ELSEVIER

Journal of Alloys and Compounds 452 (2008) 258–262

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

TEM investigation on the initial stage growth of carbon onions synthesized by CVD

C.N. He, C.S. Shi, X.W. Du, J.J. Li, N.Q. Zhao*

School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China

Received 16 September 2006; received in revised form 3 November 2006; accepted 7 November 2006
Available online 4 December 2006

Abstract

We report an investigation on the initial stages of growth of carbon onions synthesized by CVD of methane. A special experimental procedure has been developed to stop the process after short duration (10 s–2 min). It has found that during the early stages (90 s), carbon atom cluster encapsulated nanoparticles were formed. With increasing synthesis time (2 min), the carbon clusters began to graphitize to form graphitic layers. High resolution transmission electron microscope observations showed that many catalytic particles were partially encapsulated with graphitic layers, which were responsible for the hollow carbon onion formation.

Keywords: Carbon onions; Chemical vapor deposition; Transmission electron microscopy

1. Introduction

Carbon onions, which are quasi-spherical carbon nanoparticles consisting of concentric graphitic shells, are expected to be a new conformation of nanosize carbon materials and have good prospects for several applications of composite materials, magnetic storage media and wear-resistant materials [1,2]. Since the first observation of carbon onions [2], many attempts have been made to fabricate these onions and understand their formation mechanism [3,4]. Iijima [2] once tried to describe this new structure with a model involving a mixed sp^2/sp^3 hybridization of carbon atoms. However, the scientific community did not pay much attention to this explanation before the fullerene one [5] and it is only in 1987 [6,7] that the structures characterized by Iijima were reconsidered and discussed in terms of fullerene structures. Actually, the intense interest devoted to the carbon onions was in 1992, when Ugarte [8] discovered a reproducible technique to realize their formation that consists in irradiating carbon soot by an intense electron beam in a transmission electron microscope (TEM). Except for this production technique, several other methods were also developed to synthesize carbon onions. Thermal treatment of fullerene black [9], shock-wave treatment of carbon soots [10], dc arc-discharge of graphite electrode [11], pulsed laser deposition [4], and catalytic decomposition of carbon containing gases [12,13] at elevated temperatures appears as the most promising technique for producing numerous carbon onions with high purity.

Previously, we have obtained a mass of carbon onions in the process of catalytic decomposition of methane over Ni/Al catalyst at low temperature [12]. Compared with above carbon onion synthesis method [4,9–11], our carbon onions synthesized were in large quality and with diameters ranging from 5 to 50 nm, and that the synthesis equipment was relatively inexpensive. We have since paid much attention to this kind of carbon nanostructure. Because a thorough understanding of the formation mechanism for such carbon nanostructure is crucial to design procedures for controlling the growth conditions in order to obtain structures which might be directly used in different fields in nanotechnology, and that some models describing the formation of nano-onions fabricated by the methods including electric arc, high-energy electron irradiation of carbonaceous materials, and thermal treatment of "fullerene black" have been suggested in Refs. [14–17]. However, the growth mechanism of carbon onions by CVD is still under discussion. Therefore, the understanding of carbon onion formation during the initial stages of the growth is of particular importance. To the best of our knowledge, no experimental study of the initial stages of carbon onion growth by CVD of methane is reported.

---

* Corresponding author. Tel.: +86 22 27891371; fax: +86 22 27891371.
E-mail address: nqzhao@tju.edu.cn (N.Q. Zhao).

0925-8388/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2006.11.016

In this study, we report an investigation on the initial stages of the carbon onion growth performed to understand the mechanism operating in the formation of nano-onions. We developed a specific synthesis procedure in order to control precisely the synthesis duration for short times. A particular interest was devoted to the study of the location of catalyst particles and their chemical nature, morphology and size distribution when nano-onions started to grow in order to get information related to their growth mechanism. The understanding of the parameters involved would allow the development of efficient production procedures.

2. Experimental

The fabrication procedures of catalyst are similar to those described in Ref. [12]. In brief, the right amounts of $Ni(NO_3)_2 \cdot 6H_2O$ and aluminum powder were mixed in 1 l distilled water to yield the final weight ratio of Ni/Al equal to 3/1, and appropriate NaOH dissolved in 50 ml distilled water was added to the previous mixture with constant stirring. The colloid obtained was then washed for several times with distilled water and dried in a vacuum furnace. Finally, the colloid was calcined in N_2 atmosphere at 400 °C for 4 h to form fine NiO/Al composite powder, which was employed in the following carbon onion synthesis experiment.

In the catalytic decomposition processes, some catalyst of the NiO/Al was put in a quartz boat and placed in a horizontal quartz tube reactor. In order to convert the nickel oxides in the catalyst to metallic Ni, the catalyst was firstly reduced at 600 °C in a hydrogen atmosphere for 2 h. Then, carbon onions were grown at 600 or 550 °C for some time (10 s–2 min) by introducing a mixture of CH_4/N_2 into the reactor at a flow rate of 60 ml/min/420 ml/min. Then the gas flow was switched back to nitrogen with a very large flow rate (2000 ml/min) after the growth process to purge the methane from the tube in short order and to prevent back flow of air into the tube. The furnace was then allowed to cool to room temperature before exposing the carbon nanomaterials to the air.

A small quantity of the as-prepared carbon nanomaterials has been dispersed in ethanol and dispersed onto copper grids in order to perform detailed observations on individual nano-onion by transmission electron microscopy (TEM) and high resolution TEM (HRTEM) (Philips Tecnai G^2 F20, 200 kV). Energy-dispersive X-ray (EDX) analyses were coupled to TEM observations to determine the nature of the products.

3. Results and discussion

TEM images (Fig. 1) show the changes in the morphology of the products when varying the synthesis duration from 10 s to 2 min, for 600 °C catalytic decomposition temperature. For duration of 10 s (Fig. 1a and b) and 20 s, essentially few things

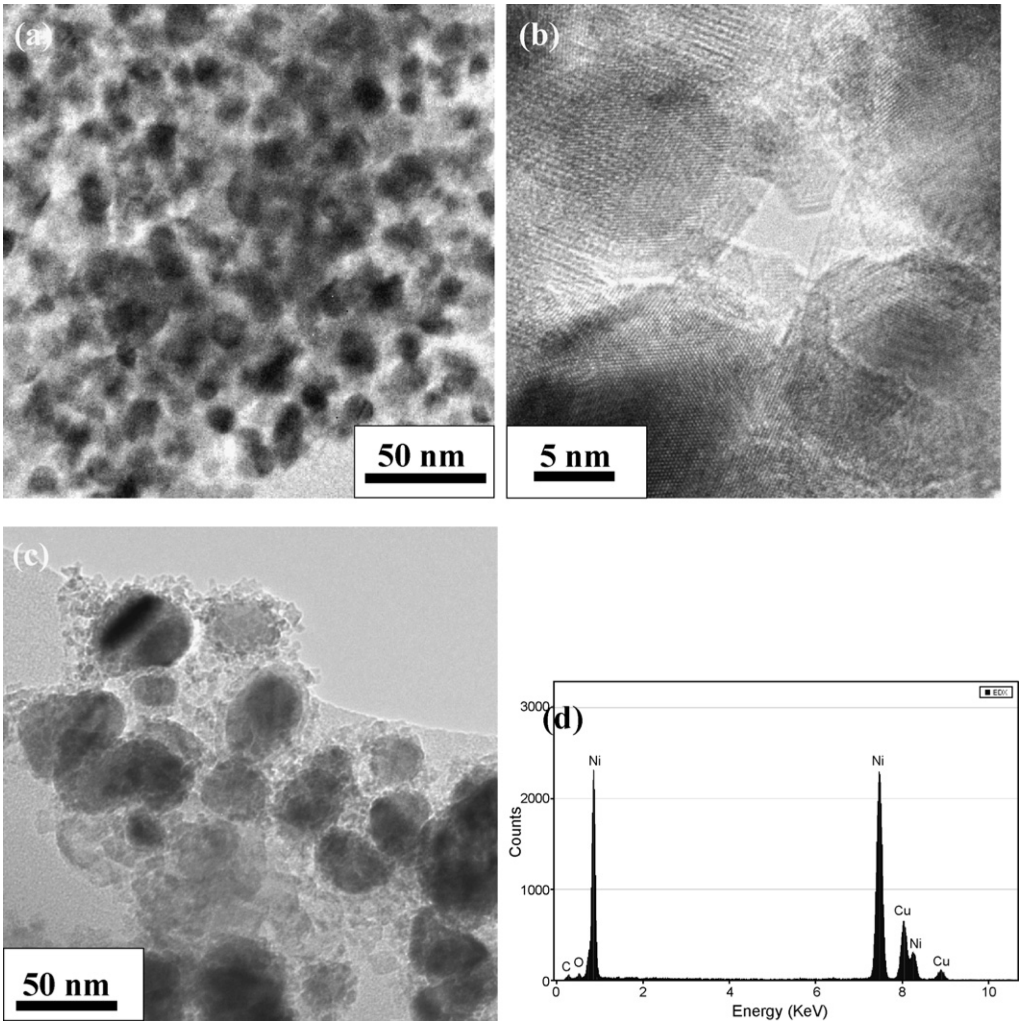

Fig. 1. (a) TEM and (b) HRTEM image of the early stages of nano-onion growth for 10 s at 600 °C from catalytic decomposition of methane. (c) TEM image of the early stages of nano-onion growth for 2 min at 600 °C from catalytic decomposition of methane; this image reveals catalytic particles encapsulated by carbon atom clusters. (d) EDX analysis of catalytic particle encapsulated by carbon atom clusters (600 °C, 2 min).

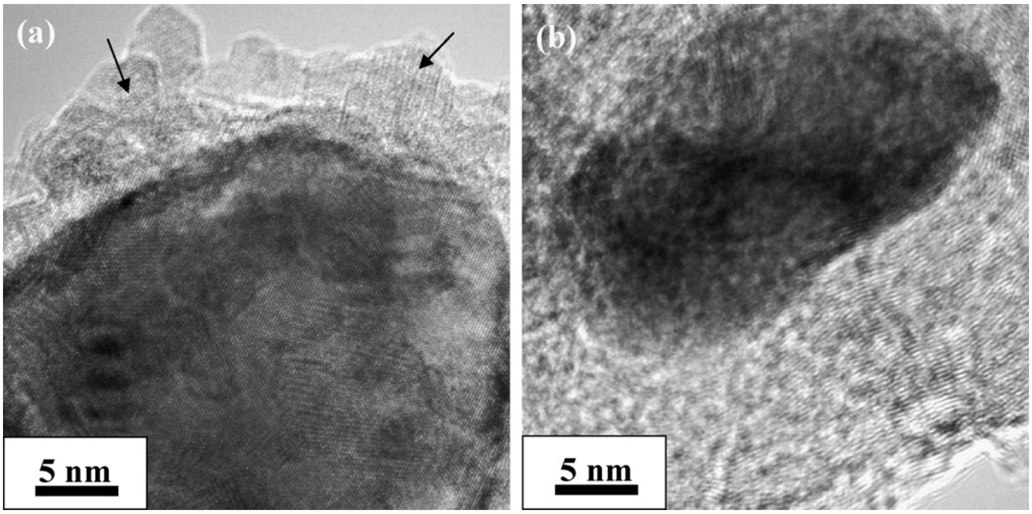

Fig. 2. HRTEM observation of: (a) a larger catalytic particle encapsulated by carbon atom clusters obtained by CVD at 600 °C for 2 min and (b) a smaller catalytic particle encapsulated by graphitic layers obtained by CVD at 600 °C for 2 min.

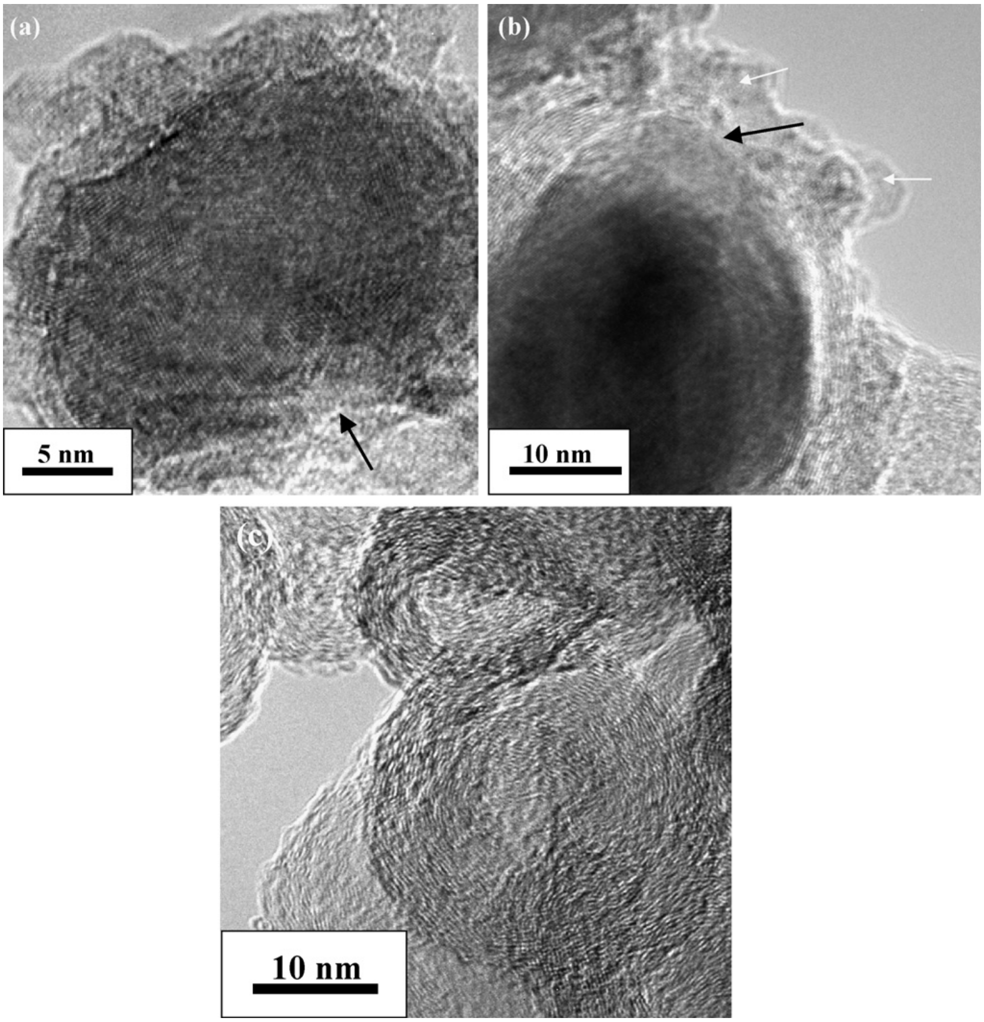

Fig. 3. (a and b) HRTEM observation of individual catalytic particle partially encapsulated by graphitic layers obtained by CVD at 600 °C for 2 min, the black arrows indicate the parts without graphite layers encapsulated, and the white arrows indicate the carbon atom clusters; (c) HRTEM observation of hollow carbon onions obtained by CVD at 600 °C for 10 min.

were found on the surfaces of the catalytic particles with the diameters ranging from 5 to 30 nm. A few of these nanoparticles were growth seeds for carbon-encapsulated particles. Among the few carbon nanostructures observed, only carbon-encapsulated particles were growing, but no hollow carbon onions formed, and most of the particles were not leading to carbon nanostructure growth. After 2 min synthesis duration (Fig. 1c), a mass of carbon-encapsulated nanoparticles was obtained and yet no hollow carbon onions existed. This indicated that the number of carbon-encapsulated nanoparticles was increasing with synthesis duration during the initial stages of carbon onion growth. For a lower synthesis temperature (550 °C), only catalytic particles were also observed for 10 s synthesis duration while no carbon-encapsulated nanoparticles formed after 20 s synthesis duration. The analysis of several images recorded at different places all over the copper grid allowed us to give an estimation of the sizes of the carbon-encapsulated nanoparticles synthesized at 600 °C for 2 min. Similar results were obtained at 550 and 600 °C decomposition temperature and for 10 s and 2 min synthesis duration. A majority of the carbon-encapsulated nanoparticles exhibited diameters ranging between 10 and 40 nm. Large diameters in the 50–100 nm range could also be found, but they were looking like agglomerates of smaller individual particles. EDX analysis performed on the catalytic nanoparticles encapsulated obviously detected Ni and Cu while the O and C signals were very feeble (Fig. 1d). The copper peaks due to the sample holder should be ignored. Furthermore HRTEM clearly presented the crystal plane of nickel, therefore the dominating ingredient of the catalytic particle was Ni and no carbide has formed, which was consistent with our previous work [12].

When investigating the carbon-encapsulated nanoparticles obtained by catalytic decomposition of methane at 600 °C for 2 min in detail using HRTEM, as illustrated in Fig. 2a and b, we can observe that larger catalytic particles (approximately above 25 nm) were just wrapped by carbon atom clusters (as shown in Fig. 2a) (though a few carbon atom clusters were graphitizing, most of them had not changed to graphite), but most smaller catalytic particles were encapsulated with graphitic layers (as can be seen in Fig. 2b). The reason for the above distinct effects might be that the catalytic nanoparticle played an important role in the formation and growth of carbon-encapsulated nanoparticles. Our catalytic synthesis experiment is very similar to CNT growth processes, and it is also widely accepted that carbon-encapsulated nanoparticle growth processes involve the adsorption and the decomposition of gases (or gas phase molecular) containing carbon on metal surfaces, the dissolution and diffusion of the released carbon atoms in catalyst [14,15,18]. The decomposition of methane and graphitization are exothermal processes [18]. Further, the amount of heat due to exothermal processes is proportional to the surface area of the catalytic nanoparticle. Normalizing this heat to the nanoparticle mass (a proportionality with surface to volume ratio results), and it may be seen that the heat per unit mass of nanoparticle is lower for larger particles. Consequently, in this work, the smaller catalytic nanoparticles might reach higher temperature than the larger catalytic nanoparticles during carbon-encapsulated nanoparticle growth. On the basis of Cui et al. [19], the temperature had important effect on the etching rate of C-species on the catalytic particle surface, which decides on the type of carbon nanostructures. As the synthesis time (2 min) was very short, and that the cooling rate and the final environment temperature were fixed, the smaller catalytic nanoparticles with higher surface temperature had faster etching rate of C-species, which made for the faster graphitizing of the carbon atom clusters segregated on the nanoparticle surfaces and graphite-like layers were grown. Analogically, the etching rate of C-species of the larger catalytic

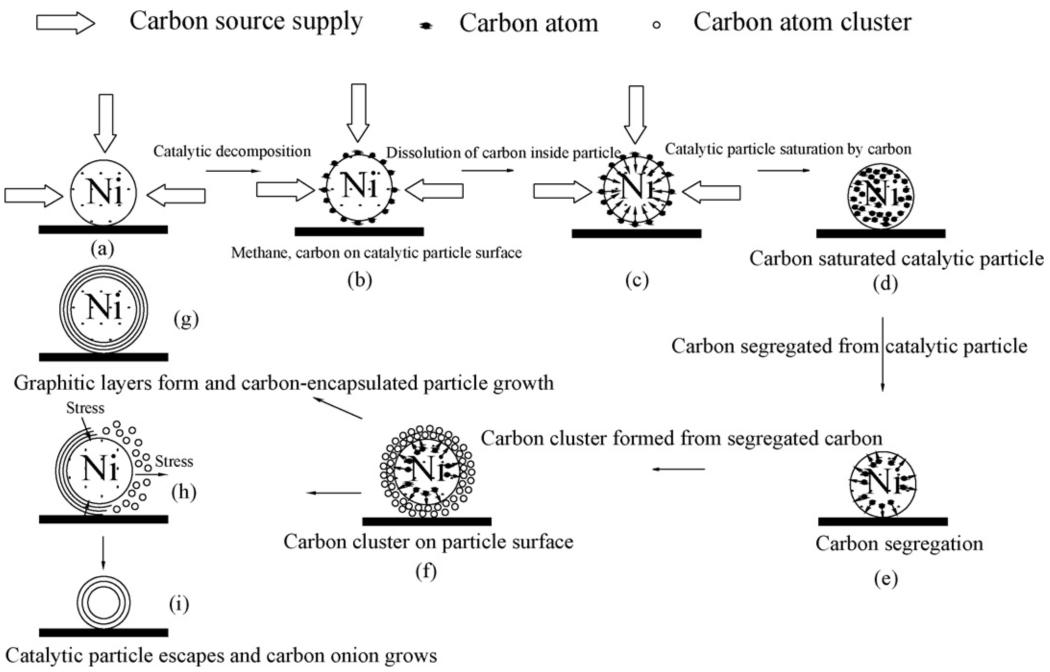

Fig. 4. Schematic models for the growth processes of the carbon-encapsulated catalytic particles and hollow carbon onions by CVD.

nanoparticles with lower surface temperature was slower, then the graphitizing rate of the carbon atom clusters was very slow and graphitic layers were unable to develop. In addition, we have also apparently observed that many smaller catalytic nanoparticles were partially encapsulated by graphite layers, and their residual parts were encapsulated with carbon atom clusters (as shown in Fig. 3a and b), indicating that the graphitizing course of the carbon atom clusters was gradual and not homogeneous. Here, we speculated that these carbon-encapsulated nanoparticles might lead to the growth of hollow carbon onions. Fig. 3c shows the hollow carbon onions obtained for 10 min. It can be seen that the quasi-spherical carbon onions consisted of several concentric carbon layers surrounding a hollow core, and that the interlayer spacing between graphitic layers was 0.34 nm, which was very close to the ideal graphitic interlayer space (0.335 nm).

Based on above-mentioned experimental evidence, we proposed a model to explain the growth of hollow carbon onions synthesized by CVD, which was presented in Fig. 4. Firstly, after the catalytic decomposition of methane, the process of the dissolution of the decomposed carbon in the catalytic particles occurred (Fig. 4b). Then, at some points, the catalytic particles became saturated by carbon due to the carbon solubility limit (Fig. 4d) and carbon segregation began (Fig. 4e), which resulted in the formation of carbon atom clusters on the catalytic particle surfaces (Fig. 4f). When carbon cluster encapsulation was complete, the graphitizing of the carbon clusters occurred. The formation of graphitic layers on the catalytic particle surfaces led to the stress on the catalytic particle, which would give a pull stress to the catalytic particle to make it escape from the encapsulation (Fig. 4h). If the existed graphitic layer encapsulation was defective and the pull stress was enough, the catalyst particle would escape and the graphite layers closed upon themselves to form hollow carbon onions.

4. Conclusion

The investigation of the early stages of carbon onion growth by CVD of methane highlighted different steps in the nano-onion birth and growth. First, carbon atom clusters were segregated on catalytic particle surfaces. With prolonging growth time up to 2 min, continuous graphitizing of the carbon atom clusters occurred and particles partially encapsulated with graphitic layers developed. Further, the catalyst particle escaped from encapsulation due to the generated stress by the graphite layers, and the graphite layers closed upon themselves to form hollow carbon onions.

Acknowledgements

The authors acknowledge the financial support by Tianjin Municipal Science and Technology Commission (No. 05YFGHHZ01000) and Doctor Fund from the Educational Ministry of China (No. 20050056062).

References

[1] H.W. Kroto, Nature 359 (1992) 670–672.
[2] S. Iijima, J. Cryst. Growth 5 (1980) 675–677.
[3] H. Yokomichi, F. Sakai, M. Ichihara, et al., Nanotechnology 16 (2005) 1204–1207.
[4] G. Radhakrishnan, P.M. Adams, L.S. Bernstein, Thin Solid Films 515 (2006) 1142–1146.
[5] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, Nature 318 (1985) 162–163.
[6] S. Iijima, J. Phys. Chem. 91 (1987) 3466–3470.
[7] H.W. Kroto, K. Mckay, Nature 331 (1988) 328–330.
[8] D. Ugarte, Nature 359 (1992) 707–708.
[9] T. Cabioch, M. Jaouen, E. Thune, P. Gue'rin, C. Fayoux, M.F. Denanot, Surf. Coat. Technol. 128/129 (2000) 43–50.
[10] R. Selvan, R. Unnikrishnan, S. Ganapathy, T. Pradeep, Chem. Phys. Lett. 316 (2000) 205–210.
[11] R.S. Ruoff, D.C. Lorents, B. Chan, R. Malhotra, S. Subramoney, Science 259 (1993) 346–348.
[12] C. He, N. Zhao, X. Du, C. Shi, J. Ding, J. Li, Y. Li, Scripta Mater. 54 (2006) 689–694.
[13] A.G. Nasibulin, A. Moisala, D.P. Brown, E.I. Kauppinen, Carbon 41 (2003) 2711–2724.
[14] D. Ugarte, Carbon 33 (1995) 989–993.
[15] P.E. Nolan, D.C. Lynch, A.H. Cutler, Carbon 34 (1996) 817–819.
[16] M. Audicr, M. Coulon, Carbon 23 (1985) 317–323.
[17] Y. Saito, T. Yoshikawa, M. Okuda, M. Ohkohchi, Y. Ando, A. Kasuya, Y. Nishina, Chem. Phys. Lett. 209 (1993) 72–76.
[18] R.B. Little, J. Cluster Sci. 14 (2003) 135–185.
[19] S. Cui, C.Z. Lu, L.Y. Qiao, L. Cui, Carbon 37 (1999) 2070–2073.