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The influence of the chemical treatment on the ferromagnetic behavior of carbon nanotubes synthesized using ferromagnetic catalyst

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In this contribution we report results of our investigations on the ferromagnetic behavior of pristine and chemically treated carbon nanotubes, synthesized by AC arc discharge method using iron powder as catalyst. The magnetic properties of the carbon nanotubes samples before and after chemical treatment were measured at room temperature in a vibrating - sample magnetometer. We observed significant changes of the ferromagnetic behavior of carbon nanotubes after the purification and concluded that the magnetic properties of carbon nanotubes synthesized using ferromagnetic catalyst are governed by the ferromagnetic catalyst nanoparticles attached to their walls during synthesis.

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Keywords: Carbon nanotubes, Magnetic behavior, Arc discharge, Vibrating sample magnetometer

1. Introduction

Carbon nanotubes have been in focus of intense research since their discovery [1], due to their unique properties including extreme mechanical strength, or peculiar electrical properties [2], which make them useful materials for a variety of applications in electronic, magnetic or optical devices. Recently, several authors have published papers on the synthesis and properties of metal-filled carbon nanotubes [3-5]. Different synthesis methods have been attempted and various materials encapsulated have been tested [6], particularly those involving magnetic or ferromagnetic materials. Carbon nanotubes that contain encapsulated magnetic nanoparticles have potential applications in magnetic storage [7], spin polarized scanning tunneling microscopy [8] and in the emerging field of spintronics [9]. In this work we have studied the ferromagnetic behavior of carbon nanotubes synthesized by AC arc discharge method using ferromagnetic catalyst, both before and after purification.

2. Experimental and results

Carbon nanotubes were synthesized by the AC arc discharge method in argon ambient at 250 mbar pressure using iron nanoparticles as catalyst [10]. The as-prepared sample normally includes sp^2-bonded carbon nanospheres, other carbon allotropes - such as fullerenes and aromatic carbons, as well as catalyst nanoparticles as impurities that could mask the intrinsic magnetic properties of the synthesized carbon nanostructures [11]. Therefore, the resulting carbonaceous material was treated following two purification steps. In the first step the amorphous carbon has been removed, while in the second one the catalyst has been eliminated from the carbon nanostructures [12].

The morphology and structure of the synthesized materials before and after purification were studied by scanning electron microscopy (SEM) using a Nova NanoSEM 630 equipment, by transmission electron microscopy (TEM) and electron diffraction (ED) in a JEOL 200CX instrument and by powder X-Ray diffraction (XRD) using the X-ray diffractometer (D8 ADVANCE Nova) with CuKα radiation ($\lambda = 0.15406$ nm), while their magnetic properties were measured at room temperature with a vibrating - sample magnetometer (VSM, Lake Shore).

In the followings, the as synthesized sample was named D_Ar_Fe, and the same sample after purification was noted as D_Ar_Fe_HCl.

Fig. 1 shows the SEM image of the D_Ar_Fe sample. This image reveals carbon nanotubes with catalyst nanoparticles attached to their walls. After purification the metal catalyst nanoparticles were removed as it can be observed in Fig. 2.

Fig. 3 presents TEM images of the D_Ar_Fe sample at different magnifications (a), (b), (c) and the selected area electron diffraction pattern (d) corresponding to the TEM image at the lowest magnification (a), revealing the general morphology of the sample. The TEM images (Figs. 3a-c) reveal carbon nanostructures of different morphologies: the white arrows indicate carbon nanotubes, while the black arrows in Fig. 3a reveal the presence of very thin graphitic foils. In addition, we observed on the side-walls of the carbon nanotubes the presence of agglomerates of catalyst nanoparticles with an average dimension of 20 nm.

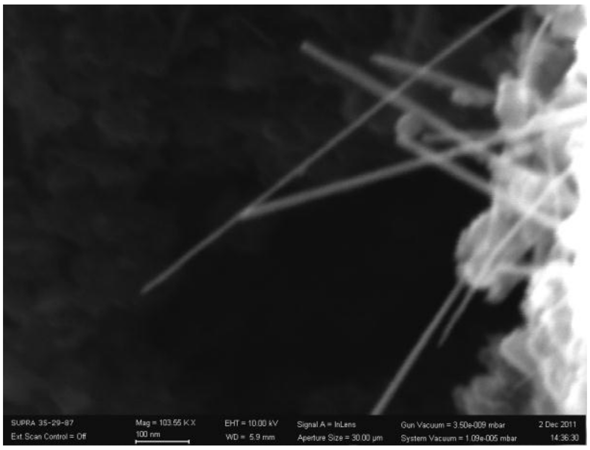


Fig. 1. SEM image of D_Ar_Fe sample.

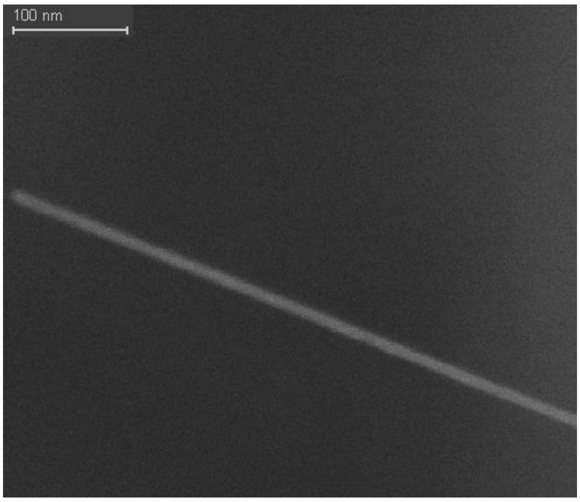
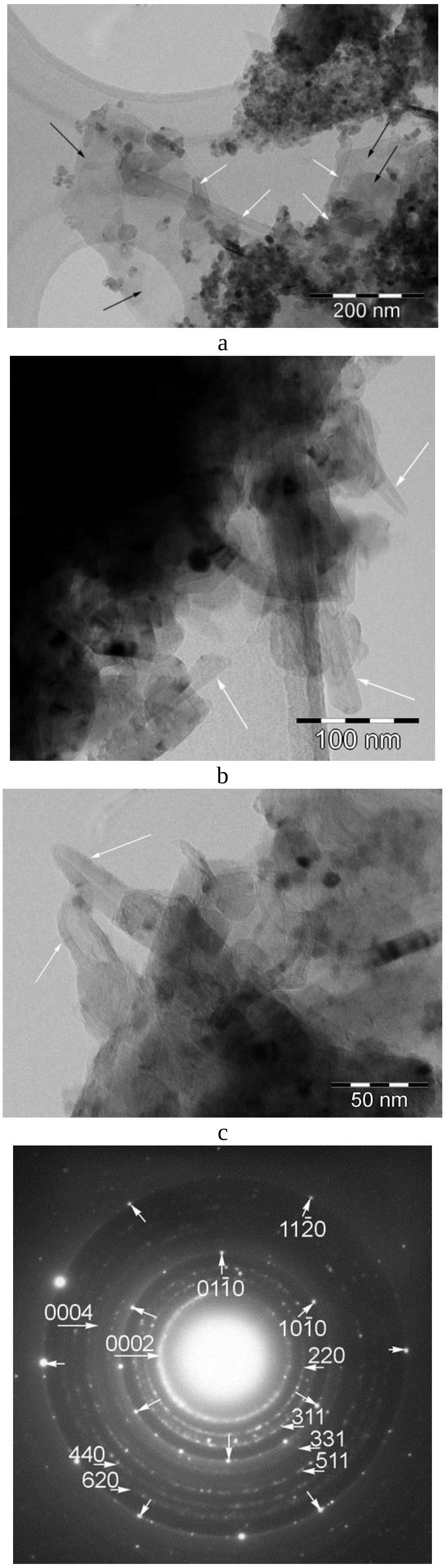


Fig. 2. SEM image of purified D_Ar_Fe_HCl sample.



a

b

c

d

Fig. 3. TEM images of D_Ar_Fe sample (a), (b), (c) and the electron diffraction pattern (d).

In the electron diffraction pattern (Fig. 3d), all the diffraction maxima (circles) are indexed. Some diffraction maxima indexed with four Miller indices correspond to the graphite structure of the carbon nanotubes and foils, while the remaining diffraction maxima corresponding to the catalyst nanoparticles can be indexed with the cubic structure of magnetite (Fe_3O_4).

Fig. 4 presents the TEM image of the purrified D_Ar_Fe_HCl sample. It shows a carbon nanotube without catalyst nanoparticles attached to it.

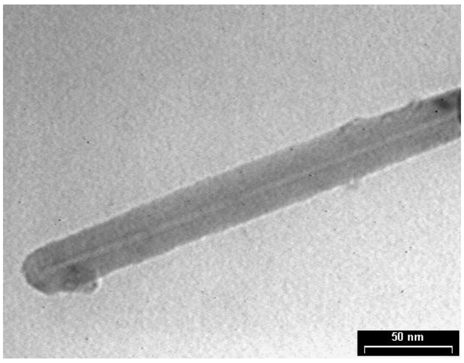


Fig. 4. TEM images of purified D_Ar_Fe_HCl sample.

The X-ray paterns of both samples, before and after purification, are presented in Fig. 5. As it can be seen, in contrast to the diffractogram (in pink) of the chemically treated carbon nanotubes sample, which clearly show the four characteristic peaks of the graphite structure for the multiwall carbon nanotubes at $2\theta=26.1^o$, 42.6^o, 54.8^o and 77.4° (green arrows) [13, 14], the XRD pattern of the unpurified carbon nanotubes sample (in black) show extra diffraction peaks at 2θ values of 35.4^o, 43.1^o (red arrows) and 44.7^o (blue arrow). The diffraction peaks at 35.4^o and 43.1^o correspond to an iron oxide called magnetite (Fe_3O_4) [15] and the peak at 44.7^o might be originated from an intermediate phase between Fe_3O_4 and FeO [16]. As in the case of electron diffraction (Fig. 3 d), this result shows that during the synthesis process, an oxidation of the Fe catalyst nanoparticles occurs. The average size of the catalyst nanoparticles as determined with the Debye-Scherrer formula is about 27.7 nm, in fair accordance with the size distribution observed in TEM.

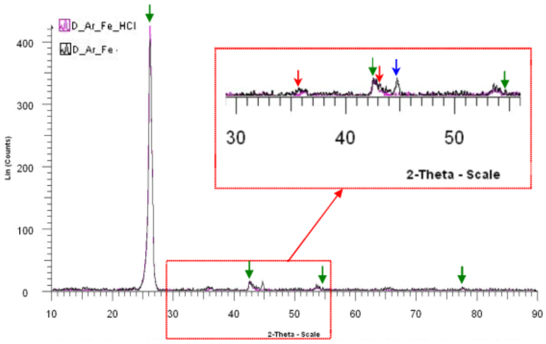


Fig. 5. XRD patterns of samples before and after purification.

The results of the magnetization measurements at room temperature are presented in Figs. 6 and 7 depicting the magnetic moment as a function of the applied field (hysteresis loops). The hysteresis loop show ferromagnetic behavior. From the magnetization hysteresis loop measured between -10 and +10 kGauss we determined the remanence magnetization and the coercivity as M_r=0.1 emu/g and H_c=110 Oe, respectively, for the D_Ar_Fe sample.

In contrast to the pristine sample, the purified D_Ar_Fe_HCl sample shows diamagnetic behavior, as seen in Fig. 7. The curve clearly indicates a diamagnetic response and suggests the absence of any measurable contribution of magnetic species.

The diamagnetism is due to induced currents opposing an applied field resulting in a small negative magnetic susceptibility, χ. The value found for the magnetic susceptibility was $-6,5\times10^{-3}$emu/g for D_Ar_Fe_HCl sample. As a result, the magnetic field in the material is weakened by the induced magnetization. Therefore, the magnetic characteristics of the sample after the purification treatment became diamagnetic with negative magnetic susceptibility. Based on these measurement we provide clear evidence that carbon nanostructures obtained by the AC arc discharge method in presence of ferromagnetic catalyst particles are rather non-magnetic, as they do not show any permanent magnetization without external magnetic field.

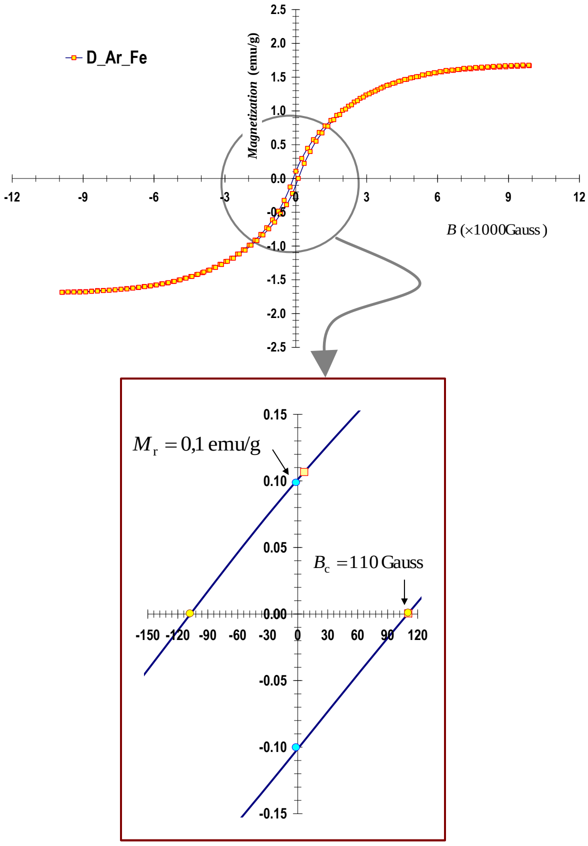


Fig. 6. Hysteresis loop for D_Ar_Fe sample.

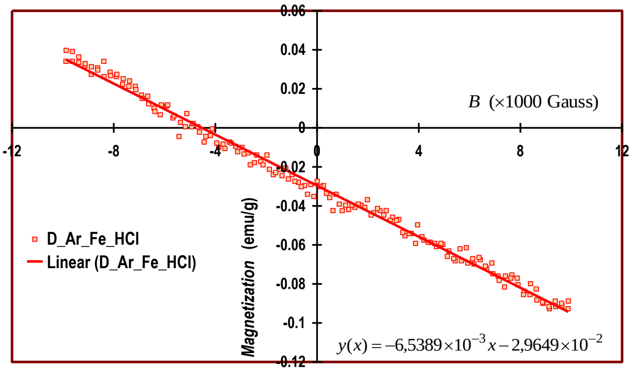


Fig. 7. Diamagnetic behavior of purified D_Ar_Fe_HCl sample.

The observed ferromagnetic behavior of pristine carbon nanostructures is most likely generated by the overlapping of the diamagnetic signal of the carbon nanostructures on the ferromagnetic signal of the catalyst nanoparticles attached on their walls. Thus, the ferromagnetic behavior of the D_Ar_Fe sample is most likely due to the presence of catalyst nanoparticles attached on the walls of carbon nanotubes during the synthesis procedure.

3. Conclusions

We have studied the ferromagnetic behavior of carbon nanotubes, synthesized by the AC arc discharge method, both before and after purification. The purification of carbon nanotubes has been carried out by burning off the amorphous carbon, followed by the oxidative dissolution of the catalyst nanoparticles with hydrochloric acid, which ensures good efficiency for the metal removal process. We conclude that, the pristine carbon nanotubes possess magnetic properties governed by the catalyst particles attached to their walls and enabling them to react to external magnetic fields, while the purified carbon nanostructures obtained by the AC arc discharge method show diamagnetic behavior.

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