One-Step Synthesis of Metal-Encapsulated Carbon Nanotubes by Pulsed Arc Discharge in Water

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Metal-encapsulated carbon nanotubes (M@CNTs) have attracted considerable attention because of their numerous potential applications. However, there have been only a few reports on the encapsulation of CNTs with high boiling point metals. We investigated the encapsulation of CNTs with such metals by using a pulsed arc discharge method in water. When the melting points of the metals were higher than the sublimation temperature of carbon, the CNTs were encapsulated. In contrast, M@CNTs could not be synthesized with lower melting point metals. The reason for this difference is attributed to the eutectic temperature of the alloys that are generated during precipitation of the carbon atoms. [DOI: 10.1380/ejssnt.2012.414]

Keywords: Carbon nanotubes; Pulsed arc discharge in water; Transmission electron microscopy (TEM); Catalysis; X-ray scattering, diffraction, and reflection

I. INTRODUCTION

Carbon nanotubes (CNTs) are distinctive in their mechanical, chemical, and physical properties [1]. In particular, metal-encapsulated CNTs (M@CNTs) are expected to have a wide range of applications, such as in magnetic recording media [2], field emission sources [3], nanoswitches [4], nanothermometers [5], and drug delivery systems [6, 7].

There are two types of methods for synthesizing M@CNTs: one requires post-processing after CNT synthesis, such as the use of capillary action [8, 9], a template method [10], or a condensed-phase electrolysis method [11]. The second approach is post-process free technique based on catalytic chemical vapor deposition (CCVD) [12] or arc discharge [13].

To synthesize nano-carbon materials including CNTs, we have performed an arc discharge method in water [14, 15], in foam [16–19], or in sucrose solution [20, 21]. The formation of M@CNTs by using metal, which is incorporated into CNTs, as the cathode was also reported [14]. A vacuum apparatus is unnecessary for the arc discharge in water method, requiring only simple equipment [22, 23].

In addition, the arc discharge in water method consumes only about 1 kVA, and thus, the electric power savings are considerable when compared to the electricity consumption for the vacuum arc discharge method, which is about 7 kVA [24–28].

We report here our investigation of the metal incorporation into CNTs using a pulsed arc discharge in water because the use of pulsed discharge is expected to increase yield of M@CNTs. The tendency of different metals to undergo encapsulation and its mechanism are discussed.

II. EXPERIMENTAL

A schematic diagram of the experimental setup is shown in Fig. 1. Distilled water (300 mL, Otsuka Pharmaceutical Co. Ltd.) was placed into a glass beaker, and electrodes (φ = 5 mm) that were attached to clips were sunk in the water. A graphite rod was used as the anode, while rods of eight different metals including tungsten (W), tantalum (Ta), molybdenum (Mo), niobium (Nb), vanadium (V), zirconium (Zr), titanium (Ti), and cobalt (Co) were used as the cathode. The voltage between the electrodes and the upper current limit of the power supply (KENWOOD; PD36-20A) were set at 30 V and 20 A, respec-

FIG. 1. Schematic diagram of the experimental setup for the arc discharge in water.

FIG. 2. High-resolution (HR) TEM images of the metal-encapsulated CNTs when the following materials were used as the cathode: (a) W, (b) Ta, (c) Nb, (d) Mo, and (e) Zr. On the other hand, the metal-encapsulated nanocapsules were observed when (f) V, (g) Ti, or (h) Co was used as the cathode.

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Fig. 3 EDX patterns of the as-grown samples when the following materials were used as the cathode: (a) W, (b) Ta, (c) Nb, (d) Mo, (e) Zr, (f) V, (g) Ti, and (h) Co.

Fig. 4 XRD patterns of the as-grown samples when the following materials were used as the cathode: (a) W, (b) Ta, (c) Nb, (d) Mo, (e) Zr, (f) V, (g) Ti, and (h) Co. The red lines in each figure indicate the peaks of standard materials.

III. RESULTS AND DISCUSSIONS

The high resolution TEM images of the as-grown samples are shown in Fig. 2. The figure shows that when W, Ta, Mo, Zr, and Nb were used as the cathode, metal-encapsulated CNTs were synthesized. These metals possess boiling points higher than 3370°C, which is the sublimation temperature of carbon. The encapsulated metal particles were approximately 5 nm in diameter, as observed by TEM. On the other hand, when V or Ti, which are metals with boiling points near the sublimation temperature of carbon, were used as the cathode, metal-carbide-encapsulated nanocapsules were synthesized. The diameter of the carbides was 10 to 100 nm. Furthermore, in the case of Co, a pure Co particle was encapsulated into the nanocapsule.

Figure 3 shows the EDX spectra of the samples. The Cu peaks in these spectra are due to the background copper TEM grid. Because no oxygen peaks can be observed in the spectra, it can be concluded that the metals used to encapsulate the nanocarbon materials were not oxidized.

The results of the XRD analyses are shown in Fig. 4. Both carbide and carboxide peaks appeared when W was used as the cathode. However, when Ta, Nb, Mo, Zr, or Ti was used as the cathode, only a carbide peak was detected. In the case when Co was used as the cathode, the spectrum indicated the presence of only pure Co. These results suggest that when W, Ta, Mo, Nb, V, Zr, or Ti was used as the cathode, the metals encapsulating the CNTs existed as carbides (W2C, TaC, Mo2C, NbC, V6C7, ZrC, or TiC, respectively). Only Co remained as a pure metal.

The reason that the synthesis depends on the metal boiling point is as follows. Metals that have boiling points higher than the sublimation temperature of carbon can be in the liquid phase when carbon is in the gaseous phase.

http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/) 415
If the metal is in the liquid phase, it is believed that it can more readily capture the carbon. When the CNT is growing, if an encapsulating metal is in the liquid phase when it comes in contact with the carbon, the carbon can be deposited continuously. As a result, metal-encapsulated CNTs can be synthesized. Metals with boiling points lower than the sublimation temperature of carbon, however, will be in the gaseous phase when carbon is in the gaseous phase, and therefore, it is believed that they are not able to capture the carbon. A metal encapsulated nanocapsule is therefore synthesized.

Saito et al. reported that W and Mo can be encapsulated into carbon nanocapsules using the vacuum arc discharge method [29]. It is assumed that the chilling effect of water in the arc discharge in water method influences the formation of metal-encapsulated CNTs.

IV. CONCLUSIONS

We investigated that the tendency of different metals to encapsulate CNTs using a pulsed arc discharge in water method. When the boiling point of the metal used as the cathode was higher than the temperature for carbon sublimation (3370°C), a metal-carbide-encapsulated CNT was synthesized. However, when V or Ti, which are metals with boiling points near the temperature for carbon sublimation, were used as the cathode, metal-carbide-encapsulated nanocapsules were synthesized. Furthermore, in the case when Co was used as the cathode, the pure Co was encapsulated in a nanocapsule. These results imply that the boiling point of metals is important to synthesize M@CNTs in one-step.

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