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Synthesis of Co-Doped Fullerene Nanowhiskers and Cobalt-Encapsulated Carbon Nanocapsules

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1. Introduction

Carbon nanocapsules (CNCs) showing high chemical and thermal stabilities have been synthesized by arc discharge and chemical vapor deposition [1, 2]. In this paper, we demonstrate the synthesis of Co-doped fullerene nanowhiskers (FNWs) and Co-encapsulated CNCs. Their structures were investigated by transmission electron microscopy.

2. Method

We synthesized Co-doped FNWs by the liquid-liquid interfacial precipitation method [3]. C_{60} powders were dissolved in toluene to obtain a C_{60}-saturated solution [4]. Co nitrate hexahydrate ($Co(NO_3)_3 \cdot 6H_2O$) was dissolved in isopropyl alcohol (IPA). The C_{60} toluene solution was poured into a glass vial, and then the IPA dissolved cobalt nitrate hexahydrate was gently added. After the vial was kept still at 278 K, the solution was filtered. The precipitates were dried in vacuum and heated in high vacuum at 973, 1073, 1173, and 1273 K.

3. Results and Discussion

Figure 1(a) shows a secondary-electron image of scanning electron microscopy (SEM) of a FNW in an as-precipitated specimen. The diameter of the FNW in Fig. 1(a) is 625 nm. The diameter of the FNWs ranged from 190 to 941 nm with an average of 440 nm. Figure 1(b) shows a high-resolution image of a FNW. The lattice of the FNWs was tetragonal. The lattice spacings seen in the high-resolution image were 0.83 nm and 0.49 nm, corresponding to (002) and (220). No Co cluster was observed.

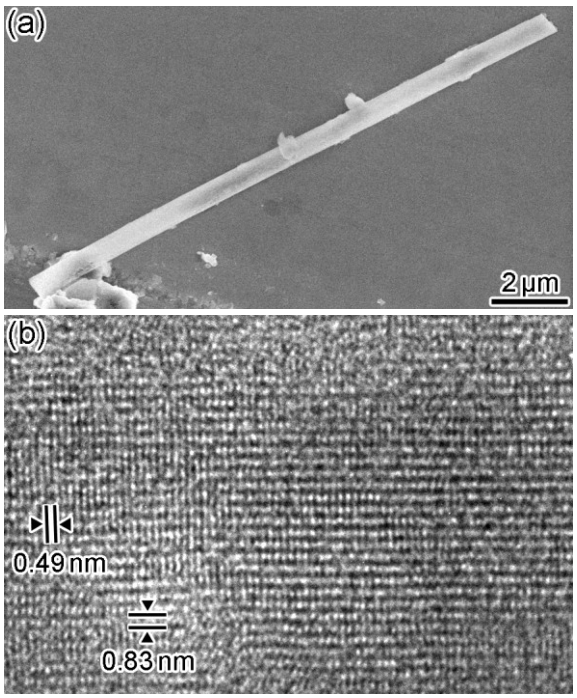

Fig. 1 (a) Secondary-electron image and (b) high-resolution image.

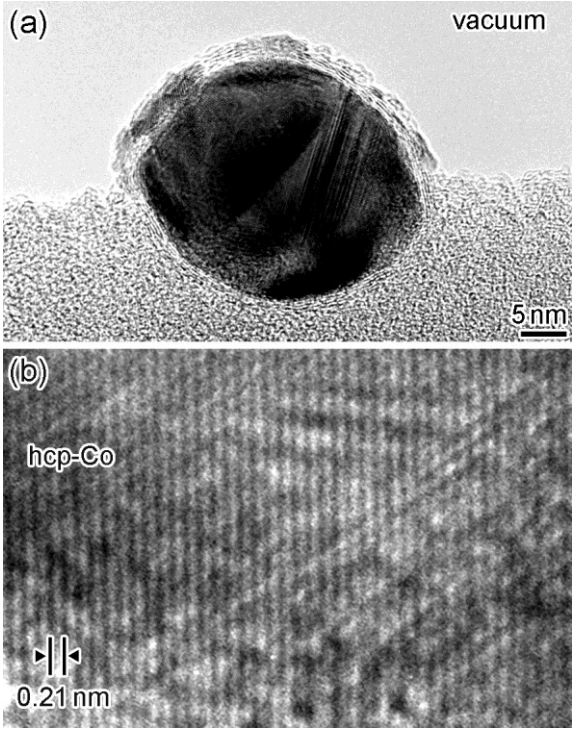

Fig 2 (a) Bright-field image, (b) selected-area electron diffraction pattern and (c) high-resolution image of CNC in specimen heated at 973 K.

Figure 2 shows a bright-field image and a high-resolution image of a CNC in the specimen heated at 973 K. The outer layer of the CNC shown in Fig. 2(a) was three-dimensionally closed, and a cluster was encapsulated. The cluster was a Co crystal with a hexagonal-closed-packed (hcp) structure. Its lattice constant was estimated to be a = 0.25 nm and c = 0.40 nm. The lattice spacing seen in Fig. 2(b) was 0.21 nm, corresponding to (100) of hcp-Co. The diameters of the CNC and the Co cluster shown in Fig. 2(a) are 36 nm and 28 nm, respectively. The diameter of the CNCs and Co clusters ranged from 12 to70 nm with an average of 35 nm and 9–41 nm with an average of 21 nm, respectively. All CNCs in this specimen encapsulated Co-clusters. The

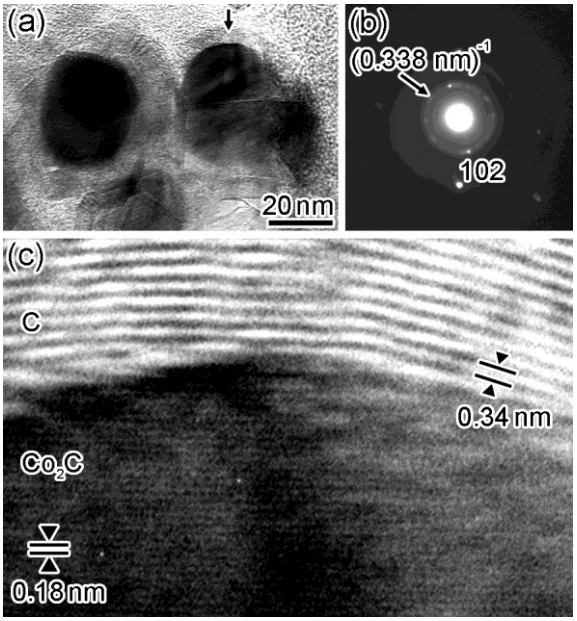

Fig 3 (a) Bright-field image, (b) selected-area electron diffraction pattern and (c) high-resolution image of CNC in specimen heated at 1273 K.

specimens heated at 1073 and 1173 K also contained hcp-Co-encapsulated CNCs.

Figure 3 shows a bright-field image and a high-resolution image of CNCs in the specimen heated at 1273 K. As is the specimen heated at 973 K, the outer layers of the CNCs were closed, and clusters were encapsulated. The SAEDP indicated that the encapsulated clusters were Co_2C crystals. The lattice spacings of the Co_2C cluster and graphite layers seen in the high-resolution image were 0.18 nm and 0.34 nm, respectively, corresponding to (102) of Co_2C and (002) of graphite, respectively. The diameters of the CNC and the Co_2C cluster in Fig. 3(a) (the black arrow) are 44 nm and 34 nm, respectively. The diameter of the CNCs ranged from 44 to 66 nm with an average of 54 nm. The diameter of the Co_2C clusters ranged from 29 to 34 nm with an average of 32 nm, respectively. Figure 4 shows the diameters of the CNCs and the encapsulating clusters. It is found that the size of the CNCs and the Co clusters became larger as heating temperature increases.

In the pristine FNWs, no Co cluster was observed. However, the specimen after heating contained Co clusters. Thus, the pristine FNWs contain Co atoms. It is known that an atom can intrude in interstices of C_{60} crystals [5]. A hard sphere with a radius of 0.21 nm can enter in the tetrahedral interstices. The radius of Co atoms is 0.125 nm. It is inferred that Co atoms are contained in the interstices of the pristine FNWs.

The synthesis process encapsulated CNCs is explained as follows. First, Co atoms in the FNWs aggregate and form Co-C clusters by heating. Second, clusters of Co-C solid solution are formed. When specimen's temperature exceeds their eutectic temperature, the solid solution transformed to Co_2C. Although eutectic temperature of bulk Co and Co_2C is 1593 K, it is known that phase transition temperature of clusters decreases [6]. In the present case, eutectic temperature decreases to lower than 1273 K. Third, as the solid solubility limit decreases during cool down process, graphite layers precipitate on the cluster surfaces, i.e., CNCs are formed.

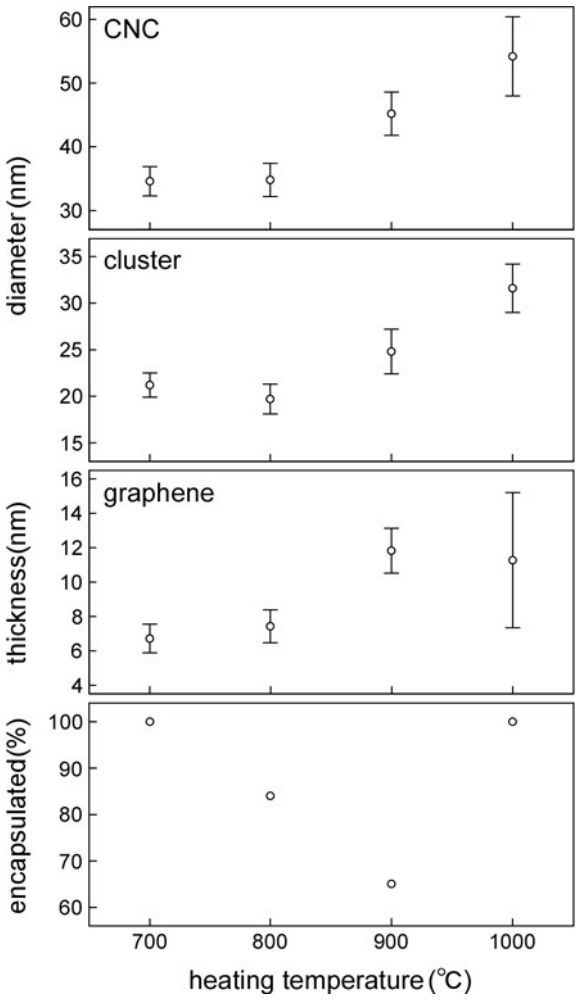

Fig. 4 The diameter of CNCs and cluster, the thickness of graphen layers, and the ratio of encapsulation of Co and Co_2C clusters against heating temperature.

4. Conclusions

It was found that (1) Co-doped FNWs can be synthesized by the liquid-liquid interfacial precipitation method, and (2) Co- and Co_2C-encapsulated CNCs can be synthesized by heating of Co-doped FNWs in a vacuum.

Acknowledgements

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