



Growth of linear Ni-filled carbon nanotubes by local arc discharge in liquid ethanol



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ABSTRACT

The cylindrical geometry of carbon nanotubes (CNTs) allows them to be filled with metal catalysts; the resulting metal-filled CNTs possess different properties depending on the filler metal. Here we report the synthesis of Ni-filled CNTs in which Ni is situated linearly and homogeneously by local arc discharge in liquid ethanol. The structural characteristics of synthesized Ni-filled CNTs were determined by transmission electron microscopy (TEM), and the relationship between pyrolysis conditions and the length and diameter of Ni-filled CNTs was examined. The encapsulated Ni was identified by a TEM-equipped energy-dispersive X-ray spectroscopy and found to have a single-crystal fcc structure by nano-beam diffraction. The features of linear Ni-filled CNT are expected to be applicable to probes for magnetic force microscopy.

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1. Introduction

A carbon nanotube (CNT) is a cylindrical structure made of rolled sheet graphene, formed of six-membered rings of carbon atoms, and its hollow can be filled various materials [1]. Many researches on the synthesis of metal-filled CNTs have developed since Iijima and Ajayan synthesized Pb-filled CNTs using the arc discharge method [2]. The chemically stable hollows of CNTs preserve pure metal nanoparticles or nanorods from reaction or contamination, which makes them applicable in various settings: e.g., Pd-filled CNTs absorb hydrogen [3], Ga-filled CNTs can serve as nanothermometers [4], and CNTs filled with ferromagnetic metals (Fe, Co, Ni) can serve as magnetic storage devices and probes for magnetic force microscopy (MFM) [5,6].

MFM, which uses a kind of scanning probe microscope, determines the magnetization of the nano region, and its performance depends on probe specifics including the magnetic property of the material, the aspect ratio, and the tip curvature radius [7].

Commercially-supplied probes for MFM consist of Si probes coated with a thin film of ferromagnetic metal and are known to have a resolution of approximately 10 nm. However, this structure for the probe results in a large tip curvature radius, which restricts the resolution. A ferromagnetic metal-filled CNT may

be better suited for an MFM probe because it has such a small tip radius, preserves the quality of inclusion, and can vary according to the ferromagnetic material selected. In recent research, Tanaka et al. reported the improvement of MFM probe resolution by synthesizing a Co particle of 20-nm diameter encapsulated by a CNT on a Si probe; it had a resolution of approximately 7.6 nm [8]. The resolution of such probes is still restricted by the fact that the filler ferromagnetic metals are particles; i.e., structurally heterogeneous. For an MFM probe to have much higher resolution would require the ferromagnetic metal filling the CNT to be thin, linear, and homogeneous.

Here we report the synthesis and structure of Ni-filled CNT having features suitable for MFM probe; namely, a diameter of around 10 nm and a length in the range of 20 nm to 150 nm. There are various methods of synthesizing metal-filled CNTs: for example, the arc discharge method [2,4,9], thermal chemical vapor deposition (CVD) method [5,6,10,11], microwave plasma CVD method [3,12], laser vaporization method [13], and so on. However, our method employs local arc discharge in liquid ethanol. This method is based on a technique developed by Nishitani-Gamo et al. [14,15], which is focused on discharge phenomenon around nearby cathode electrodes. This paper is organized follows: first, we describe the experimental procedure with the evaluation method; next we provide surface observations of the sample, and deduce the structure of the synthesized Ni-filled CNT; then we examine the relationship of the CNT diameter and length to pyrolysis conditions; and finally, we discuss the applicability of our Ni-filled CNT as an MFM probe.

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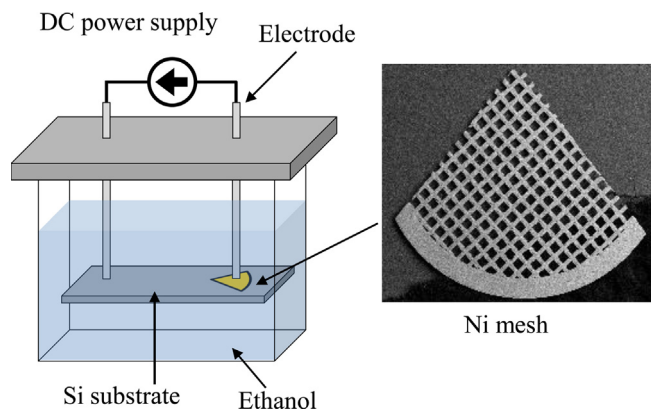


Fig. 1. Experimental apparatus and Ni mesh processed into a fan shape. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Experimental

Local arc discharge in liquid ethanol is performed by applying a direct electrical current to a specimen material on a semiconductor substrate. The experimental equipment was fabricated in our laboratory, and was the same as described in our previous work [16]. The experimental set-up is illustrated in Fig. 1; it uses a direct current power supply, stainless steel electrodes (ISO/TS 15510 X5CrNi18-10), an Si substrate ($10 \times 40 \times 0.525$ mm, $1\text{--}10\ \Omega\text{ cm}$, n-type), an Ni mesh as catalyst metal bulk for growth of CNTs (yellow part in Fig. 1), and a quartz vessel filled with ethanol solution (99.5%) as a carbon precursor. In this study, Ni-filled CNTs are directly synthesized on the surface of the Ni mesh (diameter of 3 mm, thickness of $20\ \mu\text{m}$, 200 grid per an inch); thus, they need no purification after the experiment, and can be observed directly with a transmission electron microscope (TEM). The inserted SEM image shows a Ni mesh which was processed into a fan shape in order to have the electrical current converge at the apex of the Ni mesh; this mesh was set on a Si substrate by cathode electrode. Arc discharge is locally generated at the apex of the Ni mesh by passing an electrical current through the electrode, Si substrate and Ni mesh; hence, the term “local arc discharge”. The current value ranged from 1.0 A to 5.0 A, and the heating period or time during which the current was applied was 60 s. In one experiment, using a current of 4.5 A, heating periods of 1 s and 30 s were investigated in order to observe the influence of the heating period on the surface complexion of the Ni mesh. Heating temperatures were estimated by applying Plank’s law of radiation to spectra that were measured with multichannel optical spectroscopy (EPP-2000-UVN-SR Stellarnet), which was calibrated using a standard light source (Mazda 1753K). In evaluating, we observed the surface of the Ni mesh under a scanning electron microscope (SEM, S-3000N Hitachi) with an energy-dispersive X-ray spectroscopy (EDS, Genesis2000 EDAX) detector and the structure of Ni-filled CNTs under a TEM-equipped (HF-2000S Hitachi, operating 200 kV acceleration voltage) EDS (Sigma KeveX) detector.

3. Results and discussion

The heating temperatures corresponding to current value are shown in Fig. 2. The insert photograph of Fig. 2 shows the appearance of the Ni mesh during the heating experiment. As can be seen in the photograph, the apex of the Ni mesh emitted a bright white spot which is supposed to include the cathode spot of the arc discharge, and it similarly hopped when the current moved from one point of grid to another on the mesh. It is noted that the measured spectra of the cathode spot was not a line spectrum of plasma that

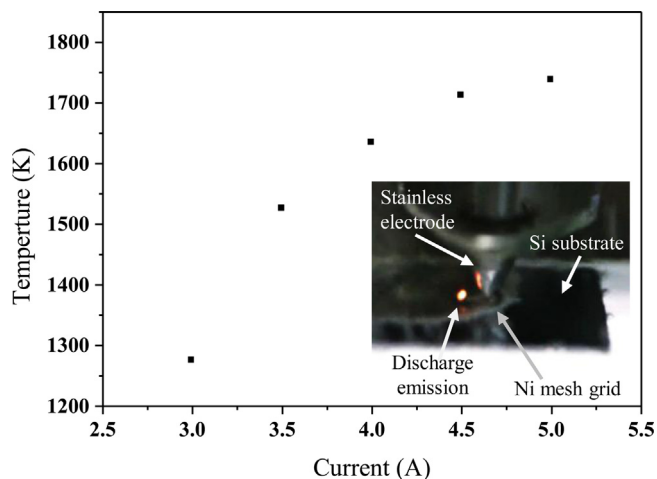


Fig. 2. Heating temperature of discharge emission; inserted image is a photograph of the experimental set-up.

typically accompanies arc discharge but rather a continuous spectrum. Therefore, as described in Section 2, the heating temperature was calculated by applying Plank’s radiation law to the continuous spectrum [17]. Although these temperatures are lower than the melting temperature of Ni, the apex of the Ni mesh was chipped because of arc discharge erosion.

After the experiment, the Ni mesh had a chipped place, which acted as a cathode spot, as shown in the SEM–EDX element mapping image in Fig. 3. Most of the disappeared part of the Ni mesh was welded onto the Si substrate or sputtered. In Fig. 3(a), showing the element mapping around the chipped place, the red part is nickel and the yellow part is carbon, indicating that carbon was included in the chipped place and in the current pathway. Fig. 3(b) is an SEM image around the carbon-deposited area, and shows the synthesis of a lot of CNTs whose content – i.e., whether or not Ni had filled them in – was uncertain. If we assume that the value of the current flow in one grid of Ni mesh equals the impressed current value of experimental conditions, we can estimate that since the thickness and width of one grid were, respectively, $20\ \mu\text{m}$ and $50\ \mu\text{m}$, the current density flowing through the grid was $3.0 \times 10^5\text{--}5.0 \times 10^5\ \text{A/cm}^2$, excluding from consideration the flow at the interface between the Ni mesh and Si substrate. These values of current density are near the cathode spot current density of the arc discharge range of $2.07 \times 10^4\text{--}1.24 \times 10^5$ [18].

Fig. 4(a) and (b) shows low-magnification TEM images of the surface of the Ni mesh in the 1- and 30-s heating periods, respectively. Graphite and amorphous carbon membrane are deposited on the surface in Fig. 4(a), while Ni particles on the order of 10–50 nm deposited on the surface in Fig. 4(b). Fig. 4(c) shows a typical Ni-filled CNT in the 60-s heat period, and it can be seen that CNT is filled with Ni continuously, homogeneously, linearly, and almost completely. The CNT’s diameter is 13 nm at the tip, 38 nm at the root, and the length is approximately 185 nm. The Ni filling also shows a diameter, length, and aspect ratio (the length divided by the diameter) of around 10 nm, 175 nm and 17.5, respectively. These results from varying heat periods indicate that Ni nano-particles increase in size with increasing heat period, and demonstrate the necessity of a 60-s heat period for sufficient growth of Ni-filled CNTs. It seems that there are two processes in regard to growth of the Ni-filled CNT, one is formation of Ni nano-particles, and next is elongation of themselves. Fig. 4(d) and (e) are high-magnification TEM image of the tip and root of the Ni-filled CNT, respectively. One to 5 graphene layers can be seen at the tip while around 20 can be seen at the root; the CNT’s shape is like a tapered needle because of the stair-like decrease of the CNT periphery. The

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