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Synthesis and Characterization of Cobalt-Carbon Core-Shell Microspheres in Supercritical Carbon Dioxide System

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The synthesis of cobalt-carbon core-shell microspheres in supercritical carbon dioxide system was investigated. Cobalt-carbon core-shell microspheres with diameter of about 1 μm were prepared at 350 $^{\circ}\text{C}$ for 12 h in a closed vessel containing an appropriate amount of bis(cyclopentadienyl)cobalt powder and dry ice. Characterization by a variety of techniques, including X-ray powder diffraction, X-ray photoelectron spectroscopy, Transmission electron microscope, Fourier transform infrared spectrum and Raman spectroscopy analysis reveals that each cobalt-carbon core-shell microsphere is made up of an amorphous cobalt core with diameter less than 1 μm and an amorphous carbon shell with thickness of about 200 nm. The possible growth mechanism of cobalt-carbon core-shell microspheres is discussed, based on the pyrolysis of bis(cyclopentadienyl)cobalt in supercritical carbon dioxide and the deposition of carbon or carbon clusters with odd electrons on the surface of magnetic cobalt cores due to magnetic attraction. Magnetic measurements show 141.41 emu/g of saturation magnetization of a typical sample, which is lower than the 168 emu/g of the corresponding metal cobalt bulk material. This is attributed to the considerable mass of the carbon shell and amorphous nature of the magnetic core. Control of magnetism in the cobalt-carbon core-shell microspheres was achieved by annealing treatments.

Key words: Cobalt-carbon core-shell microspheres, Supercritical carbon dioxide system

I. INTRODUCTION

Magnetic materials including Co [1-3], Fe [4,5], Ni [6,7], and their oxides have been studied for many years. Over the past decade magnetic materials with various shapes and sizes have attracted intensive interest because of their potential applications in high density magnetic recording, magnetic sensors and addressing some basic issues about magnetic phenomena [8-11]. Various approaches have been developed to prepare magnetic materials with various shapes and sizes [12-15]. For instance, magnetic materials coated with carbon constitute the group of especially interesting magnetic materials because of their fascinating magnetic properties and the carbon coating, which can protect the magnetic particles against environmental degradation [16]. The application of the encapsulated magnetic materials is significant owing to their novel properties and commercially valuable potential applications such as magnetic inks, magnetic recording media, a toner for xerography, ferrofluids for biomedical applications such as magnetic drug delivery carriers (MDDC) and contrast agents in magnetic resonance imaging in particular [17]. A method of magnetic drug delivery proposed by Widder *et al.* is to inject a magnetically susceptible material coated with a drug-laden matrix and then to

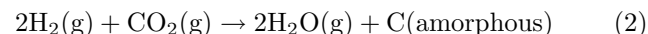
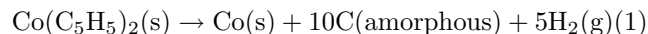
use an externally placed magnet to guide the drug matrix to the target site. A composite of activated carbon and ferromagnetic material is generally used for such purpose. The ferromagnetic material such as iron provides the magnetic characteristic while activated carbon (AC) works as drug adsorption matrix. Another method to prepare the magnetic target carrier (MTC) is by a high impact ball milling process in which fine Fe particles are welded to AC by utilizing the so-called mechanochemical effect. However, the major disadvantage is that it is easily separated into Fe and AC while being transferred in veins. In addition, the tissues are in direct contact with metal as Fe is not enclosed by the carbon matrix [18]. Cobalt is another excellent model system for cobalt-carbon core-shell microspheres for the application of magnetic drug delivery carrier. Cobalt dispersed carbon spheres were prepared from chelate resin [19,20]. Cobalt exhibits fantastic magnetism, but displays a little toxicity. If cobalt is used as MDDC, it must be coated to form a core-shell structure just like nickel [21]. The purpose of this paper is to discover a method to synthesize cobalt-carbon core-shell particles in one stage.

Supercritical fluids as solvents for chemical and material processing can be advantageously exploited for new kinds of materials processing because of their unusual combination of physical properties (i.e., easy separations, variable density, low viscosity, low surface tension, and polymer plasticization) [22]. Supercritical carbon dioxide (scCO_2) has attracted much interest as an alternative solvent for materials synthesis and pro-

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cessing, and has been promoted as a sustainable and "green" solvent because it is non-toxic, non-flammable, and naturally abundant. These characteristics have led to wide acceptance that the advantages associated with this solvent are likely to lead to a number of new CO₂-based processes [23].

In this work the preparation of cobalt-carbon composite microspheres is investigated using a single precursor, bis(cyclopentadienyl)cobalt under a supercritical carbon dioxide system. An annealing treatment for controlling the magnetism of the cobalt-carbon core-shell microspheres is also studied. The chemical reactions in the system can be represented as follows:



II. EXPERIMENTS

The reaction was carried out in a stainless steel autoclave (10 mL) that is a 110-mm long cylindrical tube with outer diameter of 85 mm and an inner diameter of 13 mm, respectively. A typical reaction used 0.3 g of bis(cyclopentadienyl)cobalt, which was placed in the cell in a glovebox filled with the argon at room temperature. Then, as soon as 12.0 g of dry ice was added outside the glovebox, the vessel was immediately closed tightly and heated to 350 °C, and kept at this temperature for 12 h. The reaction took place at an autogenic pressure depending on the amount of dry ice added. After cooling of the sample to room temperature, the black solid product was collected and was washed with distilled water and absolute ethanol several times, and dried in air at room temperature, yielding about 0.22 g of products.

The annealing treatment of the cobalt-carbon core-shell microspheres was done via quartz boat heating by a tube furnace in N₂ stream, with its flow rate of 100 mL/min. The heating rate of the system was 10 °C/min, and the temperature was held for 120 min when it came to a certain temperature point of 800 °C, then the product was cooled to the room temperature naturally.

Bis(cyclopentadienyl)cobalt was purchased from Alfa Aesar and used without further purification. Dry ice was freshly made from high purity CO₂ gas (99.9% purity) in liquid nitrogen. Transmission electron microscope (TEM) images were taken on JEOL-2010 with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was performed on a VG ESCALAB MKII Electron Spectrometer with the X-ray source of Mg K α . The Raman spectroscopy analysis was carried out on a LABRAM-HR Confocal Laser Micro-Raman spectrometer with an argon-ion laser at the excitation wavelength of 514.5 nm and the resolution factor of $\pm 1 \text{ cm}^{-1}$ at room temperature. Fourier transform infrared spectrum (FT-IR) of the sample

was recorded at the ambient temperature on a Nicolet MAGNA-IR 750 Fourier Transform Infrared Spectrometer with a resolution factor of $\pm 0.1 \text{ cm}^{-1}$. The X-ray diffraction (XRD) analysis was performed on a Rigaku (Japan) D/Max-rA X-ray diffractionmeter equipped with graphite monochromatized Cu K α radiation ($\lambda=0.154178 \text{ nm}$). Magnetic hysteresis loops were measured on a Vibrating Sample Magnetometer (VSM, BHV-55), for magnetization measurements the powder samples were pressed strongly and fixed in a small cylindrical plastic box.

III. RESULTS AND DISCUSSION

The morphology of the microspheres was studied by TEM observation. It shows the spherical particles consisted of a core covered with a layer of 200 nm low contrasting material. The diameters of these cores are less than 1 μm (Fig.1). The core sizes vary somewhat, but most of the particles were covered with a uniform shell, which helps to stabilize the core from being oxidized at room temperature. The three-dimensional core-shell structure was demonstrated when the TEM grid was tilted and the picture remained unchanged. It is well-known that the density of cobalt is much larger than that of the carbon. Taking into account the data of XRD, it is suggested that the as-prepared microspheres consisted of an amorphous carbon shell and amorphous cobalt core.

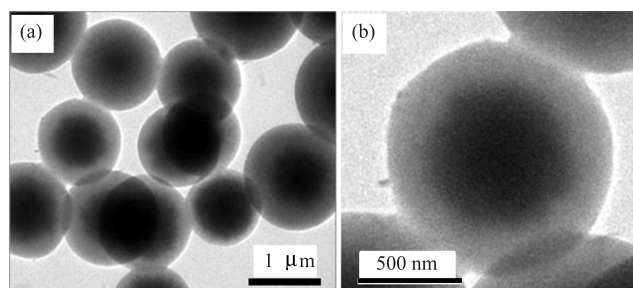


FIG. 1 (a) TEM image of cobalt-carbon core-shell microspheres synthesized in supercritical carbon dioxide system at 350 °C. (b) The enlarged image of a core-shell microsphere observed in (a).

The calculated elemental percentages of Co and C in the Co(C₅H₅)₂ reactant are 4.76% and 47.62%, respectively. We could determine the elemental content in the surface of microspheres by XPS analysis (Fig.2). The measured amount of carbon in the sample is 88.89%, while the amount of cobalt element is reduced to 0.19%. Here, the content of carbon in the surface of the sample is increased, while the content of cobalt is reduced in the surface of the sample, which suggests core-shell structure of the microspheres. Because XPS can only give surface composition information, according to conservation of mass, cobalt element must exist in the inner

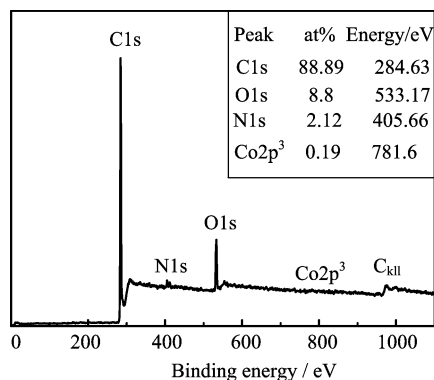


FIG. 2 XPS of a powder sample of cobalt-carbon core-shell microspheres.

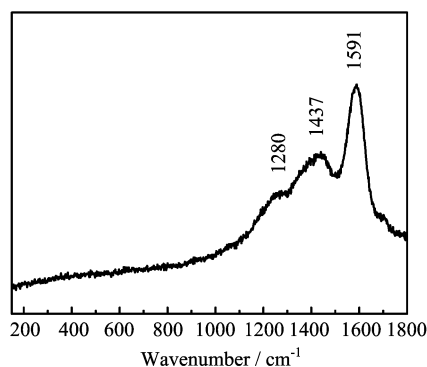


FIG. 3 Raman spectrum of cobalt-carbon core-shell microspheres with an excitation wavelength of 514.5 nm. The measurements were performed on a LABRAM-HR Confocal Laser MicroRaman spectrometer.

layer of the microspheres mostly and form the cobalt core.

Raman spectroscopy measurements were performed to understand the nature of the coated carbon (Fig.3). The peak at around 1591 cm^{-1} involves the in-plane bond stretching motion of pairs of carbon sp^2 atoms, which also exists as the G mode with the E_{2g} symmetry [24]. The peak around 1437 cm^{-1} was assigned to $\text{sp}^3\text{-CH}_n$ [25]. The D mode of graphite around 1280 cm^{-1} is related to the degree of disorder in carbon sp^2 bonded clusters in amorphous carbon. The intensity of the G-band associated with graphitic carbon is more intense than the D-band associated with amorphous carbon. It is not strange that no Co peaks were observed due to the core-shell structure of the spheres. Figure 4 shows FT-IR spectrum of the surface of microspheres. It reveals the coexistence of sp^2 and sp^3 hybridized C—C, C=C and C—H bonds, in which 2926 , 2859 , and 1456 cm^{-1} were assigned to hydrogen-bonded sp^3 carbon, and 1690 , 1093 , 822 , and 515 cm^{-1} to C=C and C=C—H bonds, which reveals the presence of complex structure of amorphous carbon and can explain why the Raman spectroscopy peak at 1280 cm^{-1} (D-band) is broadened. These bonds are useful for the application

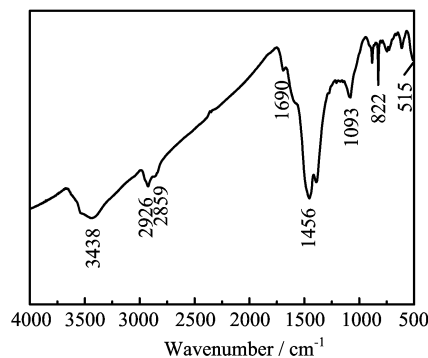


FIG. 4 FT-IR spectrum of a powder sample of cobalt-carbon core-shell microspheres.

of magnetic drug deliver carrier, because they can be oxidized forming carboxyl for further amidation, which is helpful for drug molecules or antibody bonding [26].

After annealing treatment, the XRD pattern of a powder sample is compatible with the literature values (Fig.5(a)). Compared with the PDF card, it is found that the major peaks appear at 2θ values of 44.14° , 51.44° , and 75.78° , which correspond to the reflection lines of the face-centered cubic phase of Co. These values are in agreement with the diffraction peaks, peak intensities, and cell parameters of crystalline fcc Co of $a=3.544\text{ \AA}$ (PDF card, JCPDS89-4307). This indicates that the amorphous cobalt starts to change to crystallite cobalt. To understand the annealing treatment of the product, DTA and TG data were shown in Fig.5 (b) and (c). DTA data displayed that the exothermic reaction appeared most intensively at $620\text{ }^\circ\text{C}$, and TG data revealed that the weight of the sample decreased sharply between 270 and $340\text{ }^\circ\text{C}$.

M-H hysteresis loop was measured at room temperature to identify the magnetism of the product. It was discovered that cobalt-carbon core-shell microspheres display superparamagnetism because of their amorphous cobalt cores. Figure 6(a) shows that the cobalt-carbon core-shell microspheres exhibit typical superparamagnetism curves with a saturation magnetization $M_s=141.41\text{ emu/g}$, remnant magnetization $M_r=4.86\text{ emu/g}$, and coercive field $H_c=34.69\text{ Oe}$, which is much lower than the corresponding values of the bulk sample of metal cobalt ($H_c=1500\text{ Oe}$). That the value of M_s is smaller than the bulk value ($M_s=168\text{ emu/g}$) is not surprising; the cobalt-carbon core-shell structure should be responsible for the phenomenon because of the existence of significant amounts of carbon, and magnetic particles are expected to exhibit reduced magnetization due to disordered magnetization orientation [27]. The particles with superparamagnetism could be possibly used in biomedical area or as ferrofluids in other areas [28].

After annealing treatment, M-H hysteresis loop of the cobalt-carbon core-shell microspheres was measured at room temperature. The results are shown in Fig.6(b).

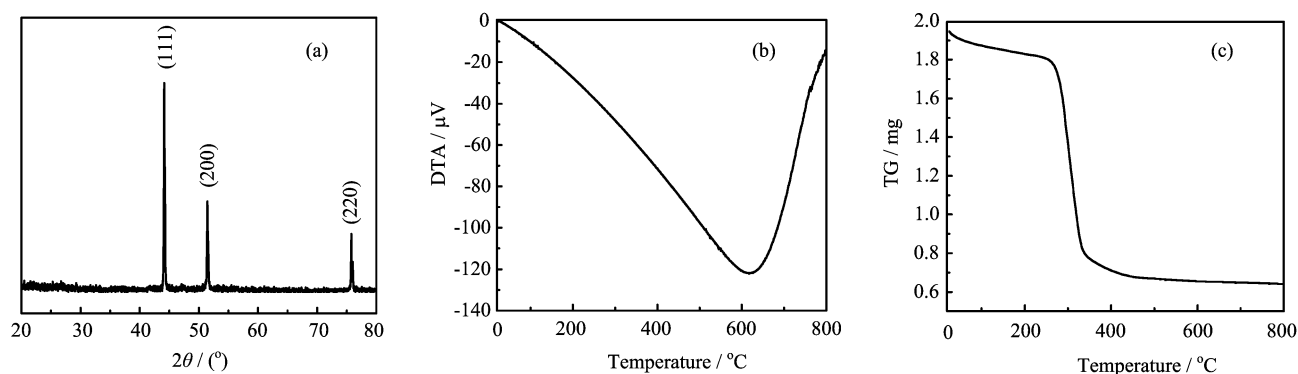


FIG. 5 X-ray diffraction pattern of a powder sample after annealing (a), DTA data (b), and TG data (c) of the sample.

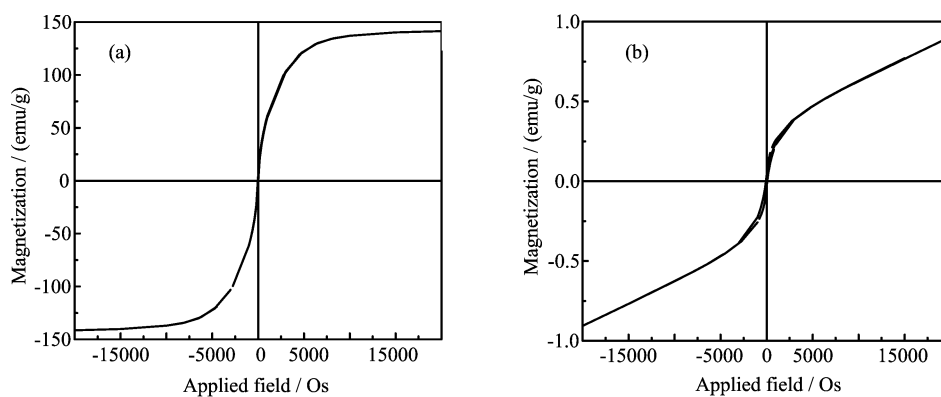


FIG. 6 (a) The M-H hysteresis loop for a powder sample of cobalt-carbon core-shell microspheres measured at room temperature. (b) The M-H hysteresis loop of cobalt-carbon composite microspheres after annealing treatment.

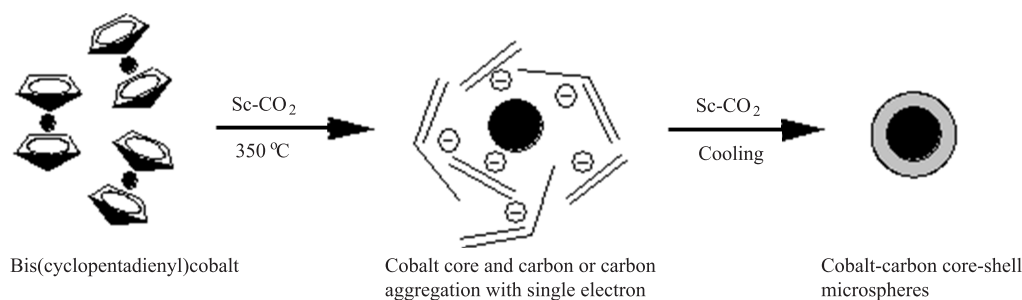


FIG. 7 A model of growth mechanism of cobalt-carbon core-shell microsphere.

It can be seen that M-H hysteresis loop is made up of two parts, one is ferromagnetism part and another is that of paramagnetism, which is because of the formation of multi-shell structure. That amorphous cobalt core was accomplished by crystallization of a thin layer on the surface (Fig.7), which was confirmed by XRD analysis. It is, therefore, possible to control magnetism of cobalt-carbon core-shell microspheres through annealing treatments.

From TEM, XPS, XRD, DTA, and TG analysis, it is clear that the product formed by the thermal dissociation of $\text{Co}(\text{C}_5\text{H}_5)_2$ in supercritical carbon dioxide system is composed of a Co core surrounded by amor-

phous carbon shell. One hypothesis is that the thermal decomposition of $\text{Co}(\text{C}_5\text{H}_5)_2$ takes place at a temperature between 300 and 350 °C, and forms a vapor of bis(cyclopentadienyl)cobalt in carbon dioxide, and then undergoes decomposition, just like the thermal dissociation of other organometallic compounds [29]. The metallic cobalt particles are formed by vapor nucleation. On the other hand, the released carbon or carbon clusters form the ion flux [30], and carbon or carbon clusters with odd electrons in the flux are deposited on the surface of Co cores due to magnetic attraction.

After annealing treatment at 800 °C, only one layer of amorphous cobalt core crystallized (Fig.8) and amor-

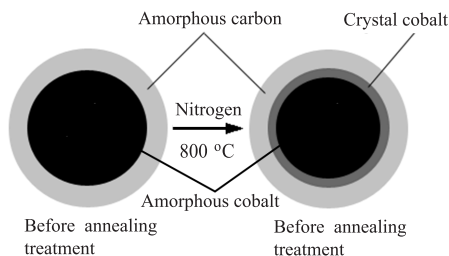


FIG. 8 The structural model of the annealing treatment of cobalt-carbon core-shell microspheres.

phous carbon shell did not graphitize because of low annealing temperature, which leads to the formation of multi-shell spherical structures. XRD pattern reveals that the layer of crystalline cobalt is the face-centered cubic phase. The magnetism measurement of the sample displays a curve consisting of signals of two parts, ferromagnetism and paramagnetization. It is, therefore, possible to control magnetism of cobalt-carbon core-shell microspheres by annealing treatment.

IV. CONCLUSION

Cobalt-carbon core-shell microspheres were produced by a one-step process in supercritical carbon dioxide system, and the resulting microspheres are made up of cobalt core with diameter less than 1 μm and amorphous carbon shell with thickness about 200 nm. The microspheres were formed by the nucleation of magnetic cobalt core and the deposition of carbon or carbon clusters with odd electrons on the surface of magnetic core due to magnetic attraction. Results show that the magnetic cobalt core can be well coated with the amorphous carbon by this simple process. C=C and C-H bonds on amorphous carbon shell could be oxidized forming carboxyl for further amidation, which is helpful for drug molecules or antibody bonding, and the magnetism of the microspheres can be controlled by the annealing treatment, making the microspheres potentially useful in biomedical or ferrofluid areas.

V. ACKNOWLEDGMENT

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- [1] D. P. Dinega and M. G. Bawendi, *Angew. Chem. Int. Ed.* **38**, 1788 (1999).
- [2] J. Osuna, D. Caro, C. Amiens, B. Chaudret, E. Snoeck, M. Respaud, J. M. Brot, and A. Fert, *J. Phys. Chem.* **100**, 14571 (1996).

- [3] J. J. He, Z. L. Liu, Y. Yoneyama, N. Nishiyama, and N. Tsubaki, *Chem. Eur. J.* **12**, 8296 (2006).
- [4] S. J. Park, S. Kim, S. Lee, Z. G. Khim, K. Char, and T. Hyeon, *J. Am. Chem. Soc.* **122**, 8581 (2001).
- [5] D. Caro, T. O. Ely, A. Mari, B. Chaudret, E. Snoeck, M. Respaud, J. M. Broto, and A. Fert, *Chem. Mater.* **8**, 1987 (1996).
- [6] N. Cordente, M. Respaud, F. Senocq, M. J. Casanove, C. Amiens, and B. Chaudret, *Nano. Lett.* **1**, 565 (2001).
- [7] T. O. Ely, C. Amiens, B. Chaudret, E. Snoeck, M. Verelst, M. Respaud, and J. M. Broto, *Chem. Mater.* **11**, 526 (1999).
- [8] Y. Jun, Y. Jung, and J. Cheon, *J. Am. Chem. Soc.* **124**, 615 (2002).
- [9] Y. H. Ni, X. W. Ge, Z. C. Zhang, and Q. Ye, *Chem. Mater.* **14**, 1048 (2002).
- [10] B. Kim, S. L. Tripp, and A. Wei, *J. Am. Chem. Soc.* **123**, 7955 (2001).
- [11] M. P. Pileni, *J. Phys. Chem. B* **105**, 3358 (2001).
- [12] D. N. Srivastava, N. Perkas, A. Gedanken, and I. Felner, *J. Phys. Chem. B* **106**, 1878 (2002).
- [13] Y. H. Wu, P. W. Qiao, J. J. Qiu, T. Chong, and T. S. Low, *Nano. Lett.* **2**, 161 (2002).
- [14] J. A. López, M. A. Pérez, Q. López, J. Mira, J. Rivas, and S. W. Charles, *J. Phys. Chem. B* **101**, 8045 (1997).
- [15] R. Amigó, J. Asenjo, E. Krotenko, F. Torres, J. Tejada, and E. Brillas, *Chem. Mater.* **12**, 573 (2000).
- [16] A. Leonhardt, A. M. Ritschel, R. Kozhuharova, A. Graff, T. Muhl, R. Huhle, I. Monch, D. Elefant, and C. M. Schneider, *Diamond Relat. Mater.* **12**, 790 (2003).
- [17] D. K. Kim, Y. Zhang, J. Kehr, T. K. Lason, B. Bjelke, and M. Muhammed, *J. Magn. Mater.* **225**, 30 (2001).
- [18] S. R. Rudge, T. L. Kurtz, C. R. Vessely, L. G. Catterall, and D. L. Williamson, *Biomaterials* **21**, 1411 (2000).
- [19] H. Konno, R. Matsuura, M. Yamasaki, and H. Habazaki, *Synth. Met.* **125**, 167 (2001).
- [20] A. Sharma, H. Nakagawa, and K. Miura, *Carbon* **44**, 2090 (2006).
- [21] L. Fu, V. P. Dravid, K. Klug, X. Liu, and C. A. Mirkin, *Eur. Cell. Mater.* **3**, Suppl. 2, 156 (2002).
- [22] C. A. Eckert, B. L. Knutson, and P. G. Debenedetti, *Nature* **383**, 313 (1996).
- [23] A. I. Cooper, *Adv. Mater.* **13**, 1111 (2001).
- [24] A. C. Ferrari and J. Robertson, *Phys. Rev. B* **61**, 14095 (2000).
- [25] J. Ristein, R. T. Stief, L. Ley, and W. Beyer, *J. Appl. Phys.* **84**, 3836 (1998).
- [26] J. Liu, A. G. Rinzler, H. J. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y. S. Shon, T. R. Lee, D. T. Colbert, and R. E. Smalley, *Science* **280**, 1253 (1998).
- [27] H. R. Kodoma, A. E. Berkovitz, E. J. Jr. Mcniff, and S. Foner, *Phys. Rev. Lett.* **77**, 394 (1996).
- [28] S. W. Lee, S. J. Kim, I. B. Shim, S. Bae, and C. S. Kim, *IEEE T. Magn.* **41**, 4114 (2005).
- [29] A. G. Nasibulin, A. Moisala, D. P. Brown, and E. I. Kauppinen, *Carbon* **41**, 2711 (2003).
- [30] U. E. Steiner and T. Ulrich, *Chem. Rev.* **89**, 51 (1989).