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The purity and thermal stability in air of metal-encapsulating carbon nanocapsules (MECNCs)

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Abstract: Rare earth elements (Y, La, Ce, Nd, Gd and Dy) encapsulated by carbon nanocapsules (CNCs) were synthesized and their purity and air oxidation stability were estimated. The purity was estimated as the rare earth carbide content. Gd- and Dy-encapsulating CNCs had higher than 30wt% and others 15 to 20wt%. Encapsulated rare earth carbide was oxidized by heating in air at 400°C or higher. This suggested oxidation damage to the graphene capsules of CNCs.

Keywords: Metal encapsulating carbon nanocapsules, rare earth, carbide, purity, thermal stability

INTRODUCTION

Metal-encapsulating carbon nanocapsules (MECNCs) are several tens of nanometers in diameter and consist of a graphene sheet structure encapsulating a metallic carbide. MECNCs have a surface covered by a graphene sheet, so they have quite high chemical stability (1-10). In the capsule synthesized by using a direct current arc-discharge method with a lanthanide-loading graphite anode, lanthanide is usually encapsulated as a carbide. The formation of MECNCs was suggested as the segregation of excess carbon composition from the metal carbide droplets while they are cooling (4). Metallofullerenes have been studied as contrast agents in X-ray or magnetic resonance imaging (11, 12). MECNCs also contain metallic elements in the graphite capsule, but the size of the capsule and the amount of encapsulated metallic elements are a hundred times larger than metallofullerenes. In addition, the graphene capsules have high chemical stability and the encapsulated metals are stable in air, water and concentrated sulfuric acid, and these features will provide higher imaging and tracing efficiencies as contrast agents or tracers as the authors have reported the low cytotoxicity of MECNCs (13). In the application of MECNCs, their purity and the chemical stability of the graphene capsules must be estimated.

EXPERIMENTAL PROCEDURES

MECNCs were synthesized by a direct current arc-discharge between a pure graphite cathode and a metal-loaded graphite anode in a helium atmosphere. A pure graphite rod (purity 99.9%, Wakomu Denso Co., Japan) and a graphite rod loaded with Y_2O_3, La_2O_3, CeO_2, Nd_2O_3, Gd_2O_3 and Dy_2O_3 powder (99.9%, Wako Pure Chemical Industries, Japan) as the source of rare earth were used as the cathode and anode, respectively. The arc-discharge was carried out in helium gas at 500 Torr. A carbonaceous deposit on the cathode was corrected and the synthesis of the MECNCs was confirmed with TEM observation (TEM: Hitachi, HF-2000, Japan), energy-dispersive X-ray spectroscopy analysis (EDXS: NORAN Instruments, VANTAGE, USA) and X-ray diffraction (XRD: Rigaku, Multiflex, Japan). As-grown MECNCs, MECNCs heated at 350 to 450°C in air for 30 minutes and MECNCs heated at 450°C in vacuum (10^{-6} torr) were subjected to X-ray diffraction to estimate the crystalline state of encapsulated rare earth. Some MECNCs were heated at 800°C for 2 hours to burn out the graphene capsule and the rare earth oxide that

remained was weighed. The rare earth carbide contents in as-grown MECNCs were converted from the final oxide weight and the chemical formulae of the rare earth carbides and oxides were assigned.

RESULTS AND DISCUSSION

MECNCs encapsulating Y, La, Ce, Nd, Gd and Dy were successfully synthesized. Below, those MECNCs are abbreviated as Y-CNCs. Figure 1 shows the TEM image of Ce-CNCs. We observed many MECNCs as well as non-encapsulating carbon nanocapsules. The single-crystal CeC_2 compounds were encapsulated in the multi-walled carbon layers. The fact that the CeC_2 interior was single-crystalline was confirmed by electron diffraction (9) and EDXS. The estimated rare earth carbide contents in various MECNCs are presented in Table 1. The weights of the MECNCs were mostly obtained from the rare earth carbide cores. Therefore, the carbide contents were close to the purity of the MECNCs. The purity levels of Gd- and Dy-containing CNCs were more than 30wt% and others were less than 20wt%. Therefore, graphite, amorphous carbon and vacant carbon nanocapsules were contained as impurities.

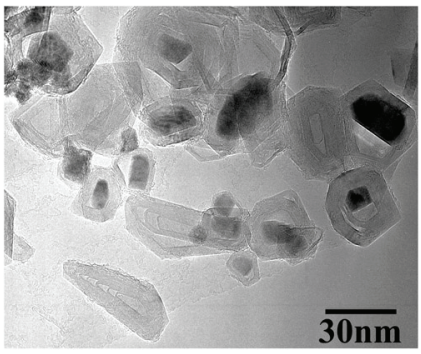


Figure.1 High magnification TEM image of MECNCs (Ce-CNCs)

Table 1. Rare earth carbide content in raw MECNCs.

MECNCs	Chemical formula of encapsulated carbide	Carbide content (wt%)
Y-CNCs	YC_2	16
La-CNCs	LaC_2	19
Ce-CNCs	CeC_2	19
Nd-CNCs	NdC_2	20
Gd-CNCs	GdC_2	35
Dy-CNCs	DyC_2	31

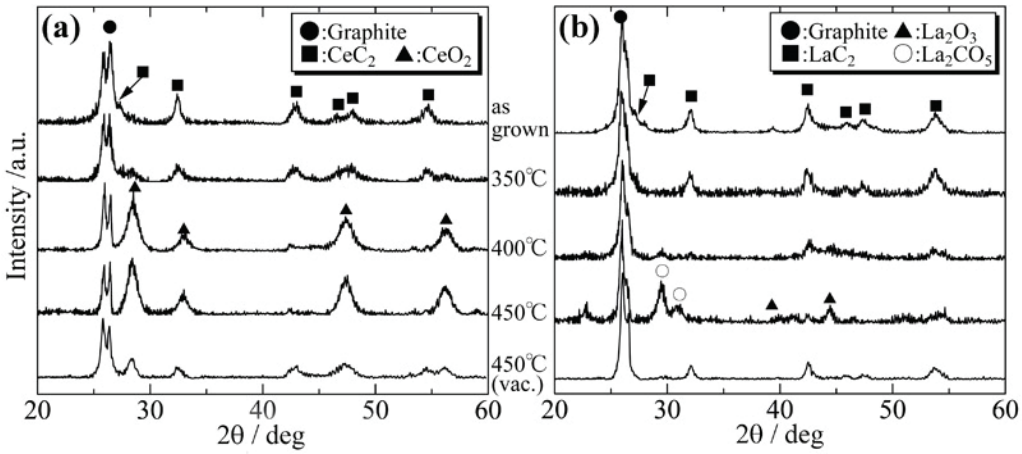


Figure.2 Changes in X-ray diffraction spectra of Ce- and La-CNCs with heat treatment.

Figure 2(a) shows the X-ray diffraction spectra of Ce-encapsulating nanocapsules (Ce-CNCs) as grown and heated at 350 to 450°C. As-grown Ce-CNCs show diffraction peaks derived from the graphite and CeC_2. The spectrum was not changed after heating at 350°C, but CeO_2 appeared after heating at higher than 400°C. Rare earth carbides are instable in air and easily oxidized. In MECNCs, however, the graphene capsule is airtight, therefore the rare earth carbide is isolated from the air. When heated at higher than 400°C in air, the graphene capsule was damaged by oxidation and the encapsulated CeC_2 was oxidized to CeO_2. Similarly, Y-CNCs showed peaks derived from the oxide species (Y_2O_3) after heating at 400°C or higher. Figure 2(b) shows the X-ray diffraction spectra of La-CNCs as grown and heated at 350 to 450°C. As-grown La-CNCs show diffraction peaks derived from the graphite and LaC_2. After heating at 400°C, peaks of LaC_2 became weak and peaks of La_2O_3 and La_2CO_5 appeared at above

450°C. Nd-CNCs showed $Nd_2O_2CO_3$ after 450°C. These results showed that La- and Nd-CNCs were stable at lower than 350°C and that carbonate or oxicarbonate species were formed at 450°C. After heating at 450°C in vacuum, Ce-CNCs showed CeO_2 peaks, however, La-CNCs were not changed. Also, Y-CNCs and Nd-CNCs were not changed after heating at 450°C in vacuum. Then, Ce-CNCs would be less stable for heating.

Figure.3 Changes in X-ray diffraction spectra of Dy- and Gd-CNCs with heat treatment.

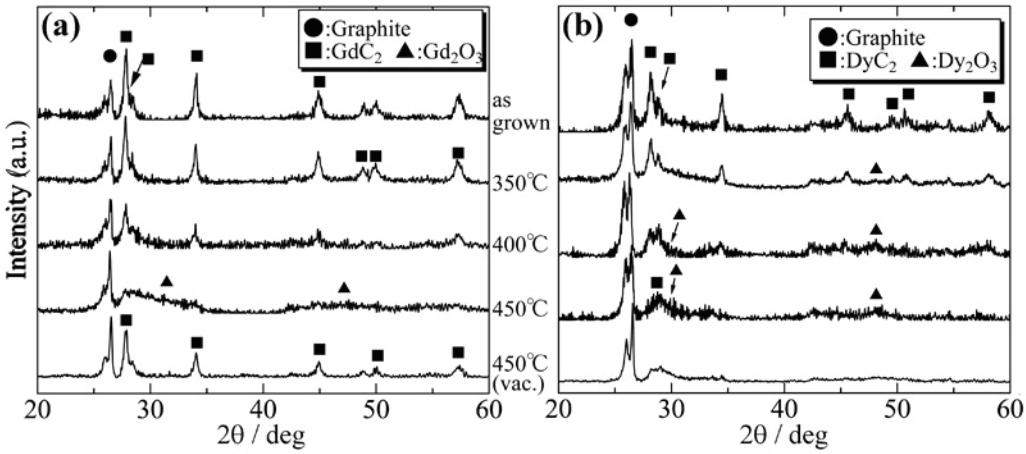


Figure 3(a) shows the X-ray diffraction spectra of Gd-CNCs as grown and heated at 350 to 450°C. The peaks derived from GdC_2 remained after heating at 400°C. At 450°C, peaks assigned to GdC_2 disappeared and unclear peaks assigned to Gd_2O_3 were slightly increased. Gd-CNCs was not changed after heated at 450°C in vacuum. As shown in Figure 3(b), the peaks derived from DyC_2 remained after heating at 400°C, but the peaks were broadened. Dy-CNCs after heated at 450°C in vacuum was similar to that after heated in air. Therefore, Gd-CNCs would have the highest stability for heating in air and vacuum.

Figure 4 shows the TEM images of Gd- and Dy-CNCs after heated at 450 °C. Gd or Dy encapsulating CNCs (point 1 and 3 in Figure 4) were remained and large granules (point 2 and 4) were generated after heating. The compositions of each point analyzed by EDXS were tabulated in Table 2. Point 1 and 3 contain the rare earth (Gd or Dy) and C. Then, the remaining of Gd- and Dy-CNCs after heated at 450°C could be confirmed. Point 2 and 4 which were generated large granules showed high oxygen content. Those granules could be assumed that the most of MECNCs were oxidized and degraded by heating, and then encapsulated rare earth was formed oxide particles. In Y-, La-, Ce- and Nd-CNCs that showed no carbides in XRD spectra after heated at 450°C, the remained MECNCs could not observed by TEM observation. Therefore, the heating stability estimated by XRD was confirmed by TEM observation.

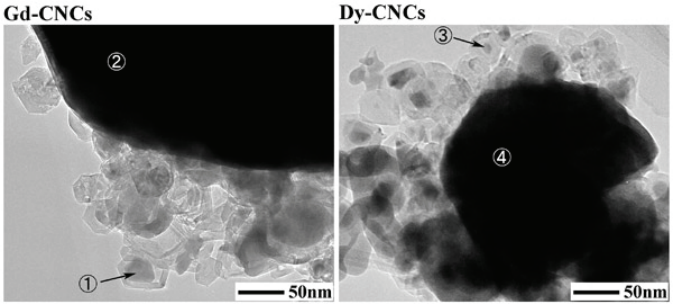


Figure.4 TEM images of Dy- and Gd-CNCs after heat treatment at 450°C.

Table 2. EDXS analysis of Gd- and Dy-CNCs after heated 450°C shown in Figure 4 (at%)

Elements / Analyzed point	Gd	Dy	C	O
1	7.0	----	92.4	0.6
2	10.6	----	66.1	23.3
3	----	76.9	20.9	2.2
4	----	27.5	51.9	20.6

Oxidation treatment at around 500°C was useful for the purification of carbon nanotubes because the impurities, e.g. amorphous carbon or hydrocarbon, were burned out before nanotube oxidation. In this study, the encapsulated

rare earth carbides in MECNCs were oxidized by heating at 400 to 450°C in air. Ajayan et al. suggested that both the strain at the tip and the presence of pentagons might help to initiation of the oxidation at the caps of carbon nanotubes (14). MECNCs have tips which would contain pentagons, thus, heating in air would promote the oxidation at the tips of the graphene capsules of MECNCs and airtightness is lost. Then the encapsulated rare earth carbide is oxidized. The airtightness of the graphene capsule means that the encapsulated elements are isolated from the outside. Oxidation of encapsulated rare earth elements indicates damage to the graphene capsules and loss of their airtightness. Therefore, MECNCs heated at higher than 400°C in air lose their chemical stability and the encapsulated elements become erosive. In other words, MECNCs are stable at lower than 350°C and the erosion of encapsulated elements is negligible. This feature is important for biomedical application as the authors have reported the low cytotoxicity of Ce-CNCs(13). In this study, various rare earth elements were encapsulated in carbon nanocapsules. Gd-CNCs had the highest purity (35wt%) among the synthesized MECNCs and slightly better stability for heating in air up to 450°C. Concerning to the Gd-CNCs, paramagnetic propery and magnetic separation was suggested (15, 16). Thus, Gd-CNCs would be favorable for biomedical and other applications.

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