

Research Article

Ferromagnetic Property and Synthesis of Onion-Like Fullerenes by Chemical Vapor Deposition Using Fe and Co Catalysts Supported on NaCl

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Metal-encapsulating onion-like fullerenes (M@OLFs) were synthesized by CVD at relatively low temperature (420°C) using Fe and Co nanoparticles impregnated into NaCl as catalyst. The morphology and structure of the products were characterized by field emission scanning electron microscopy, high-resolution transmission electron microscopy, X-ray diffraction, and Raman spectroscopy. The results show that Fe@OLFs and Co@OLFs with stacked graphitic fragments were prepared using Fe/NaCl or Co/NaCl as catalysts; after Co@OLFs were immersed in concentrated HCl for 48 hours, Co nanoparticles encapsulated by carbon shells were not removed, meaning that carbon shells can protect the encapsulated Co cores against environmental degradation. The coercivity value (750.23 Oe) of Co@OLFs showed an obvious magnetic property.

1. Introduction

Since the report by Ugarte in 1992 [1], onion-like fullerenes (OLFs) have been expected to have good prospects in some aspects of energy materials, high-performance/high temperature wear-resistance materials, superconductive materials, and biomaterials [2]. Metal-encapsulating OLFs (M@OLFs) have potential application in many fields such as magnetic data storage, xerography, and magnetic resonance imaging [3]. At present, M@OLFs have been prepared by various techniques, such as electron irradiation [4], arc discharge [5], plasma [6], explosive decomposition of organometal [7], and chemical vapor deposition (CVD) [8, 9]. Among these methods, CVD appears promising because of its relatively low cost and potentially high yield. The catalyst, which can be categorized into floating catalyst and supported catalyst, plays essential role in CVD. Compared with the floating precursors, the supported catalyst plays the role of dispersing active components and adjusting catalyst properties via the chemical or physical interaction of support with metal

nanoparticles. Various kinds of catalyst supports such as Al₂O₃, MgO, CaCO₃, and zeolite were used to synthesize nanocarbon materials [10–13]. However, it is difficult to separate these supports from the final products. On the other hand, water-soluble materials as catalyst supports can be easily separated from the product. Soluble silicate, carbonate, and chloride were employed as catalyst supports to synthesize carbon nanofibers or carbon nanotubes (CNTs) [14–16]. However, little attention was paid to the synthesis of M@OLFs using water-soluble materials as catalyst supports. Liu et al. [17] employed cobalt supported on NaCl prepared by mechanical milling as catalyst to synthesize carbon-encapsulated cobalt nanoparticles, but the method to fabricate catalyst was somewhat complicated.

In the present study, M@OLFs were synthesized by CVD at relatively low temperature (420°C) using Fe and Co nanoparticles impregnated into NaCl support as catalysts, and the magnetic property of Co@OLFs was also studied. This work is of interest for the low cost production of OLFs.

2. Experimental

2.1. Synthesis of Fe/NaCl and Co/NaCl Catalysts. Fe/NaCl and Co/NaCl with about 2 wt% Fe or Co were prepared by means of impregnation. First, 1.76 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ or 1.49 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in an appropriate amount of distilled water. Then 14.85 g of NaCl was added into $\text{Fe}(\text{NO}_3)_3$ or $\text{Co}(\text{NO}_3)_2$ solution. To get homogeneous mixture, the mixture was stirred for 1 h and then dried at 120°C . The obtained catalysts were ground into fine particles.

2.2. Synthesis of $M@\text{OLFs}$. The catalytic decomposition of C_2H_2 was carried out at 420°C in a horizontal furnace, using Fe/NaCl and Co/NaCl as catalysts separately. An 18 mm-long quartz boat with about 2.50 g of catalyst was placed at the isothermal zone in a horizontal quartz tube reactor. Initially, the tube was heated up to 420°C in $100 \text{ ml} \cdot \text{min}^{-1}$ of steady Ar flow. The catalysts were reduced at 420°C in a hydrogen atmosphere for 1 h. Then synthesis reactions were carried out at 420°C by introducing a mixture of C_2H_2 -Ar (C_2H_2 : $30 \text{ ml} \cdot \text{min}^{-1}$, Ar: $300 \text{ ml} \cdot \text{min}^{-1}$) into the reactor. After 1 h, the reactor was cooled to room temperature in Ar atmosphere ($80 \text{ ml} \cdot \text{min}^{-1}$) and the black powders were collected.

2.3. Purification of $M@\text{OLFs}$. To separate NaCl, the products were dissolved in an appropriate amount of distilled water and filtered, which are denoted as H_2O -washed samples. In addition, to remove the residual metal catalyst, the as-synthesized samples were immersed in concentrated HCl solution at room temperature for 48 h, and then washed and filtrated with distilled water, which are denoted as HCl-washed OLFs.

2.4. Characterization of $M@\text{OLFs}$. The morphology and structure of the samples were characterized using field emission scanning electron microscope (FESEM, JSM-6700F, operated at 10 kV), high resolution transmission electron microscope (HRTEM, JEM-2010, working at an accelerating voltage of 200 kV), X-ray powder diffractometer (XRD, D/Max-3C, Cu- $K\alpha$ radiation, $\lambda = 1.54018 \text{ \AA}$), and thermogravimetric analyzer (TGA, Netzsch TG 209 F3, between room temperature and 900°C in air atmosphere at heating rate of $10^\circ\text{C}/\text{min}$). The magnetic property measurement was conducted with a vibrating sample magnetometer (VSM, Lake Shore 7307).

3. Results and Discussion

FESEM was used to investigate the morphologies of the products (Figure 1). It can be obviously observed that there were large quantities of nanoparticles in the products without accompanying CNTs or nanofibers (Figure 1(a)). To analyze the elemental composition for the products, the EDS spectra were shown in the insert. From the insert in Figure 1(a), C, Fe, and O signals were observed. And from the insert in Figure 1(b), C, Co, and O signals were clearly

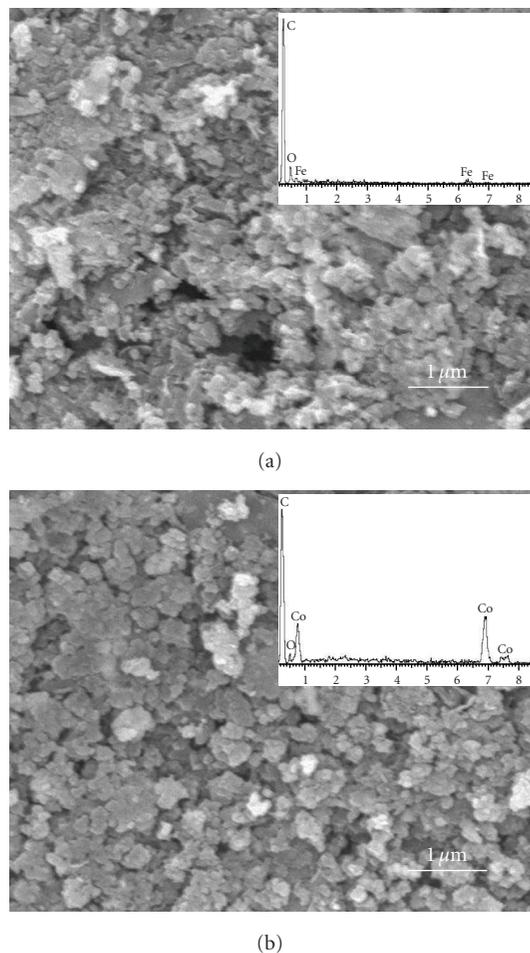


FIGURE 1: FESEM images of H_2O -washed products prepared on different catalysts. (a) Fe/NaCl, (b) Co/NaCl.

observed. No Na and Cl signals were exhibited, indicating the complete removal of NaCl.

The products were further characterized by HRTEM to study the particle size and structure. Figure 2(a) shows the TEM image of H_2O -washed OLFs synthesized using Fe/NaCl as catalyst. Most metal nanoparticles were wrapped by carbon layers, and the sizes were in the range of 10–50 nm. The diversity in the shapes of the carbon nanocages encapsulating metallic particle reflects the shapes of the encapsulated metallic particles. Figure 2(b) shows the TEM image of H_2O -washed OLFs synthesized using Co/NaCl as catalyst. A mass of metal-encapsulating carbon nanoparticles can be seen ranging in diameter from 10 to 60 nm besides little hollow carbon indicated by an arrow. Figures 2(c) and 2(d) show the TEM images of HCl-washed OLFs synthesized using Fe/NaCl and Co/NaCl as catalysts, respectively. The metal nanoparticles encapsulated by carbon shells were not removed after immersing in concentrated HCl for 48 h. It means that carbon shells can protect the encapsulated metal cores against environmental degradation. The HRTEM images of HCl-washed OLFs synthesized using Fe/NaCl and Co/NaCl as catalysts (Figures 2(e) and 2(f)) indicate that the

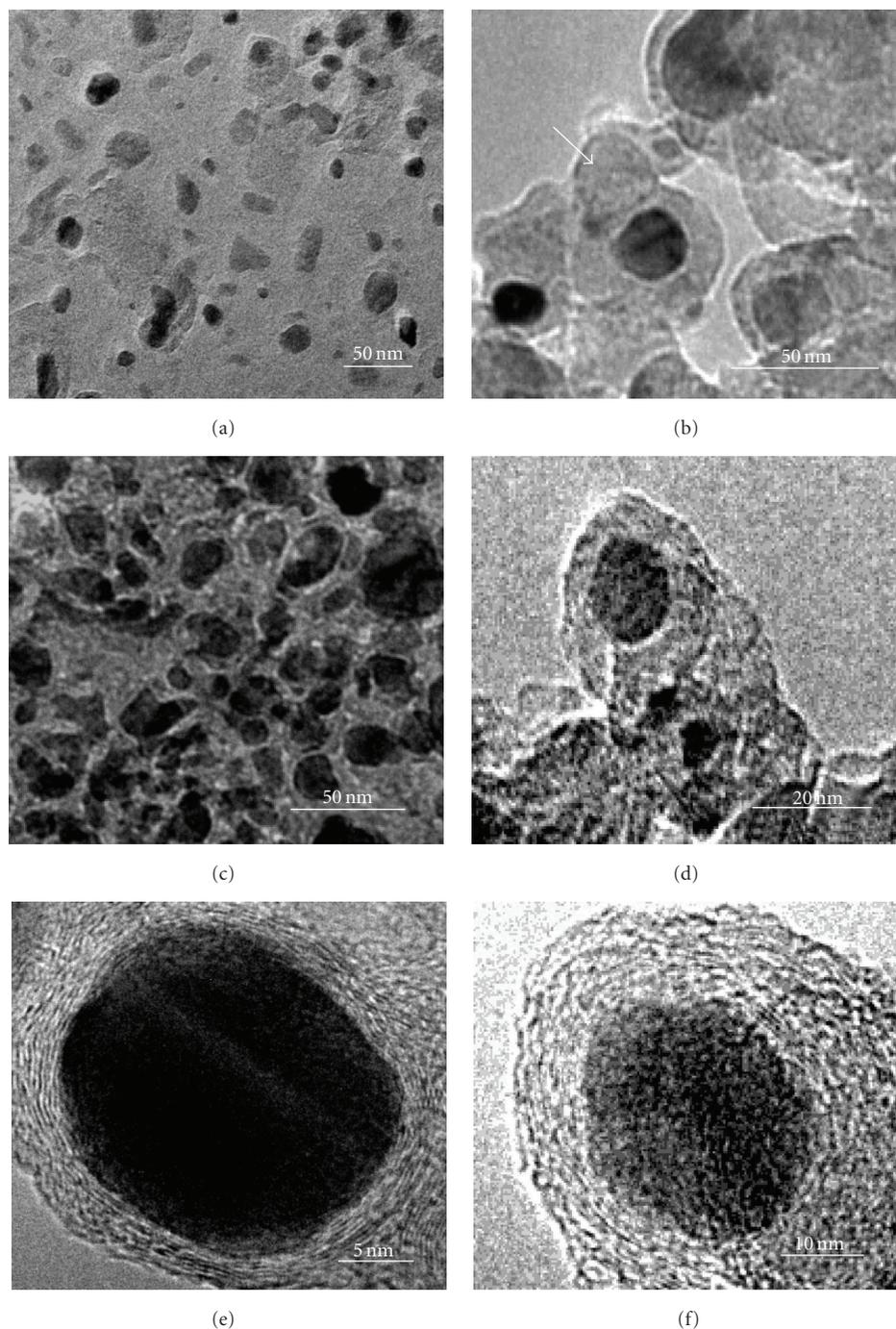


FIGURE 2: TEM images of H_2O -washed OLFs synthesized using Fe/NaCl (a) and Co/NaCl (b) as catalysts, hollow OLF as indicated by an arrow; TEM images of HCl-washed OLFs synthesized using Fe/NaCl (c) and Co/NaCl (d) as catalysts; HRTEM images of HCl-washed OLFs synthesized using Fe/NaCl (e) and Co/NaCl (f) as catalysts.

metallic cores were encapsulated by graphitic sheets. This implied that both Fe/NaCl and Co/NaCl can be used as catalysts to synthesize M@OLFs by CVD using acetylene as carbon resource at 420°C , and carbon shells can protect the encapsulated metallic cores.

Based on our experimental results and previous investigations, a vapor solid (VS) growth model of M@OLFs

at low temperature was suggested [18]. Firstly, C_2H_2 was absorbed onto metal nanoparticle surface and decomposed into carbon atoms; secondly, assembled carbon atom clusters began to diffuse in the crystal lattice of metal particles until carbon species got supersaturated; thirdly, carbon species precipitated and nucleated on catalyst nanoparticle surface, resulting in the formation of small graphitic fragments with

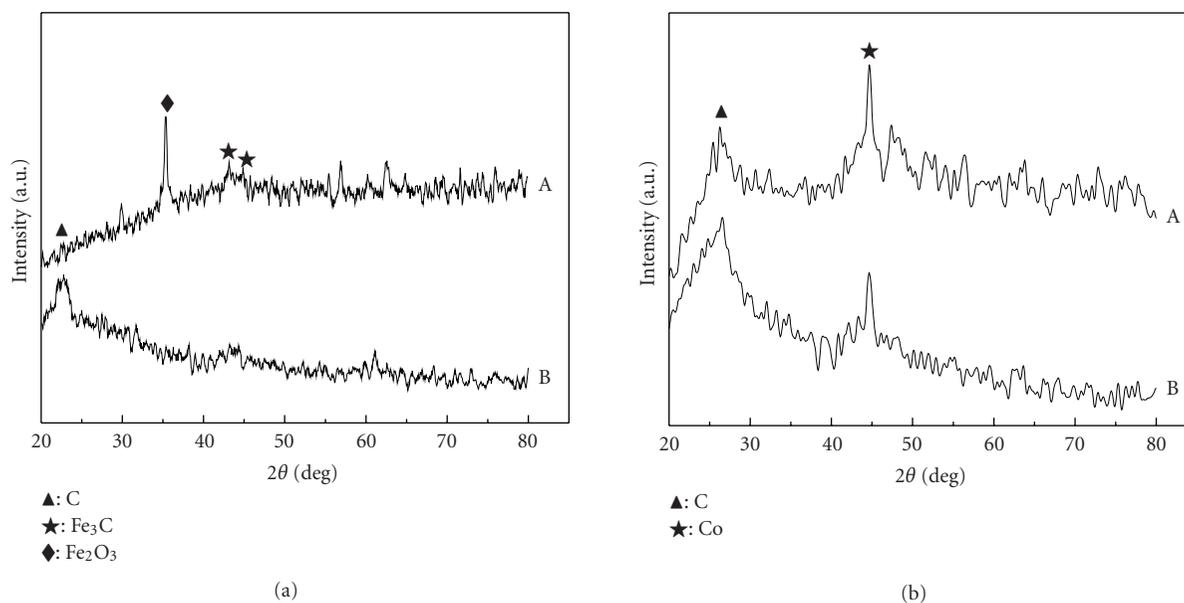


FIGURE 3: (a) XRD patterns of H₂O-washed OLFs (A) and HCl-washed OLFs (B) synthesized using Fe/NaCl as catalyst; (b) XRD patterns of H₂O-washed OLFs (A) and HCl-washed OLFs (B) synthesized using Co/NaCl as catalyst.

a lot of defects. The small graphitic fragments combined with each other by their dangling bonds in order to reach a more stable state, and at the same time, the defects on the surface of the graphitic fragments might act as nucleation sites for the deposition of decomposed carbon species followed by the nucleation of pentagonal or hexagonal rings. Thus OLFs grew in isotropic way continuously until no carbon source was supplied. Because the reaction temperature was too low to supply enough energy to induce the rearrangement of carbon atoms in the graphitic fragments, the formed OLFs had a structure of stacked graphitic fragments.

The products were further characterized by XRD (Figure 3). Figure 3(a) shows the XRD patterns of Fe@OLFs synthesized using Fe/NaCl. The peak attributed to the diffraction of carbon at $2\theta = 22.6^\circ$ indicates that OLFs had a structure of stacked graphitic fragments, which was between amorphous carbon and concentric graphitic layers. The peaks at $2\theta = 43.75^\circ$ and 44.95° can be ascribed to the diffraction of Fe₃C, indicating that the metallic cores inside the OLFs were Fe₃C. And the peak attributed to the diffraction of Fe₂O₃ at $2\theta = 35.4^\circ$ was also observed. After immersing the products in concentrated HCl for 48 h, the peak attributed to the diffraction of Fe₂O₃ disappeared. It means that some catalyst nanoparticles were not encapsulated completely and converted to Fe₂O₃ when exposed to air. Figure 3(b) shows the XRD patterns of H₂O-washed OLFs (A) and HCl-washed OLFs (B) synthesized using Co/NaCl as catalyst. A broad diffraction peak at about 26.3° was assigned to the (002) planes of hexagonal graphite structure. The peak at $2\theta = 44.9^\circ$ was identified to the (111) planes of Co with a face-centered cubic (fcc) structure, indicating that the metallic cores inside the OLFs were Co. After immersing the products in concentrated HCl for 48 h, the

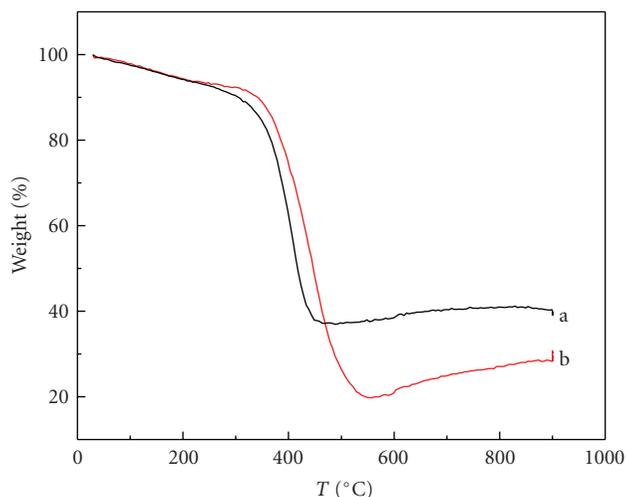


FIGURE 4: TG curves of H₂O-washed Co@OLFs (a) and HCl-washed Co@OLFs (b).

peaks attributed to the diffraction of Co became weaker, indicating the removal of bare Co nanoparticles.

Co@OLFs synthesized using Co/NaCl as catalysts were further investigated by TG. The content of Co in H₂O-washed and HCl-washed OLFs was calculated as 25.6 wt% and 14.2 wt%, respectively, in accordance with the XRD measurement.

The magnetic property of the HCl-washed Co@OLFs at room temperature is shown by the magnetization hysteresis loop (Figure 5). For magnetic nanoparticles, the magnetic properties, especially the saturation magnetization M_s and

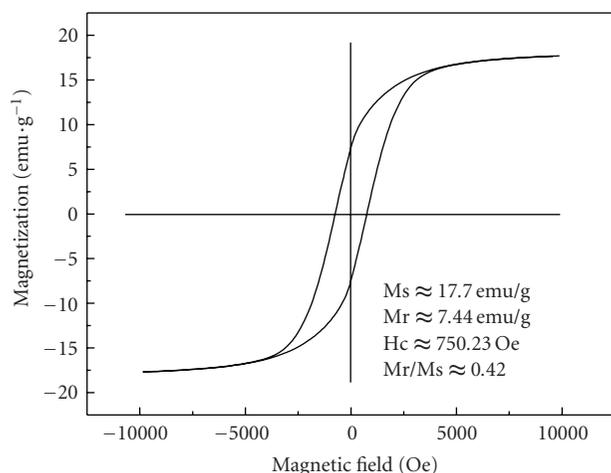


FIGURE 5: Hysteresis loops of HCl-washed Co@OLFs.

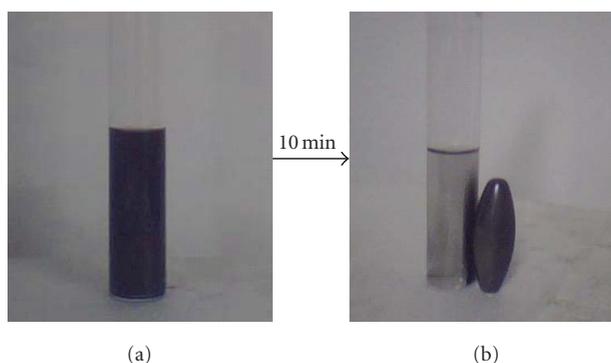


FIGURE 6: Magnetically separable HCl-washed Co@OLFs in alcohol. Before (a) and after (b) a magnet was placed on the outer wall of tube for 10 min.

coercive force H_c , are dependent upon chemical composition and particle size [19]. The curve is symmetric around $H = 0$, with a saturation magnetization (M_s) of 17.70 emu/g and a coercivity (H_c) of 750.23 Oe. Here, the M_s of Co@OLFs is much lower than that of bulk Co ($M_s = 162.5$ emu/g) [19]. The decrease of the saturation magnetization may be attributed to the inclusive phases of carbon (e.g., carbon's diamagnetic contribution), and the surface coating effects [19], in view of the fact that Co nanoparticles were entirely encapsulated by carbon. These effects are expected to become more prominent for smaller particles owing to their larger surface-to-volume ratio. Moreover, the data for the ratio of remanence to saturation magnetization ($M_r/M_s = 0.42$) indicates the good ferromagnetism of Co@OLFs at room temperature.

The magnetic property of the Co@OLFs can also be tested qualitatively, as shown in Figure 6. The Co@OLFs were dispersed homogeneously in ethanol solution in a colorimetric tube by ultrasonic vibration (Figure 6(a)). After a magnet was placed on the outer wall of colorimetric tube for 10 min, the black products were aggregated on the inner wall of tube (Figure 6(b)), suggesting the ferromagnetic property

of Co@OLFs, which may be of potential application in electronic devices, high-density magnetic memories, sensors, and electrochemical energy storage.

4. Conclusions

Fe/NaCl or Co/NaCl were used as catalysts to fabricate Fe@OLFs with diameters of 10–50 nm or Co@OLFs with diameters of 10–60 nm by CVD using acetylene as carbon resource at 420°C. NaCl was easily separable from the product just by a washing process. The metallic cores inside the OLFs were Fe_3C when Fe/NaCl was used as catalyst and Co nanoparticles when Co/NaCl was used as catalyst. After immersing the as-synthesized products in concentrated HCl for 48 h, bare metal nanoparticles were removed while the metal nanoparticles encapsulated by carbon shells were unaffected. It means that carbon shells can protect the encapsulated metallic cores against environmental degradation. The coercivity value (750.23 Oe) of Co@OLFs showed an obvious magnetic property.

Acknowledgments

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References

- [1] D. Ugarte, "Curling and closure of graphitic networks under electron-beam irradiation," *Nature*, vol. 359, no. 6397, pp. 707–709, 1992.
- [2] B.-S. Xu, "Prospects and research progress in nano onion-like fullerenes," *Xinxing Tan Cailiao/ New Carbon Materials*, vol. 23, no. 4, pp. 289–301, 2008.
- [3] S. Seraphin, D. Zhou, and J. Jiao, "Filling the carbon nanocages," *Journal of Applied Physics*, vol. 80, no. 4, pp. 2097–2104, 1996.
- [4] B. S. Xu and S.-I. Tanaka, "Formation of giant onion-like fullerenes under Al nanoparticles by electron irradiation," *Acta Materialia*, vol. 46, no. 15, pp. 5249–5257, 1998.
- [5] B. Xu, J. Guo, X. Wang, X. Liu, and H. Ichinose, "Synthesis of carbon nanocapsules containing Fe, Ni or Co by arc discharge in aqueous solution," *Carbon*, vol. 44, no. 13, pp. 2631–2634, 2006.
- [6] A.-B. Du, X.-G. Liu, D.-J. Fu, P.-D. Han, and B.-S. Xu, "Onion-like fullerenes synthesis from coal," *Fuel*, vol. 86, no. 1-2, pp. 294–298, 2007.
- [7] Y. Lu, Z. Zhu, and Z. Liu, "Carbon-encapsulated Fe nanoparticles from detonation-induced pyrolysis of ferrocene," *Carbon*, vol. 43, no. 2, pp. 369–374, 2005.
- [8] Y. Yang, X. Liu, and B. Xu, "Fe-encapsulating carbon nano onionlike fullerenes from heavy oil residue," *Journal of Materials Research*, vol. 23, no. 5, pp. 1393–1397, 2008.

- [9] B. Xu, T. Li, P. Han, X. Liu, and I. Hideki, "Several features of the iron-included onion-like fullerenes," *Materials Letters*, vol. 60, no. 16, pp. 2042–2045, 2006.
- [10] G. Gulino, R. Vieira, J. Amadou et al., "C₂H₆ as an active carbon source for a large scale synthesis of carbon nanotubes by chemical vapour deposition," *Applied Catalysis A*, vol. 279, no. 1-2, pp. 89–97, 2005.
- [11] H. Kathyayini, N. Nagaraju, A. Fonseca, and J. B. Nagy, "Catalytic activity of Fe, Co and Fe/Co supported on Ca and Mg oxides, hydroxides and carbonates in the synthesis of carbon nanotubes," *Journal of Molecular Catalysis A*, vol. 223, no. 1-2, pp. 129–136, 2004.
- [12] T. C. Schmitt, A. S. Biris, D. W. Miller et al., "Analysis of effluent gases during the CCVD growth of multi-wall carbon nanotubes from acetylene," *Carbon*, vol. 44, no. 10, pp. 2032–2038, 2006.
- [13] A. K. Sinha, D. W. Hwang, and L.-P. Hwang, "A novel approach to bulk synthesis of carbon nanotubes filled with metal by a catalytic chemical vapor deposition method," *Chemical Physics Letters*, vol. 332, no. 5-6, pp. 455–460, 2000.
- [14] E. S. Steigerwalt and C. M. Lukehart, "Preparation of graphitic carbon nanofibers with the use of water-soluble supports," *Journal of Nanoscience and Nanotechnology*, vol. 2, no. 1, pp. 25–28, 2002.
- [15] J. Geng, I. A. Kinloch, C. Singh et al., "Production of carbon nanofibers in high yields using a sodium chloride support," *Journal of Physical Chemistry B*, vol. 109, no. 35, pp. 16665–16670, 2005.
- [16] A. Eftekhari, P. Jafarkhani, and F. Moztafzadeh, "High-yield synthesis of carbon nanotubes using a water-soluble catalyst support in catalytic chemical vapor deposition," *Carbon*, vol. 44, no. 7, pp. 1343–1345, 2006.
- [17] B. H. Liu, J. Ding, Z. Y. Zhong, Z. L. Dong, T. White, and J. Y. Lin, "Large-scale preparation of carbon-encapsulated cobalt nanoparticles by the catalytic method," *Chemical Physics Letters*, vol. 358, no. 1-2, pp. 96–102, 2002.
- [18] X. Liu, C. Wang, Y. Yang, X. Guo, H. Wen, and B. Xu, "Synthesis of nano onion-like fullerenes by using Al₂O₃ as catalyst by chemical vapor deposition," *Chinese Science Bulletin*, vol. 54, no. 1, pp. 137–141, 2009.
- [19] E. Flahaut, F. Agnoli, J. Sloan, C. O'Connor, and M. L. H. Green, "CCVD Synthesis and characterization of cobalt-encapsulated nanoparticles," *Chemistry of Materials*, vol. 14, no. 6, pp. 2553–2558, 2002.



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