19.4	31.0 ΔH=1.4	-	-	20.4 ΔH=0.50	33.4 ΔH=0.6	-	18.3 ΔH=0.04	8.2 ΔH=0.02	-
ε /QS [mm/s]	< ε >=0.02	0	-	QS_1= 0.73 $ΔQS_1$=0.45 (11.9%) QS_2=1.0 $ΔQS_2$=0.16 (2.4%)	< ε >=0.03	0	-	0.65 ΔQS=0.52	< ε >=-0.001	0	-	0.16±0.14	0.01±0.07	0.65 ΔQS=0.29
IS [mm/s]	<IS>=0.03	-0.10±0.09	-	IS_1=0.08±0.04 IS_2=0.64±0.12	<IS>=0.07	-0.03±0.17	-	0.28±0.08	<IS>=0.09	-0.08±0.10	-	0.66±0.14	0.42±0.08	0.27±0.01
steel mill														
C[%]	83.8±2.3	5.6±1.5	-	10.6±2.4	24.3±2.0	19.4±1.9	18.6±3.5	37.6±3.2	40.9±3.8	6.5±2.0	-	4.8±.2.0	8.6±1.6	39.2±3.8

H_{hf} [T]	20.35 ΔH=0.51 p=0.71 17.1 ΔH=6.7 p=0.29 <H>=19.4	33.0 ΔH=0.03	-	-	20.6 ΔH=0.44	31.1 ΔH=2.0	30.0 ΔH=3.0 (p=0.40) 15.0 ΔH=3.0 (p=0.08) 10.0 ΔH=3.0 (p=0.52) <H>=18.3	-	20.5±0.1 ΔH=0.48	31.6±1.5 ΔH=1.97	-	18.0 ΔH=0.02	6.8 ΔH=0.05	-
ε /QS [mm/s]	< ε >=0.000	0	-	Q=0.63 ΔQ=0.48	0.01±0.01	0	0.0	QS_1=0.63 ΔQS_1=0.33 (27.3%) QS_2=0.83 ΔQS_2=0.02 (10.3%)	-0.001±0.025	0	-	0.17±0.16	0.20±0.18	0.68 ΔQS=0.28
IS [mm/s]	<IS> = 0.08	-0.07±0.07	-	0.18±0.05	0.10±0.01	-0.10±0.11	0.44±0.12	IS_1=0.16±0.02 IS_2=0.38±0.03	0.07±0.03	-0.1±0.1	-	0.82±0.16	0.45±0.10	0.26±0.05

Table 4. Metal and semimetal concentrations of MWCNTs obtained by use of ICP-OES method. Concentrations are given in [μg/g]. n.d. – below the detection limit.

Element	*as prepared* MWCNTs	MWCNTs-COOH	MWCNTs-COONH4
		control	
Al	154 ± 2	35.5 ± 0.1	11.9 ± 0.1
As	69.9 ± 1.4	11.7 ± 0.5	14.4 ± 0.8
B	126 ± 4	19.8 ± 0.1	24 ± 0.2
Ca	30.8 ± 0.8	143 ± 2	41 ± 1
Cd	2.1 ± 0.4	n.d.	n.d.
Cr	4.0 ± 0.7	n.d.	n.d.
Cu	6.2 ± 0.3	0.53 ± 0.01	1.1 ± 0.1
Fe	342 ± 2	54.4 ± 0.2	56.9 ± 0.3
Hg	250 ± 38	4.2 ± 1.1	4.9 ± 3.0
K	5.8 ± 1.5	12.4 ± 0.8	3.1 ± 0.3
Mg	n.d.	4.26 ± 0.05	1.64 ± 0.06
Mo	3.2 ± 0.5	n.d.	n.d.
Na	21.4 ± 0.5	12.1 ± 0.3	5.6 ± 0.1
Sb	29 ± 3	1.4 ± 0.5	n.d.
Si	23.9 ± 0.5	19.2 ± 0.9	12.5 ± 1.1
V	1.6 ± 0.2	n.d.	n.d.
W	15.2 ± 1.7	n.d.	1.3 ± 0.1
		agate mill*	
Fe	330 ± 3	53.1 ± 0.4	54.6 ± 0.4
		steel mill*	
Fe	334 ± 4	54.0 ± 0.4	55.5 ± 0.4

*The contents of other elements in the ground samples did not change.

Figure 3. Temperature dependencies of the magnetic moment (μ) measured in the field of 4 T for MWCNTs-COOH obtained from MWCNTs prepared in the agate (blue squares) and steel (red circles) mill. Empty symbols denote the data as measured and full symbols correspond to the values corrected for the carbon contribution.

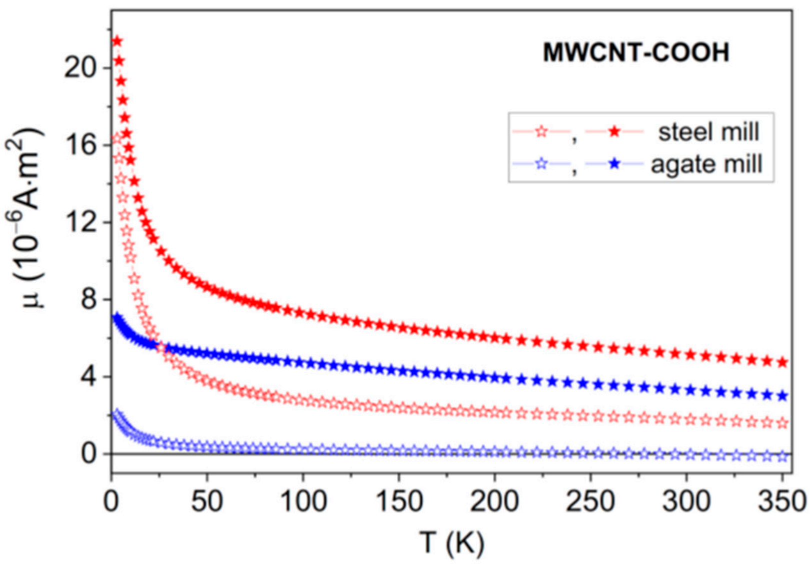
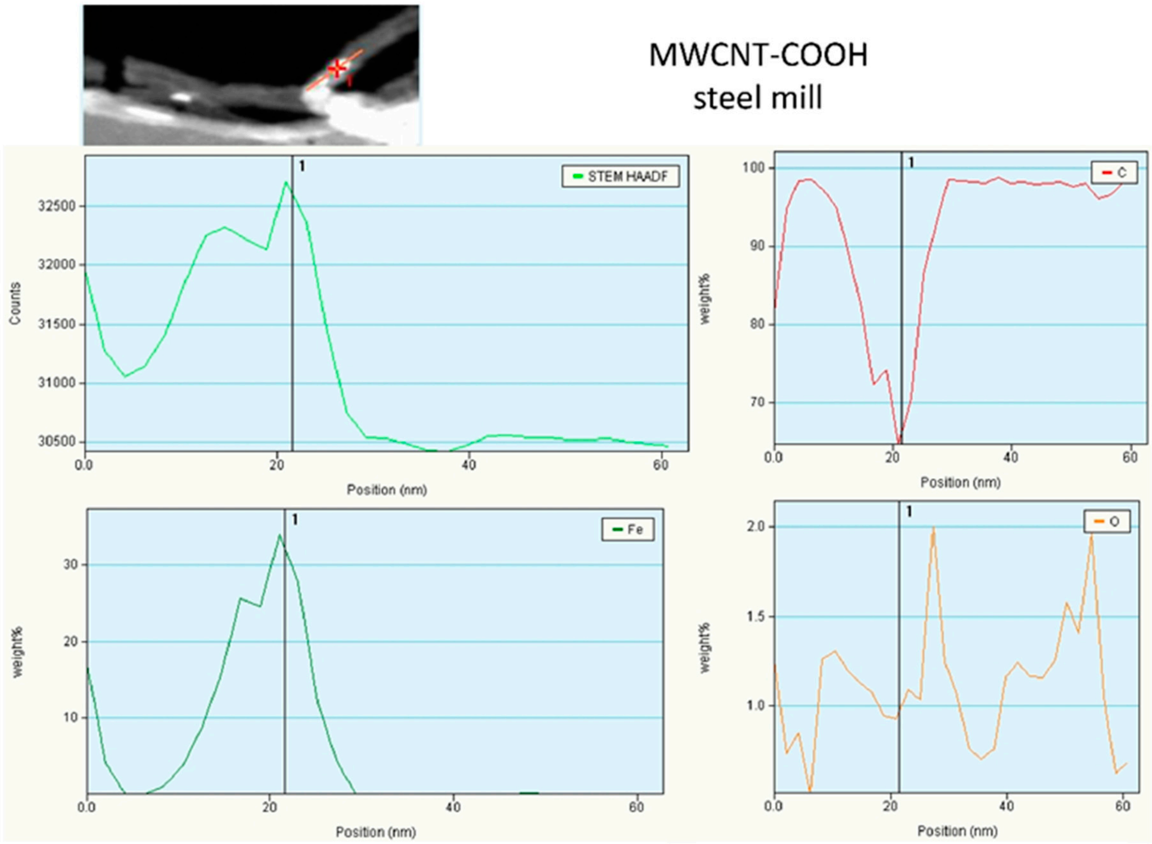


Figure 4. TEM image of a large nanoparticle in MWCNTs-COOH and an experimental evidence (EDX measurements) that it contains Fe, C and O is given.


MWCNT-COOH
steel mill
STEM HAADF
Counts
Position (nm)
C
weight%
Fe
O
1