Applied Surface Science 255 (2009) 9622–9625

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Structural characterization of single-wall carbon nanohorn aggregates hybridized with carbon nanocapsules and their formation mechanism

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ARTICLE INFO

Article history:
Available online 21 April 2009

PACS:
61.48.De
68.37.Lp
81.15.Fg

Keywords:
Carbon nanohorn
Nanocapsule
Hybrid
Laser vaporization

ABSTRACT

Three types of single-wall carbon nanohorn (SWNH) aggregates hybridized with carbon nanocapsules (CNCs) containing Fe_3C, Co, or Ag were produced by laser vaporization of graphite mixed with Fe, Co, or Ag in Ar gas. Characterization by transmission electron microscopy revealed that although the three hybrid structures had different diameter distributions with average diameters of 96, 90, and 85 nm, respectively, their SWNH layers had similar thicknesses (17–18 nm on average). The diameter difference is explained by the sizes (16–24 nm on average) of the encapsulated CNCs, the formation of which depended on the carbon solubility of the three metals and the precipitation of the graphitic layers. In addition, there was a stronger correlation between the diameters of the hybrids and the thicknesses of the SWNH layers for the three types. We suggest that the formation mechanism of the three structures is based on the assembly of SWNHs around a molten metal–carbon particle with certain ranges of lengths and diameters, respectively.

1. Introduction

Single-wall carbon nanohorn (SWNH) aggregates hybridized with carbon nanocapsules (CNCs) filled with a metal or a metal carbide have been formed using a submerged arc method [1] or laser vaporization [2]. The yield with the arc discharge method was less than 1%, while it was up to ~70% with the laser vaporization of metal-containing graphite in the presence of Ar gas. The formation of a hybrid structure using laser vaporization of graphite mixed Al, Si, Fe, Co, Ni, Cu, Ag, La, Gd, or Y has been attempted [2]. A hybrid structure was formed only for the Fe, Co, Ni, Cu, and Ag, which have relatively low carbon solubilities. The cores of the CNCs were carbide (Fe_3C) for the Fe and were metals for the Co, Ni, Cu, and Ag. Among the products from the laser vaporization, only small-diameter (5–100 nm) Fe_3C particles contributed to the formation of the hybrid structures, although large-diameter (up to 140 nm) Fe_3C particles forming CNCs were also found. A growth model of the hybrid structures, based on the formation of tubule-like SWNH structures and their aggregation around a molten carbon–metal particle in Ar gas, was proposed. However, the complicated processes resulting in the formation of the hybrid structures from laser-vaporized carbon and metal confined by Ar atmosphere are still not well understood.

In this study, we synthesized three types of hybrid structures by laser vaporization of graphite mixed with Fe, Co, or Ag (hereafter Fe, Co, and Ag hybrids) and characterized their structures. As shown by previously reported binary phase diagram [3], Fe, Co, and Ag have different carbon solubilities: 25, 4.2, and 0.036 atomic (at.) %, respectively. Analysis of each hybrid structure using transmission electron microscopy (TEM) was performed for more than 200 samples of each type. The diameters of the hybrids and the encapsulated CNCs and the thicknesses of the SWNH layers surrounding the CNCs were measured and compared. By investigating the correlation of the hybrid diameters with the CNC diameters or the SWNH layer thicknesses, the formation mechanism of the hybrid structures was examined.

2. Experimental

The experiment of laser vaporization of metal-containing graphite targets in Ar gas and TEM observation of the products were carried out as done in a previous study [2]. A powder of Fe, Co, or Ag was mixed with a graphite powder. The metal content ranged from 10 to 30 at.%. The mixed powder was pressed into pellets (10-mm diameter, 2-mm thickness). A continuous wave Nd:YAG laser (600-W peak power) was used for the vaporization at room temperature. The laser beam was focused on the pellets through a quartz window installed in a stainless-steel chamber filled with Ar gas at pressures ranging from 0.1 to 0.3 MPa. The size of the laser spot and the power density were adjusted to 2 mm and about

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doi:10.1016/j.apsusc.2009.04.076

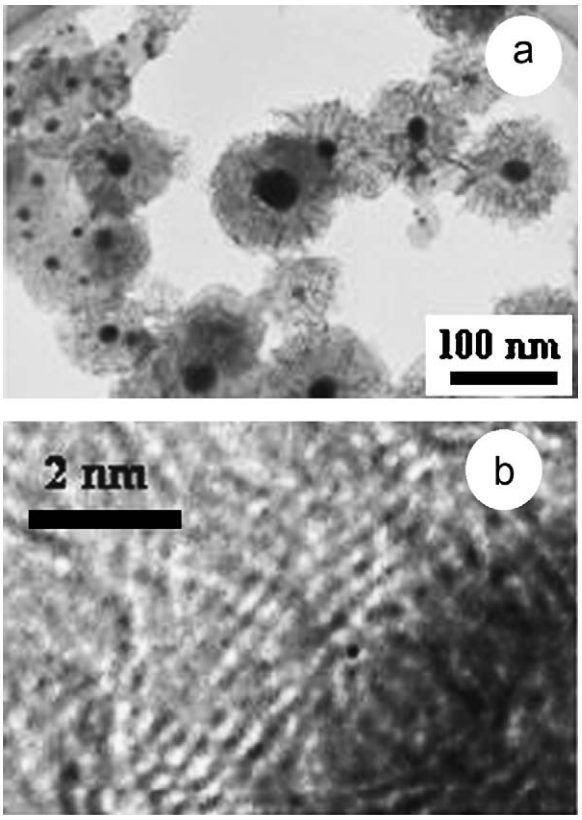

Fig. 1. TEM images of (a) hybridized SWNH aggregates and (b) core region of aggregate obtained by laser vaporization of graphite containing 20 at.% Co at Ar gas pressure of 0.2 MPa.

13 kW/cm^2, respectively, and the laser irradiation time was set to 2 s. The deposits in the chamber were collected and examined with TEMs operating at 100 or 300 kV.

3. Results and discussion

TEM observation indicated that the deposits contained Fe, Co, and Ag hybrids, and other structures such as SWNH aggregates, CNCs, and platelet graphite particles. Their yields strongly depended on the Ar gas pressure and the metal content in the graphite target as previously reported [2]. At a gas pressure of 0.2 MPa and with a metal content of 20 at.%, the maximum yield was ~70% for the three structures. The yield was roughly estimated by comparing their areas in the several TEM images measured for the product.

Fig. 1 shows example TEM images of Co hybrids obtained at 0.2 MPa and 20 at.%. Many Co hybrids with various diameters are seen in Fig. 1(a). The magnified image of the core CNC region (Fig. 1(b)) shows the presence of five graphitic layers surrounding a Co particle (dark area). The interlayer spacing is about 0.34 nm. The number of layers, which differed between samples, ranged from 5 to 15. TEM images of the Fe and Ag hybrids also revealed many structures with various diameters. Different numbers of graphitic layers were observed around the CNCs, and the number depended on the type of metal, similar to the previous findings [2]. The number of graphitic layers ranged from 10 to 25 for the Fe hybrids. It was a maximum of three for the Ag hybrids.

Figs. 2 and 3 show diameter distributions of the hybrids (d_h) and CNCs (d_c) for the three hybrid structures. They were obtained from TEM examination of more than 200 samples for each structure. Since the tubule-like SWNHs of various lengths

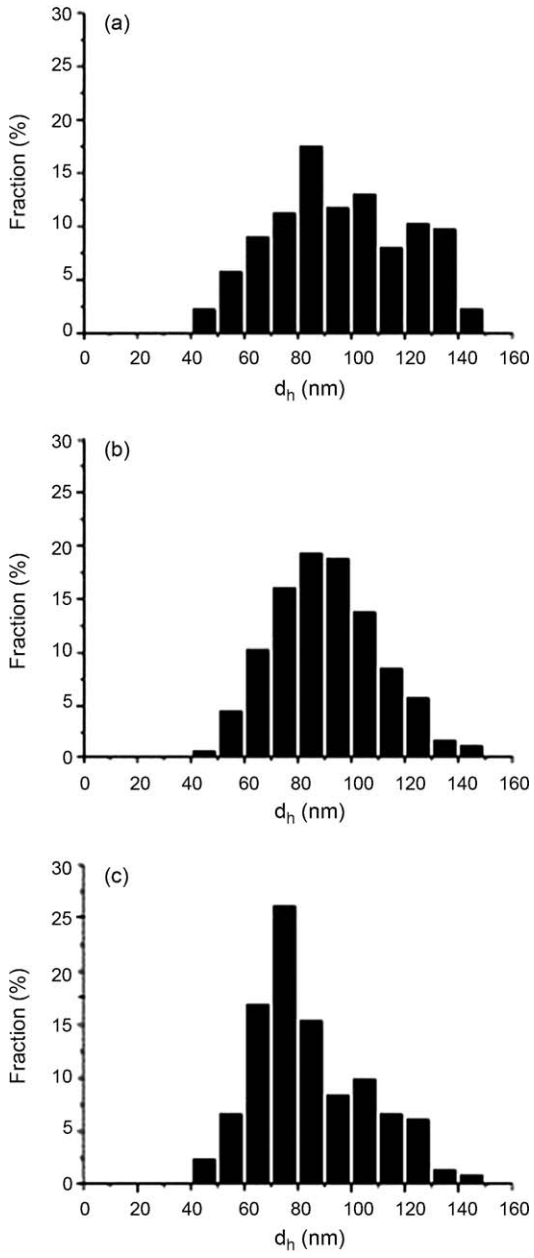

Fig. 2. Distributions of diameters (d_h) of (a) Fe, (b) Co, and (c) Ag hybrids.

were present in each structure, the length of the longest one was measured to obtain the d_h. In addition, since the CNCs did not necessarily have a perfect sphere, the longest part in the CNC was measured for the d_c. As shown in Fig. 2, the d_h values for the three structures range from 40 to 150 nm. The peak position and d_h distribution differ among the structures. The average d_h values are 96, 90, and 85 nm for the Fe, Co, and Ag hybrids, respectively. As shown in Fig. 3, the d_c values range from 5 to 55 nm. The d_c distributions differ among the structures; the average diameters are 24, 19, and 16 nm for the Fe, Co, and Ag hybrids, respectively. Note that large CNCs with diameters up to ~140 nm, which were not surrounded by SWNHs, were also observed, as in the previous study [2]. In addition to the d_h and d_c, the distributions of the thicknesses of the SWNH layers (t_n) were measured for the three hybrids (not shown). The t_n values ranged from 15 to 65 nm. The average t_n values were 18 nm for the Fe and Co hybrids and 17 nm for the Ag hybrid. Unlike for