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Synthesis of magnetic nano-composite particles

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Abstract

Carbon nano-particles were synthesized using an arc-discharge apparatus. Magnetic-metal filled nano-capsules were segregated from nonmagnetic carbon particles using a magnet. TEM, XRD, EDS and Raman scattering spectroscopic examination revealed that a magnetic iron particle, 10–50 nm in diameter, was encapsulated in each carbon nano-capsule. These magnetic-metal filled carbon nano-capsules were then coated individually with amorphous silicate to provide additional oxidation protection. These nano composite particles ranging from 100 to 300 nm in diameter can be dispersed in water solution and aligned or spatially arranged by a magnet.

Keywords: Carbon nano-capsule; Magnetic nano composite

1. Introduction

Metal nano-particles encapsulated in concentric layers of graphitic carbon, called carbon nano-capsules, have received extensive consideration (e.g., [1–5]). Particularly the interesting magnetic behavior of magnetic-metal filled carbon nano-particles have led to infer numerous potential application in future nano technologies (e.g., [6,7]).

Metal nano-particles filled carbon nano-capsules have been produced by arc-discharge [1–4,8–10], ion-beam sputtering methods [7] and via solid-state reaction [5]. However, magnetic-metal nano-particles filled carbon nano-capsules are electrically conductive and susceptible to oxidation. It would be of great interest to produce ceramic coated magnetic nano-particles.

In this paper, experimental results are reported on the synthesis and characterization of magnetic-metal filled carbon nano-capsules using an arc-discharge apparatus. An attempt was made to coat magnetic carbon nano-capsules with amorphous silicate to provide additional oxidation resistance.

2. Experimental

2.1. Synthesis of nano-capsules

The method employed to synthesize nano-capsules is based on a DC arc-discharge between a graphite rod (cathode) and an iron-loaded graphite rod (anode) in an argon gas atmosphere. The description of the arc-discharge apparatus for the production of nano-capsules and nanotubes is given in Ref. [11]. Both electrodes were 99.99% purity and 6 mm in diameter graphite rods. The length of anode and cathode were approximately 70 and 30 mm, respectively. The iron-loaded anode was prepared by packing a hole (2.8 mm diameter by 40 mm deep) drilled in the graphite rod with an 1:1 by weight mixture of 99.99% purity iron powder and 99.0% pure graphite powder.

The arc discharge between the electrodes was fired in argon gas (purity 99.9%) of 500 Torr. The voltage was typically about 20 V, and the current 80 ± 10 A. Since the anode (iron-loaded rod) was preferentially consumed by evaporation, the arc gap between the electrodes was kept constant, 1–2 mm, by manually advancing the consumed anode. The arc reaction usually takes place in 6–10 min. Approximately half of the evaporated carbon and iron directly condensed on the tip of the graphite cathode, forming a slag-like hard deposit. The remaining vapor condensed in the gas phase, forming

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soot, which finally deposited on the inner walls of the reaction chamber, called "chamber soot'. Another soot-like material was also formed around the root of the slag-like hard deposit on the metal cathode holder, called "cathode soot". All these carbonaceous products (ca. 1 g per run) were collected and examined by Transmission Electron Microscopy (TEM).

2.2. Purification of nano-capsules

The carbonaceous materials collected from the arc-discharge apparatus were not only carbon nano-capsules and nanotubes, but were also invariably accompanied by nano-particles, amorphous carbon and other graphitic debris. Purification methods for removing the various contaminants are reported in many references (e.g., [11–13]). The purification process for this experiment is as follows:

1. The raw soot was first refluxed in distilled water for 12 h, followed by filtering and drying. This treatment removed some of the graphitic particles and amorphous carbon.
2. The soot was then treated with concentrated H_2SO_4 or $KMnO_4$ at 150 °C for 2 h in order to dissolve the metal particles, followed by flushing with distilled water, filtering and drying.
3. The purified products were then stirred with a magnetic pen, such that the magnetic particles were collected and segregated from the non-magnetic soot residual.

Both types of magnetic and non-magnetic particles were evaluated by TEM, X-ray diffraction (XRD), Electron diffraction and energy dispersive spectroscopy (EDS), and Raman spectroscopy.

2.3. Synthesis of nano-composite

An attempt was made to synthesize ceramic coated magnetic nano-composite particles based on the magnetic-metal filled carbon nano-capsules. Water-glass, a mixture of inorganic oxides—soda-silica (Na_2O–SiO_2) system, is known to be used as coat on egg shell for egg preservation. In this experiment, water-glass (sodium silicate solution) was applied on the magnetic-metal filled carbon nano-capsules by mixing them at a ratio of 1:1 by volume, then rinsed with distilled water, filtered and dried. These composite particles were then characterized by SEM.

3. Results and discussion

3.1. Raw soot material

Carbonaceous products collected from three locations in the arc chamber were examined using a TEM. The typical TEM photo of raw soot (from cathode and chamber) prior to acid purification is shown in Fig. 1, which shows nano-capsules, carbon nanotubes and various debris in the soot. However, preliminary examination of the hard slag material collected from the tip of graphite cathode appeared to have more contaminants and debris than that in the soot materials. The iron filled carbon nano-capsules in soot materials before acid purification treatment was evaluated using TEM and is shown in Fig. 2. A detailed examination of iron particles encapsulated in the carbon nano-capsules is shown in Fig. 3. This TEM image looks like larva in the cocoons of silk worm. Fibrous silk web connecting between the cocoons can be seen. The iron particles encapsulated in the carbon nano-capsules appear to be less than spherical and off concentric.

Fig. 1. Typical TEM image of raw soot after water cleaning.

3.2. Purified carbon nano-capsules

The magnetic carbon nano-capsules were purified by concentrated acid treatment and segregated from the soot residual prior to TEM evaluation. Their typical TEM image is shown in Fig. 4 and detailed in Fig. 5. By comparing Figs. 4 and 5 with Figs. 2 and 3, the iron particle encapsulated in the capsule after purification appears to be smaller, spherical and more concentric than before purification. The purified carbon capsules are ranging from 10 to 50 nm in diameter, while iron particles are approximately 5–30 nm. Thickness of the carbon layer of each capsule could be varied from 5 to 20 nm. The typical thickness of carbon layer of this nano-capsule, as shown in Fig. 5, is about 10 nm.

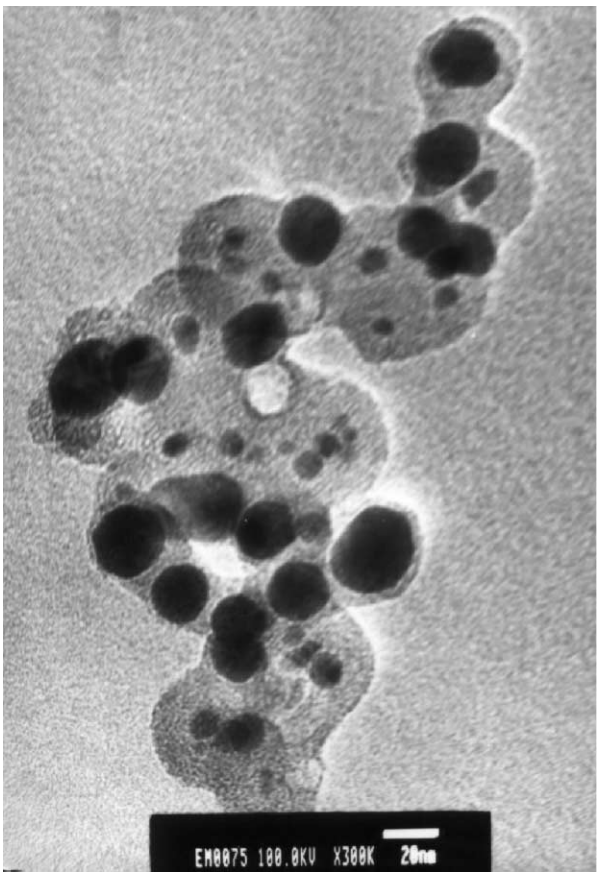

Fig. 2. Typical TEM image of iron filled carbon nanocapsules prior to acid treatment.

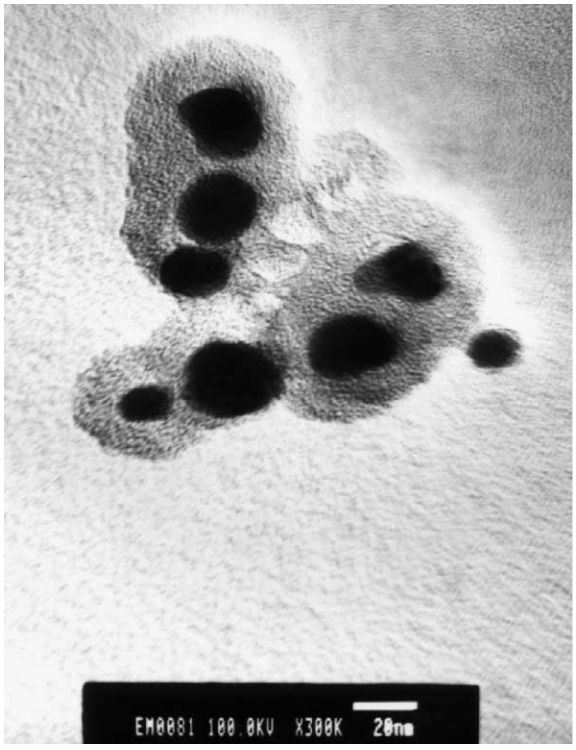

Fig. 3. Detailed TEM image of iron particles encapsulated in the carbon nanocapsules.

The XRD pattern of the iron encapsulated carbon nano-capsules is shown in Fig. 6. The peaks for graphite (26.3°) and iron materials (ca. 45°) can be easily identified.

The EDS spectrum of the metal filled carbon nanocapsules is given in Fig. 7. The Si and O found in the spectrum are due to the glass substrate on which nanocapsule samples were mounted for EDS analysis.

In addition, Raman spectroscopic analysis was used to characterize the structure of nano-capsule (Fig. 8).

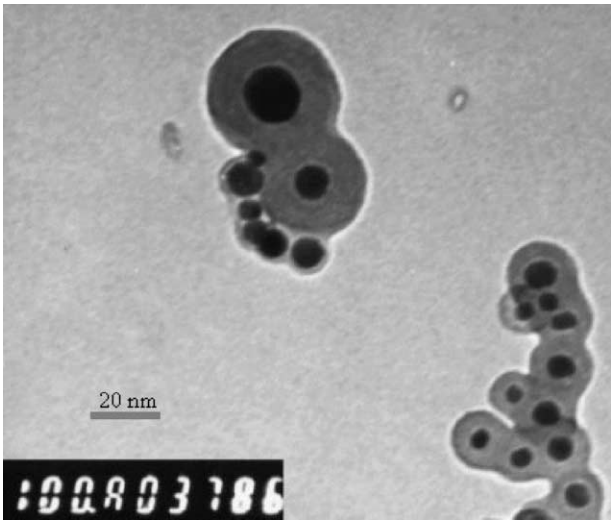

Fig. 4. Typical TEM image of purified carbon nano capsules.

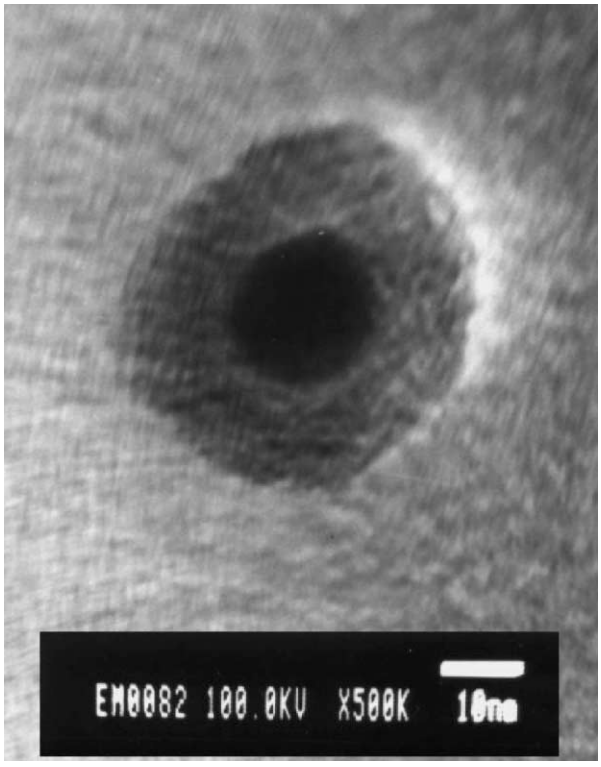

Fig. 5. An iron particle encapsulated in a carbon nano-capsule.

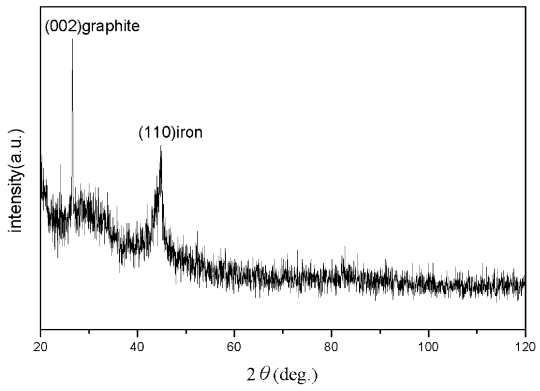

Fig. 6. XRD pattern of iron encapsulated carbon nano-capsule.

The Raman peak at 1592 cm^{-1} is corresponding to highly crystalline and defect free graphite (E_{2g} mode), while the peak around 1350 cm^{-1} corresponds to the disordered or imperfect graphite and carbon [12]. The peaks at about 853 and 929 cm^{-1} are attributed to the iron particles.

TEM, XRD, EDS and Raman spectroscopy analyses indicate that a magnetic iron particle was encapsulated in each carbon nano-capsule.

As mentioned before, the raw soot material was subjected to acid treatment followed by a magnetic particles segregation process, in which the magnetic carbon nano-capsules were removed from the residual nonmagnetic soot by a magnet. This nonmagnetic soot residual material was also examined by TEM. It should be noted, as in Fig. 1, that a considerable amount of carbon nanotubes was observed in the raw soot material before purification. However, TEM results revealed a greater amount of pure carbon nanotubes in this nonmagnetic soot material than that occurring before the segregation process. A typical carbon nanotube in the purified carbonaceous materials is shown in Fig. 9. It implies that the magnetic segregation process can be used to remove the magnetic particles and to produce pure carbon nanotubes.

3.3. Nano-composite

The amorphous silicate coated magnetic nano composite particles usually stick together as flocks or aggregates as shown by the typical SEM image of a small lump of the iron filled nano-composite of Fig. 10. A small amount of water was added to these nano composite aggregates. A drop of the resulting suspension was placed on a glass substrate, dried and examined by SEM. As shown in Fig. 11, the nano-composite particles were found to be well dispersed in the water solution. Since the outside coating of the nano-composites is sodium silicate, which can be dissolved in water,

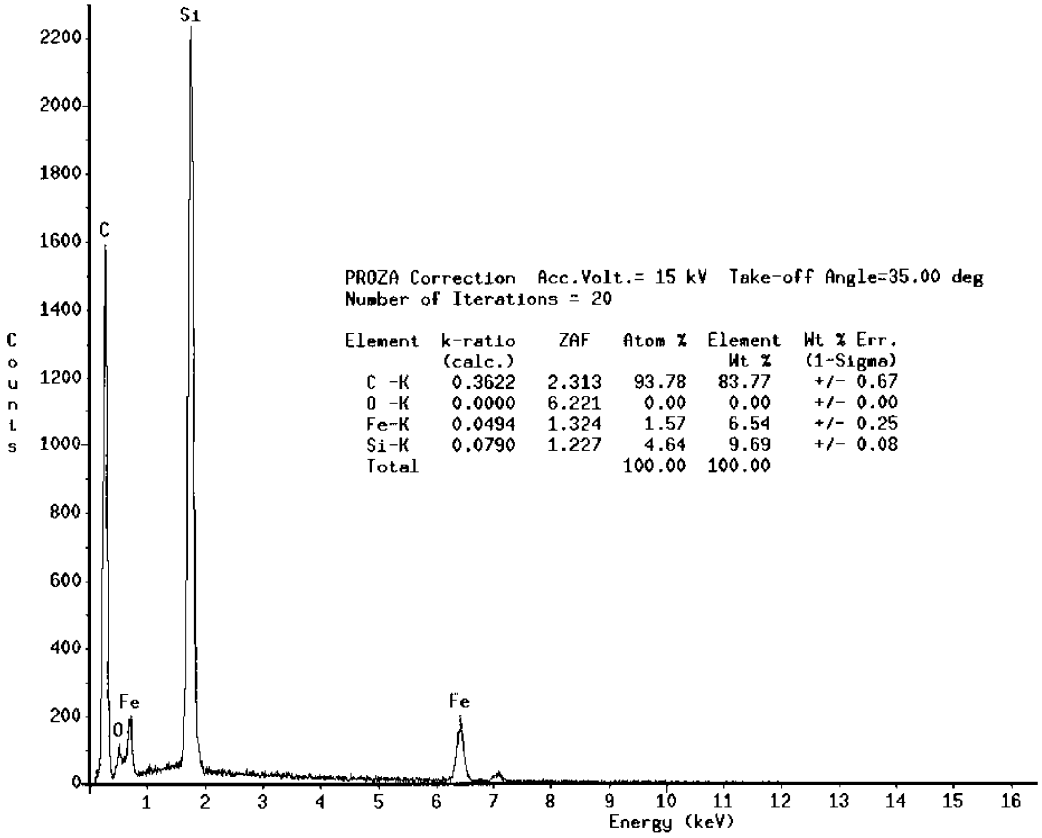

Fig. 7. EDS spectrum of iron filled carbon nano-capsule.

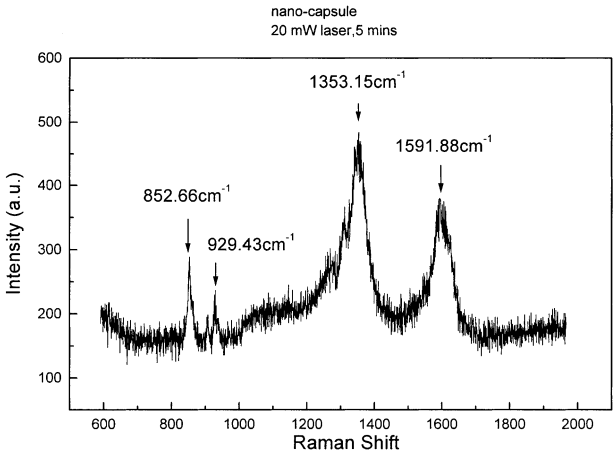

Fig. 8. Raman spectrum of nano-capsules.

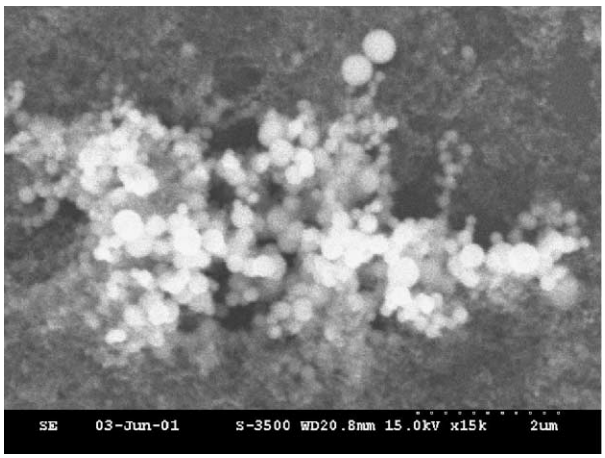

Fig. 10. The iron filled nano-composite particles.

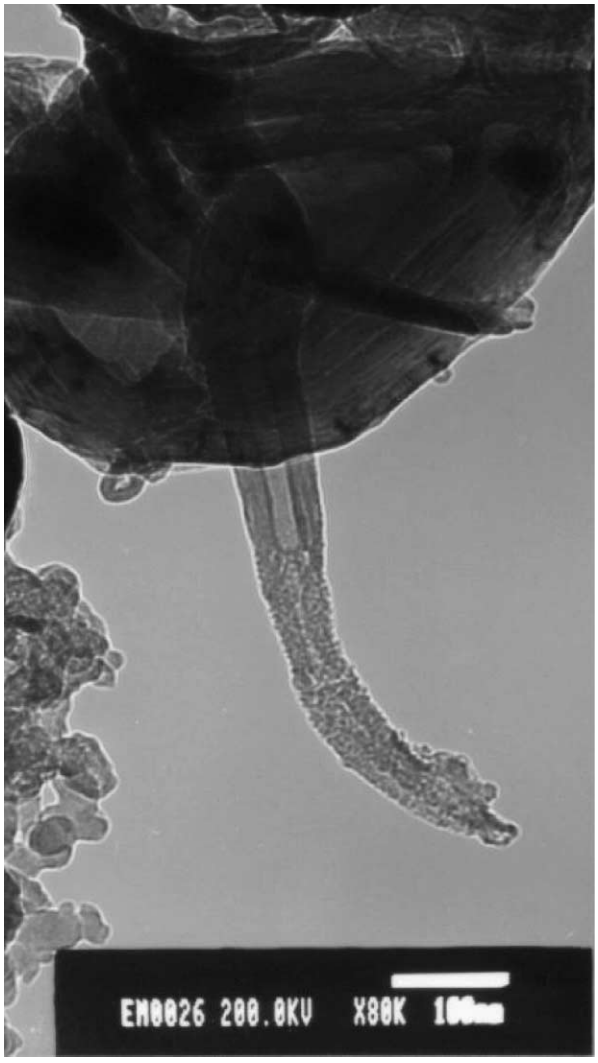

Fig. 9. A typical TEM image of carbon nanotube.

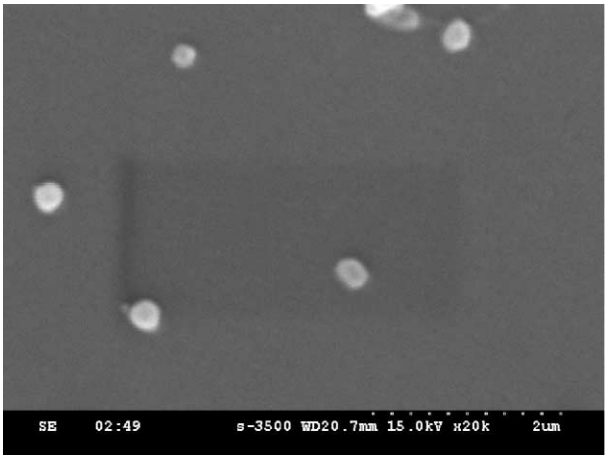

Fig. 11. Well dispersed nano-composite particles.

deflocculation of particles in the fluid must have taken place. From Fig. 11, the particle size of the composites can be estimated to be 100–300 nm in diameter. These magnetic nano-composite particles were aligned or spatially arranged by a magnet.

4. Conclusions

Magnetic-metal filled carbon nano-capsules, ranging from 10 to 50 nm in diameter, were produced using an arc-discharge apparatus and purified by concentrated acid treatment. The magnetic carbon nano-capsules were segregated from non-magnetic particles by a magnet. TEM, XRD, EDS and Raman scattering spectroscopic examination revealed that a magnetic iron particle was encapsulated in each carbon nano-capsule. The iron particle encapsulated in the carbon nano-capsule was estimated to range from 5 to 30 nm in diameter. Magnetic nano composite particles were

synthesized by coating individual iron filled carbon nano-capsule with amorphous silicate. These nano composite particles are ranging from 100 to 300 nm in diameter. The nano composite particles can be dispersed in water solution as a result of deflocculation effect. They can be aligned or spatially arranged by a magnet.

References

[1] Y. Saito, T. Yoshikawa, M. Inagaki, M. Tomita, T. Hayashi, Growth and structure of graphitic tubules and polyhedral particles in arc-discharge, Chem. Phys. Lett. 204 (1993) 277–282.
[2] Y. Saito, Nanoparticles and filled nanocapsules, Carbon 33 (7) (1995) 979–988.
[3] Y. Saito, M. Okuda, T. Koyama, Carbon nanocapsules and single-wall nanotubes formed by arc evaporation, Surface Review & Letters 3 (1) (1996) 863–867.
[4] T.W. Ebbesen, Nanotubes, nanoparticles, and aspects of fullerene related carbons, J. Phys. Chem. Solids 58 (11) (1997) 1979–1982.
[5] S. Tomita, M. Hikita, M. Fujii, S Hayashi, K. Yamamoto, A new and simple method for thin graphitic coating of magnetic-metal nanoparticles, Chem. Phys. Lett. 316 (2000) 361–364.
[6] J.H.J. Scott, S.A. Majetich, Morphology, structure, and growth of nanoparticles produced in a carbon arc, Phys. Rev. B 52 (1995) 12564–12571.
[7] T. Hayashji, S. Hirono, M. Tomita, S. Umemura, Magnetic thin films of cobalt nanocrystals encapsulated in graphite-like carbon, Nature 381 (1996) 772–774.
[8] M.E. McHenry, S.A. Majetich, J.O. Artman, M. DeGraef, S.W. Staley, Superparamagnetism in carbon-coated Co paricles produced by the Kratschmer carbon arc process, Phys. Rev. B 49 (1994) 11358–11363.
[9] A.A. Setlur, J.Y. Dai, J.M. Lauerhaas, R.P.H. Chang, Formation of filled carbon nanotubes and nanoparticles using polycyclic aromatic hydrocarbon molecules, Carbon 36 (1998) 721–723.
[10] V.P. Dravid, J.J. Host, M.H. Teng, B. Elliott, J. Hwang, D.L. Johnson, T.O. Mason, J.R. Weertman, Controlled-size nanocapsules, Nature 374 (1995) 602.
[11] P.J.F. Harris, Carbon Nanotubes and Related Structures, Cambridge University Press, 1999, pp. 18–19.
[12] R. Saito, G. Dresselhaus, M.S. Dresselhaus, Physical Properties of Carbon Nanotubes, Imperial College Press, 1998.
[13] T.W. Ebbesen (Ed.), Carbon Nanotubes Preparation and Properties, CRC Press, 1997.