Research Article

Synthesis of Nickel-Encapsulated Carbon Nanocapsules and Cup-Stacked-Type Carbon Nanotubes via Nickel-Doped Fullerene Nanowhiskers

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Nickel- (Ni) doped C₆₀ nanowhiskers (NWs) were synthesized by a liquid-liquid interfacial precipitation method using a C₆₀-saturated toluene solution and isopropanol with Ni nitrate hexahydrate Ni(NO₃)₂·6H₂O. By varying the heating temperature of Ni-doped C₆₀ NWs, two types of one-dimensional carbon nanostructures were produced. By heating the NWs at 973 and 1173 K, carbon nanocapsules (CNCs) that encapsulated Ni nanoparticles were produced. The Ni-encapsulated CNCs joined one dimensionally to form chain structures. Upon heating the NWs to 1373 K, cup-stacked-type carbon nanotubes were synthesized.

1. Introduction

Crystals of fullerene molecules have been synthesized by precipitation methods [1–13]. Such fullerene crystals show various morphologies, that is, plates, films, and rods, and the morphology can be controlled by varying the precipitation conditions. By using a liquid-liquid interfacial precipitation (LLIP) method, Miyazawa et al. have produced fullerene nanowhiskers (NWs) and nanotubes with high length-to-diameter aspect ratios [14–17]. By heating fullerene NWs, carbon nanocapsules (CNCs) are produced [18–22]. Using the LLIP method, Miyazawa et al. also found that fullerene NWs incorporate metal nanoparticles using C₆₀ derivatives or metal nitrate hydrates in solutions [23–26]. It is expected that the alloying of metals and CNCs can be performed using metal-doped fullerene NWs. In this study, metal-CNC structures were produced by the heating nickel- (Ni) doped C₆₀ NWs which were synthesized by the LLIP method.

2. Method

C₆₀ powders were dissolved in toluene to prepare a C₆₀-saturated solution with a solubility of 2.8 g/L. Ni nitrate

hexahydrate [Ni(NO₃)₂·6H₂O] was dissolved in 2-propanol with concentrations of 0.01 M and 0.68 M (hereafter labeled as specimens A and B, resp.). The C₆₀ toluene solution was poured into a glass vial, and the 2-propanol was then added to form a liquid-liquid interface. After the vial was maintained at 278 K for one week, the solution was filtered to extract precipitates. The precipitates were dried and heated in high vacuum at 973, 1173, and 1323 K for 1 h. Next, the specimens were dispersed on microgrids and observed by transmission electron microscopy (TEM). Thermogravimetric analyses (TGA) and differential thermal analyses (DTA) of the specimens were performed in a nitrogen flow.

3. Results and Discussion

Figure 1(a) shows a bright-field image of an as-precipitated Ni-doped C₆₀ NW in specimen A. The diameter of this NW is 740 nm. The surfaces of the Ni-doped NWs were porous, as shown in Figure 1(b). Figure 2(a) shows a bright-field image of an as-precipitated Ni-doped C₆₀ NW in specimen B. The diameter of this NW is 240 nm. The NWs showed undulating surfaces. Ni particles with a face-centered

FIGURE 1: (a) Bright-field image of Ni-doped C_{60} nanowhiskers synthesized using isopropyl alcohol with concentration of 0.01 M $Ni(NO_3)_2 \cdot 6H_2O$. (b) Enlarged image of (a).

cubic structure were observed in the NWs, as shown in Figure 2(b).

The surfaces of the Ni-doped NWs in both specimens A and B were rough. The roughness increases with the $Ni(NO_3)_2 \cdot 6H_2O$ concentration. Pure C_{60} NWs are surrounded by planar surfaces [14–17]. Thus, we attribute the rough surfaces of the as-precipitated Ni-doped NWs to the addition of $Ni(NO_3)_2 \cdot 6H_2O$ in 2-propanol. In particular, Ni particles were observed in the dents of Ni-doped NWs, implying that the crystal growth of the NWs was inhibited by the Ni particles. This is similar to the crystal growth of C_{60} -derivative NWs [23–25].

Figure 3 shows TGA and DTA curves of the Ni-doped NWs in specimen A and C_{60} bulk crystals. For C_{60} bulk crystals, the DTA curve starts to decrease around 773 K. On the other hand, no change is observed in the TGA curve around this temperature. This shows that the mass of the specimen remained unchanged, whereas the structure changed. The transformation from a crystalline to an amorphous configuration of C_{60} molecules starts at this temperature [27]. Around 1173 K, the TGA curve decreases, and a downward peak is observed in the DTA curve, which shows that an endothermic reaction occurred. Furthermore, it has been reported that sublimation of C_{60} molecules takes place at this temperature [27]. On the other hand,

FIGURE 2: (a) Bright-field images of Ni-doped C_{60} nanowhiskers synthesized using isopropyl alcohol with concentration of 0.68 M $Ni(NO_3)_2 \cdot 6H_2O$. The arrows indicate Ni particles in dents. (b) High-resolution image of Ni particles in the NW in (a).

FIGURE 3: (a) Thermogravimetric analysis curves and (b) differential thermal analysis curves of Ni-doped nanowhiskers (specimen A, solid lines) and pure C_{60} bulk (broken lines) in nitrogen flow.

(a)

(b)

(c)

FIGURE 4: (a) Bright-field images of Ni-encapsulated carbon nanocapsules prepared by heating Ni-doped C_{60} nanowhiskers (specimen A) at 973 K. (b) High-resolution image of Ni-encapsulated carbon nanocapsule. (c) High-resolution image of chain of Ni-encapsulated carbon nanocapsules.

for the Ni-doped NWs, an upward peak was observed in the DTA curve around 773 K, which corresponds to an exothermic reaction. No change is observed in the TGA curve around this temperature. TEM observations showed that grain coarsening of Ni particles started near this temperature. This TEM result suggests that the upward peak around 773 K was caused by the grain coarsening of Ni particles.

Around 1123 K, the TGA curve decreases and the DTA curve shows a downward peak. This implies that the sublimation of C_{60} molecules occurred, as similarly observed in C_{60} bulk crystals. Note that the sublimation temperature of C_{60} molecules in the Ni-doped NWs is approximately 50 K lower than that in the C_{60} bulk crystals. From this result, we

(a)

(b)

FIGURE 5: (a) Bright-field images of Ni-encapsulated carbon nanocapsules prepared by heating Ni-doped C_{60} nanowhiskers (specimen B) at 1173 K. The nanocapsules form chain structures. (b) High-resolution image of the chain of Ni-encapsulated carbon nanocapsules.

infer that Ni particles act as catalysts for the weakening of intermolecular C_{60} molecular bonds.

On the basis of the results of TGA and DTA, we heated the specimens to temperatures higher than 973 K and observed them by TEM. Figures 4(a) and 4(b) show bright-field and high-resolution images of specimen A after heating at 973 K, respectively. Ni-encapsulated CNCs are formed by this heat treatment. The diameter of the CNCs ranged from 12 to 51 nm. The diameter of the encapsulated Ni particles ranged from 8 to 33 nm. A portion of the CNCs aligned one dimensionally to form chain structures, as shown in Figure 4(c). Such chain structures have also been produced by arc discharge [28, 29]. As shown in Figure 4(b), Ni particles were attached on the tips of the chains, indicating that the chain structures were produced by the cycles of the precipitation of graphene shells around Ni particles and the movement of the Ni particles. Note that in Figure 4(b), the Ni particle protrudes from the center of the hollow region of the CNC. This state corresponds to the movement of the Ni particle from the precipitated graphene shell.

Figures 5(a) and 5(b) show bright-field and high-resolution images of specimen B after heating it at 1173 K. Ni-encapsulated CNCs and their chain structures were formed. The formation rate of CNC chains in this specimen was higher than that in specimen A owing to a higher concentration of Ni particles.

By heating Ni-doped C_{60} NWs in specimen B to 1323 K, cup-stacked-type carbon nanotubes (CNTs) were produced, as shown in Figure 6. Ni particles were attached to the tip

FIGURE 6: (a) Cup-stacked-type carbon nanotube synthesized by heating Ni-doped C_{60} nanowhiskers (specimen B) at 1323 K. (b) High-resolution image of the cup-stacked-type carbon nanotube depicted in (a).

of CNTs, and the graphene layers were aligned parallel to the surfaces of Ni particles. Thus, CNTs were produced by the continuous precipitation of graphene cones and the continuous movement of Ni particles. However, for CNC formation, the movement of Ni particles and the precipitation of graphene shells are intermittent.

In this experiment, cup-stacked-type CNTs were produced at the highest temperature (1373 K). As observed in Figures 4(b) and 5(a), the Ni particles in the specimens heated at temperatures lower than 1173 K formed spherical shapes, whereas Ni particles in the specimens heated to 1373 K formed clear crystal habits. At higher temperatures, the metal particles show more stable shapes surrounded by crystal planes with lower surface energies. Cup-stacked-type CNTs are formed by one-directional continuous precipitation of graphitic cones from metal particles having such clear crystal habits [30–39]. The solubility limit of carbon atoms in metals also increases at higher temperatures, and the precipitation speed increases. We infer that both the formation of crystal habits and the increase in precipitation speed promote the production of cup-stacked-type CNTs.

4. Conclusion

Ni-doped C_{60} NWs synthesized by the liquid-liquid interfacial precipitation method allow us to produce Ni-encapsulated CNCs and cup-stacked-type CNTs. In particular, the CNCs form chain structures. The two types of

one-dimensional carbon nanostructures were produced using Ni-doped C_{60} NWs by varying heating temperature.

Other transition metals such as iron and cobalt can be doped into fullerene NWs using similar synthetic methods, and CNCs encapsulating nanoparticles of various metal elements can be produced using NWs.

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