Synthesis of Carbon Nanocapsules and Nanotubes Using Fe-Doped Fullerene Nanowhiskers

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Abstract

We synthesized iron-(Fe-)doped C60 nanowhiskers (NWs) by applying the liquid-liquid interfacial precipitation method that employs a C60-saturated toluene solution and a solution of 2-propanol containing ferric nitrate nonahydrate (Fe(NO3)3·9H2O). Fe particles of 3–7 nm in diameter were precipitated in the NWs. By heating at 1173 K, the NWs were transformed into hollow and Fe3C-encapsulated carbon nanocapsules and carbon nanotubes.

1. Introduction

Fullerene nanocages, such as carbon nanocapsules (CNCs) and carbon nanotubes (CNTs), can be used to encapsulate functional nanomaterials, leading to potential applications in catalysis and drug delivery [1–13]. Encapsulation of functional nanomaterials has been performed by simultaneous evaporation of metals and diamond by arc discharge [4, 5, 8–10]. Chemical vapor deposition, electron irradiation, and thermal decomposition have also been applied to produce CNCs and CNTs [1, 3, 12, 13]. An efficient synthesis method for hollow CNCs using single-crystal fullerene nanowhiskers (NWs) was found by Asaka et al. [14–18]. Fullerene NWs can be synthesized by a simple method, that is, the liquid-liquid interfacial precipitation (LLIP) method [19–23]. In addition, in the LLIP method, fullerene NWs can be doped with metallic particles using C60 derivatives and additives such as metal nitrate nonahydrates in solution [24–26]. Such metallic particles act as catalysts in the syntheses of CNCs and CNTs. In this study, we demonstrate the synthesis of iron-(Fe-)doped C60 NWs using the LLIP method and their application to produce CNCs and CNTs.

2. Method

C60 powders were dissolved in toluene to prepare a C60-saturated solution with a solubility of 2.8 g/L. In addition, ferric nitrate nonahydrate (Fe(NO3)3·9H2O) was dissolved in 2-propanol to give a concentration of 0.1 M. Next, the C60 toluene solution was transferred to a glass vial, and the solution of 2-propanol containing Fe(NO3)3·9H2O was added to form a liquid-liquid interface. The vial was maintained at 278 K for one week, and the mixed solution was then filtered to extract precipitates. The precipitates were dried and heated under high vacuum at 1173 K for 1 h. The as-precipitated and heat-treated specimens were dispersed on microgrids and observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

3. Results

Figure 1 shows an SEM image of as-precipitated C60 NWs. Figures 2(a) and 2(b) show a bright-field image and a high-resolution image of an as-precipitated C60 NW, respectively. The diameters of the as-precipitated NWs ranged from 0.5 to 7.5 μm, as shown in Figure 3. Lattice fringes with a spacing of
0.52 nm were observed in the NWs, as shown in Figure 2(b). Figure 2(c) shows a selected-area electron diffraction pattern of the NW depicted in Figure 2(a). The high-resolution images and diffraction patterns reveal that the NWs have a tetragonal lattice with lattice constants of \( a = 0.99 \text{ nm} \) and \( c = 2.1 \text{ nm} \). The lattice fringes with a spacing of 0.52 nm depicted in Figure 2(b) correspond to the (004) plane. The long axis of the NW is parallel to the (110) direction. Figure 2(d) shows a high-resolution image of an NW surface, where Fe particles with diameters in the range 3–7 nm were observed. Thus, the LLIP method using a solution of Fe(NO₃)₃·9H₂O in 2-propanol resulted in the precipitation of Fe particles in the C₆₀ NWs. Owing to the precipitation of Fe particles, the crystal growth of the NW was inhibited; as a result, the surfaces of the NWs had a rough topography. Therefore, the Fe-doped NWs presented here differ from pure C₆₀ NWs, which are surrounded by plane surfaces [19–23].

Figure 4 shows a bright-field image of the heat-treated specimen. Hollow and encapsulating CNCs and CNTs were observed in the specimen, as were chains of CNCs.

Figure 5 shows a bright-field image and a selected-area diffraction pattern of a CNC encapsulating a particle. The 220, 230, and 050 spots of Fe₃C (cementite) are observed; the particle was identified to be Fe₃C.

Figures 6(a) and 6(b) show high-resolution images of an Fe₃C-encapsulated CNC. The diameters of the CNCs and the Fe₃C particles ranged 25–175 nm and 5–100 nm, respectively, as shown in Figure 7. The Fe₃C particle does not completely fill the empty space at the core of the CNC. Figure 6(c) shows a high-resolution image of graphene layers in an Fe₃C-encapsulated CNC. The spacing of the graphene layers around the surface is 0.34 nm, whereas the spacing decreases to 0.31 nm around the graphene/Fe₃C interface.

Figure 8(a) shows a high-resolution image of a CNT encapsulating Fe₃C particles (Figures 8(b) and 8(c)), similar to the case of the CNCs. The Fe₃C particles encapsulated by the CNTs showed rod shapes, as shown in Figure 8(a). This is different from the spherical Fe₃C particles observed in CNCs. The diameters of the CNTs and the Fe₃C particles ranged 10–70 nm and 5–50 nm, respectively, as shown in Figure 9.

The formation of CNCs and CNTs was not confirmed when the heating temperature was changed to 873 K, 973 K, 1073 K, and 1123 K. When the heating time was shortened to 0.5 h at 1173 K, the size distribution of CNCs and CNTs was similar.

4. Discussion

4.1. Formation of Fe₃C Particles. In the as-precipitated NWs, Fe particles 3–7 nm in diameter were observed. On the other hand, after heating at 1173 K, the diameter of the Fe₃C particles in the CNCs and CNTs was found to increase to 5–100 nm. This implies that the Fe particles had aggregated, and carbon was solved in them during heating. According to Ding et al., pure Fe particles that are several nanometers in
size melt at 1000 K [27]. The melting Fe particles are mobile and fuse together. Fe-carbides with a carbon concentration of more than 50 at% are formed when the melting Fe particles contact with carbon [28]. During cooling, the solubility limit of carbon in the particles decreases and is followed by the precipitation of graphene layers on the particle surfaces. In this experiment, the particles observed in CNCs and CNTs were Fe₃C. When the carbon concentration of the particles at coagulation exceeds 25 at%, Fe₃C particles can be formed in the CNCs and CNTs. Fe₃C is a quasistable phase and does not transform to other phases at room temperature.

4.2. Formation of CNCs and CNTs. According to Saito, CNCs are produced by the precipitation of carbon from catalysts, that is, metallic or carbide particles [10]. Thus, a CNC encapsulating a particle is initially formed. Jiao et al. showed from in situ TEM that in, CNCs encapsulating Fe and Fe carbide particles, the particle is removed from the CNC at 1173–1373 K [29]. As Ding et al. discussed, the driving force of the particle removal relates to the temperature and concentration gradients in the particle, which are caused by the precipitation of graphene layers [27]. By removal of the particle, the CNC is broken and a hole is formed. This hole is closed by subsequent growth of the layers [30], and hence, a hollow CNC is formed. Subsequently, the next precipitation starts. Thus, the precipitation of graphene layers occurs intermittently. By repeating the processes of precipitation and the removal of the encapsulated particle, hollow CNCs proliferate and one CNC encapsulating the particle remains. The CNCs aggregate, resulting in the formation of a chain, as shown in Figure 4. In the case of the formation of CNTs, the encapsulated Fe₃C particles showed rod shapes. Tubular graphene layers, that is, CNTs, precipitate around such rod-shaped particles. Once a CNT is formed, the encapsulated rod-shaped particle shifts along the symmetric axis of the CNT. Carbon precipitates continuously on the same region of the particle, along one direction, leading to growth of
the CNT [10]. According to Jourdain et al., a particle is encapsulated in a CNT owing to the strong interfacial tension between the inner wall of the CNT and the surface of the melting particle [31]. It is suggested that the interfacial tension of the rod-shaped particles encapsulated by CNTs is higher than that of the spherical particles in the CNCs. In this study, both CNCs and CNTs were formed in the same specimen. Whether CNCs or CNTs are formed depends on the shape of each encapsulated particle.

4.3. Decrease in the Spacing of Graphene Layers of CNCs. The spacing of the graphene layers decreases to 0.31 nm around

Figure 6: (a) High-resolution images of Fe3C-encapsulated carbon nanocapsule and (b) enlargement of the (200) and (020) lattice fringes of the Fe3C particle in (a). (c) Graphene layers of the carbon nanocapsule in (a).

Figure 7: Histograms of (a) outer diameter of carbon nanocapsules and (b) Fe3C particles encapsulated by carbon nanocapsules.

Figure 8: (a) High-resolution image of Fe3C-encapsulated carbon nanotube. (b) Enlargement of the nanotube tip in (a). (c) Selected-area electron diffraction pattern of the Fe3C particle encapsulated by the nanotube in (a).
Fe-doped C<sub>60</sub> NWs were synthesized by the LLIP method using a C<sub>60</sub>-saturated toluene solution and 2-propanol containing Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O. The additive of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O resulted in the precipitation of Fe particles in the C<sub>60</sub> NWs. Heat treatment of the NWs at 1173 K produced both hollow CNCs and CNTs. Fe<sub>3</sub>C-encapsulated CNCs and CNTs were also produced. The present method can be applied to synthesize NWs including other metals, for example, cobalt and nickel. Thus, the present method is suitable for the production of CNCs and CNTs encapsulating various foreign nanomaterials.

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### References


