



## Magnetic properties of core-shell catalyst nanoparticles for carbon nanotube growth

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### ABSTRACT

Two types of core-shell nanoparticles have been prepared by laser pyrolysis using  $\text{Fe}(\text{CO})_5$  and  $\text{C}_2\text{H}_2$  or  $[(\text{CH}_3)_3\text{Si}]_2\text{O}$  as precursors and  $\text{C}_2\text{H}_4$  as sensitizer. The first type (about 4 nm diameter) – produced by the decomposition of  $\text{Fe}(\text{CO})_5$  in the presence of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  – consists of Fe cores protected by graphenic layers. The second type (mean particle size of about 14 nm) consists also of Fe cores, yet covered by few nm thick  $\gamma\text{-Fe}_2\text{O}_3$ /porous polycarbosiloxane shells resulted from the  $[(\text{CH}_3)_3\text{Si}]_2\text{O}$  decomposition and superficial oxidation after air exposure. The hysteresis loops suggest a room temperature superparamagnetic behavior of the Fe-C nanopowder and a weak ferromagnetic one for larger particles in the Fe- $\text{Fe}_2\text{O}_3$ -polymer sample. Both types of nanoparticles were finally used as a catalyst for the carbon nanotube growth by seeding Si(100) substrates via drop-casting method. CNTs were grown by Hot-Filament Direct.

Current PE CVD technique from  $\text{C}_2\text{H}_2$  and  $\text{H}_2$  at 980 K. It is suggested that the increased density and orientation degree observed for the multiwall nanotubes grown from Fe- $\text{Fe}_2\text{O}_3$ -polymer nanoparticles could be due to their magnetic behavior and surface composition.

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## 1. Introduction

Due to size and surface effects, magnetic nanoparticles reveal different properties as compared to their corresponding bulk materials. They have been utilized in a variety of applications in fields such as medicine (sensing devices, cancer treatment by hyperthermia, drug delivery, in vivo imaging) or data storage (magnetic recording media) [1]. Moreover, it is well known that magnetic Fe, Co, Ni nanoparticles are the best catalysts for CNT growth. However, there is little information in the literature about the role of their magnetic properties in the CNT growth. Thus, magnetic interactions between nanoparticles can play a role in catalyst deposition and coalescence. Recent studies underline the role of the magnetic properties of nanocatalysts in the non-planar

nanotubular structural formation of CNTs [2]. Embedding the nanoparticles with a shell could provide a better dispersibility of catalyst in suspensions for the deposition on plain substrates and also could control the density of the deposited CNTs [3].

In this work we report about the catalytic growth of CNTs using two kinds of core-shell nanoparticles. The nanoparticles were prepared by the laser pyrolysis method, using  $\text{Fe}(\text{CO})_5$  and  $\text{C}_2\text{H}_2$  or  $[(\text{CH}_3)_3\text{Si}]_2\text{O}$  (HMDSO) as precursors and  $\text{C}_2\text{H}_4$  as sensitizer. Their structural and morphologic properties have been studied by many analytical techniques—such as transmission electron microscopy (TEM), selected area electron diffraction (SAED), X-ray diffraction (XRD) and Raman spectroscopy. Hysteresis loops at different temperatures were used in order to evaluate their magnetic properties. The nanoparticles were used as catalysts on seeded Si(100) substrates. The properties of the grown multiwall carbon nanotubes (MWCNT) (prepared by the Hot-Filament Direct Current PE CVD technique from  $\text{C}_2\text{H}_2$  and  $\text{H}_2$ ) were analysed by scanning electron microscopy (SEM) and Raman spectroscopy.

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**Table 1**  
Mean parameters for laser pyrolysis synthesis of core-shell nanoparticles.

Run	Inner flow (sccm)	Middle (flow sccm)			Ext flow (sccm)	Windows flow (sccm)	Resulted Fe(CO) <sub>5</sub> flow (sccm)	Resulted [(CH <sub>3</sub> ) <sub>3</sub> Si] <sub>2</sub> O flow (sccm)	Pressure (kPa)	Laser power (W)
	C <sub>2</sub> H <sub>4</sub> through Fe(CO) <sub>5</sub>	Ar through [(CH <sub>3</sub> ) <sub>3</sub> Si] <sub>2</sub> O	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	Ar	Ar				
CF15	20	–	10	35	1500	150	1.54	–	65.3	50
PF12	60	10	120	–	500	200	6.89	0.92	453	70

## 2. Experimental

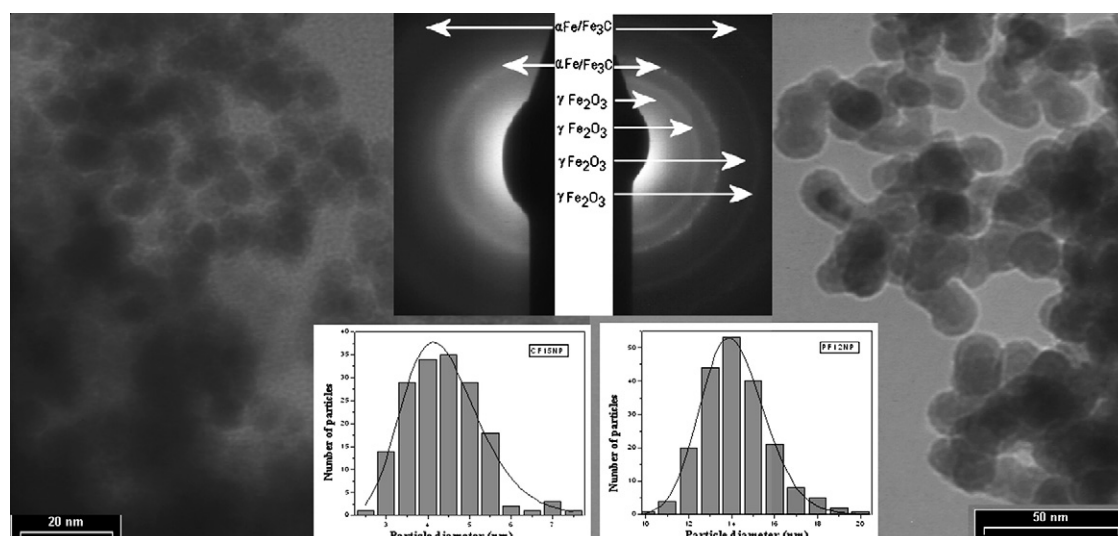
The laser pyrolysis synthesis of the two kinds of nanoparticles: Fe-C type (labeled CF15NP) and Fe- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/carbosiloxane polymer type (labeled PF12NP) is described elsewhere ([4] and [5], respectively). Briefly, a concentric three-nozzle injector allows three gaseous co-flows to reach the reaction zone where they orthogonally intersect a continuous IR laser beam. Due to the absorption of IR photons, C<sub>2</sub>H<sub>4</sub> molecules become vibrationally excited and transfer their energy to other gas-phase molecules by collisions. The temperature increase leads to the dissociation of Fe(CO)<sub>5</sub> to Fe atoms and CO molecules. Iron atoms condensate into clusters which serve as catalysts for the decomposition of hot fragments from the second co-flow. This contains mixtures where either C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> or [(CH<sub>3</sub>)<sub>3</sub>Si]<sub>2</sub>O/C<sub>2</sub>H<sub>4</sub> are present. The third co-flow consists of Ar for the inner flows confinement. As a result of the induced reactions, loosely agglomerated core-shell type nanoparticles (Fe-C or Fe-carbosiloxane) are formed. They are collected downstream, on the porous surface of a filter. After extracting the powder from the inert gas filled collecting chamber, the second type nanoparticles undergo a superficial oxidation due to the contact with the atmospheric oxygen. The main parameters of the synthesis processes are summarized in Table 1. The subsequent steps accomplished to grow CNTs were detailed in [5]. Each of the two powders was sonicated in acetone and the suspensions (0.05 mg/cm<sup>3</sup>) dripped (30 droplets  $\sim$ 0.9 cm<sup>3</sup>) onto Si(100) wafers (9  $\times$  7 mm<sup>2</sup>). The vertically oriented MWCNTs were grown onto these seeded substrates by hot-filament plasma-enhanced CVD in d.c. current flow discharge under H<sub>2</sub>-C<sub>2</sub>H<sub>2</sub> atmosphere.

The nanotube samples were observed by SEM performed on a XL30S-FEG Philips and the nanostructures were probed by TEM on a FEG TEM CM200 Philips. Raman spectra were recorded on a Renishaw spectrometer using an Ar ion laser at  $\lambda$  = 488 nm. XRD

analysis was performed with a DRON DTAR UM2 diffractometer equipped with a graphite monochromatized Cu anode. Hysteresis loops of few mg of nanopowders were recorded at five temperatures (from 5 to 295 K) with the aid of a Quantum Design SQUID Magnetometer.

## 3. Results and discussions

Fig. 1 shows TEM images of catalyst core-shell nanopowders. The as-synthesized nanoparticles present a relatively narrow monomodal log-normal distribution (inserts in Fig. 1), with mean particle diameter around 4 nm for CF15NP and 14 nm for PF12NP. From the TEM images the core-shell structure of both samples is clearly visible. The inserted SAED pictures reveal the differences between the two kinds of nanoparticles: while in CF15NP sample only diffraction rings of  $\alpha$ -Fe (and possibly Fe<sub>3</sub>C) are visible, in PF12NP sample, the rings of maghemite  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> are revealed. These rings suggest the presence of very small crystallites with random orientation. The massive presence of maghemite in the outer shell of PF12NP can be attributed to the atmospheric oxygen penetration towards the iron core through the very thin/porous or/and incomplete carbosiloxane polymer layer. The inability of this polymer layer to protect the iron core against oxidation can be correlated with the very small [(CH<sub>3</sub>)<sub>3</sub>Si]<sub>2</sub>O flow (0.92 sccm of HMDSO against 35 sccm of C<sub>2</sub>H<sub>2</sub>, in conditions of a larger Fe(CO)<sub>5</sub> flow compared to that used for the synthesis of CF15NP sample). The information deduced from SAED images are strengthened by XRD superposed diffractograms presented in Fig. 2, where the  $\alpha$ -Fe peaks are revealed by both samples and the maghemite peaks are clearly visible only for the PF12NP sample. This suggests that the graphenic shell of particles composing CF15NP sample is a rather strong protector against oxidation. Also, the revealing of Fe<sub>3</sub>C cementite/cohenite peaks is difficult for this sample, due to the partial



**Fig. 1.** TEM images of nanoparticles; inserts – up: SAED images, down: particles size distribution histograms (left part CF15 NP, right part PF12 NP).

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