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Electrochemical production of Sn-filled carbon nanotubes in molten salts①

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Abstract: Sn-filled carbon nanotubes(CNTs) were prepared in situ by electrolysis of graphite in molten $\mathrm{LiCl/SnCl_2}$ mixtures. Transmission electron microscopy(TEM) investigation shows that the as-made products contain abundance of carbon nanotubes and most of them are filled with metal nanoparticles or nanorods. Some nanotubes are even inserted with long continuous nanowires more than several micrometers in length. Selected area electron diffraction(SAED) patterns and energy dispersive X-ray spectroscopy(EDS) of the filled nanotubes confirm the presence of Sn inside the nanotubes. The encapsulated Sn was further identified as β-Sn with tetragonal structure. Based on the experimental results, a possible growth mechanism of the Sn-filled nanotubes was also discussed.

Key words: carbon nanotubes; molten salts; electrolysis; electron microscopy

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1 INTRODUCTION

Since the discovery of carbon nanotubes in arc-discharge soot materials, nanotubes have generated significant research activities in chemistry, condensed matter physics and materials science[1, 2]. The morphology and size of carbon nanotubes suggest that they might offer intriguing possibilities for fundamental studies of nanoscale well-fined structures and provide high potential for technological applications. Inserting materials into the cavity of carbon nanotubes might greatly change the physical and chemical properties. A variety of interesting applications such as catalysts in heterogeneous catalysis[3], electronics devices[4], biosensors[5] and magnetic recording media[6] have been displayed by these novel one-dimensional nano-materials.

Thus, the preparation and applications of such metal-filled carbon nanotubes now become a promising and challenging subject of research. So far, various methods have been developed for the preparation of metal-filled carbon nanotubes. Elements such as Pb, Bi, Cs, S and Se were first introduced into the nanotubes by heating them with open-ended nanotubes. This process involves in the effects of capillary and wetting, and only low-surface-tension substances can be inserted into nanotubes bv this way[7, 8]. Subsequently, the arc-discharge technique, using composite electrodes impregnated with the filling metal, was attempted to produce mainly metal carbide-encapsulated carbons nanotubes[9, 10], but the yield of filled nanotubes is very low and this method produces impurities such as encapsulated carbon clusters and soot. In addition, pyrolysis method provides an alternative production route of filling nanotubes with metal[11-14]. Sen et al[11] reported that vapor-phase pyrolysis of benzene in the presence of metallocenes could generate ferromagnetic metals(such as Fe, Co and Ni) filled carbon nanotubes. In contrast, the catalytic pyrolysis method has attracted much attention due to its simplicity, low costs, ready availability of raw materials. However, the growth mechanism and the nature of the encapsulated nano-materials are still not clear.

Recently, carbon nanotubes filled with Sn have attracted extensive interest in various applications, particularly for the lithium intercalation electrode in lithium ion batteries[15]. In this paper, we describe a new way of producing Sn-filled carbon nanotubes by electrolysis of graphite electrode in $\mathrm{LiCl/SnCl_2}$ molten salts. Compared with other synthesis methods, the products contained abundance of Sn-filled carbon nanotubes with a high overall yield and the filled carbon nanotubes were also formed in situ by the electrolytic method. Furthermore, the nature of the encapsulated materials was characterized by transmission electron

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microscopy(TEM), selected area electron diffraction (SAED) patterns and energy dispersive X-ray spectroscopy(EDS). Based on the experimental results, a possible growth mechanism of Sn-filled nanotubes was also proposed.

2 EXPERIMENTAL

As schematically shown in Fig. 1, the synthesis of Sn-filled carbon nanotubes was conducted in a vertical tube furnace located in a stainless steel vessel under argon atmosphere. The electrolyte was kept in a cylindrical graphite crucible (external: 110 mm in height and 50 mm in diameter; internal: 70 mm in height and 25 mm in diameter), which also served as the anode during electrolysis experiments. A graphite rod with 3 mm in diameter was used as cathode, and its insertion depth was set at 15 − 20 mm in the melts by means of a screw mechanism. The salt mixtures of LiCl-$SnCl_2$ were always thermally pre-dried inside the graphite crucible at 300 ℃ for at least 2 h, and then melted under an argon flow (100 cm^3/min). The electrolysis experiment was carried out by a constant current of 5 − 10 A at 700 ℃ for 3 min, which is in the optimal temperature for carbon nanotubes preparation in molten LiCl as determined in Ref. [16].

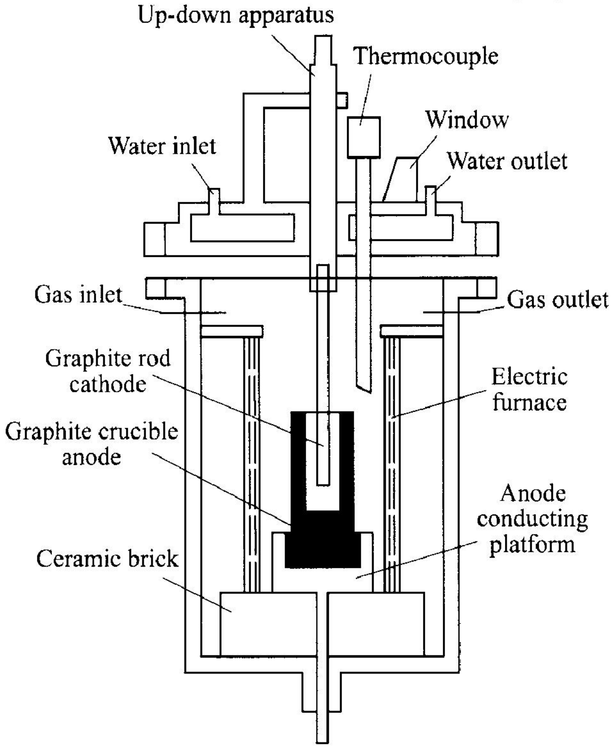

Fig. 1 Schematic diagram of experimental set-up for molten salt electrolysis

After electrolysis, the cathode was removed from the crucible immediately and the electrolyte was cooled down slowly to the room temperature under argon atmosphere. Distilled water was added to the crucible and the carbonaceous materials were received using the same methodology as reported in Ref. [17]. After being vibrated ultrasonically in the ethanol and then dispersed over a honey-carbon grid. The as-formed materials were investigated by transmission electron microscopy (TEM, Philips 200UT) operating at 200 keV. Elemental analysis was performed with energy dispersive X-ray spectroscopy(EDS, Link System QX2000).

Because the geometrical exposed area of graphite rod cathode was much smaller than that of anode, the characteristics of electrode reaction in molten salts were feasibly determined by the variation of cell voltage with current density. However, in constant current electrolysis, the surface area of cathode would decrease with time due to erosion and so would the current density. This made it difficult to correlate the change of cell voltage with the current density. Consequently, the test was required to carry out at initial stages of the electrolysis which implied that the surface area of cathode was not or a little changed. In each case, once a constant current was firstly applied to the system, the cell voltage was measured immediately at the meantime. Repeating this process several times, the cell voltage—current density curves were obtained by varying the current and logging corresponding cell voltage under the same conditions.

3 RESULTS AND DISCUSSION

Electron microscope observations revealed that the as-formed products grown from LiCl + 1.0% $SnCl_2$ melts contain abundance of nanotubes and most of them are filled with metal nanoparticles or nanorods(as shown in Fig. 2 indicated by arrows *A* and *B*). Some nanotubes are even filled with long continuous nanowires(arrow *C* in Fig. 2). The typically metal-filled nanotubes are straight with 75 − 125 nm in diameter and more than several micrometers in length. During our TEM investigation, we can also observe that the metal nanoparticles or nanorods are located in the center of the tubes or at one end of the tubes and even at two ends of a nanotube. The sizes of these nanoparticles or nanorods vary from several to tens of nanometers. In addition to the filled nanotubes, the other main constituent in the product is the aggregated metal nanoparticles which are fully encapsulated by graphite carbon, forming large spherical carbon encapsulated metal particles(arrow *D* in Fig. 2).

Fig. 3(a) shows a nanotube encapsulating a long continuous filament with the length of more than 2

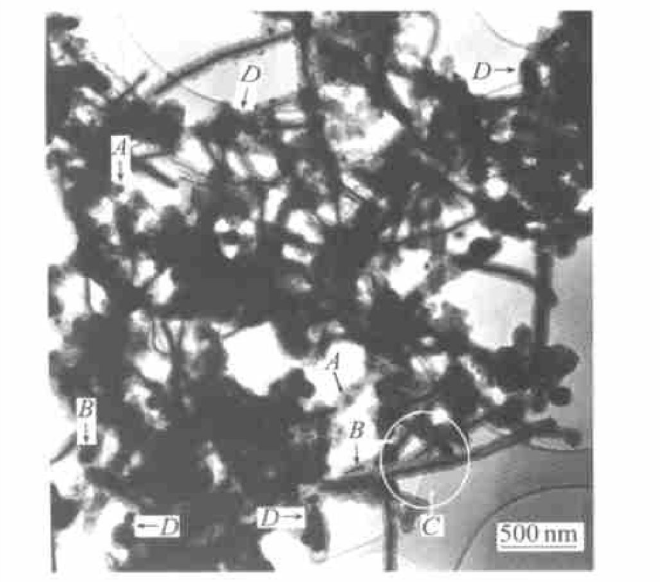

Fig. 2 TEM image at low-magnification of as-prepared products showing many nanotubes filled with nanoparticles, nanorods or long continuous nanowires collected from LiCl + 1.0% $SnCl_2$ molten salt electrolyte
(Arrows *A*, *B* and *C* point nanoparticles, short nanorods or nanowires, respectively. Arrow *D* points large carbon encapsulated metal particles)

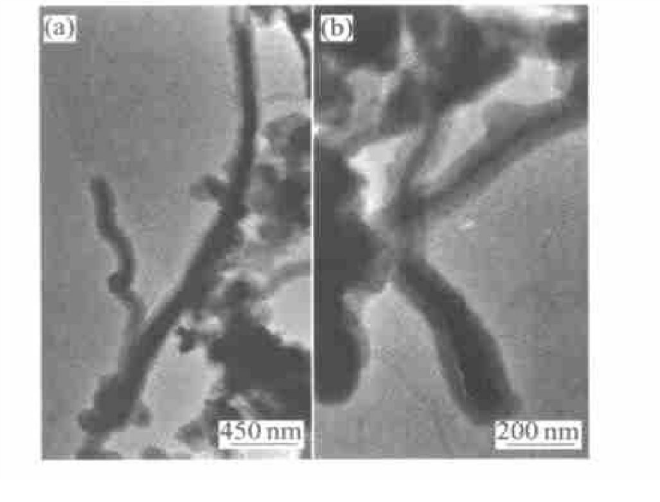

Fig. 3 TEM images of very long nanotube filled with continuous nanowires(a) and continuously filled nanotube with its diameter varied(b)

μm. Interestingly, the filled nanowires are tightly wrapped by the nanotube's wall even in a bent portion and their diameters vary with the nanotube's inner wall. Some of the metal-filled nanotubes have unusual morphologies, as shown in Fig. 3(b). The nanotube is filled with metal nanowire with the length of about 800 nm. Both of the nanotube's diameter and the metal nanowire's diameter vary greatly and decrease from bottom to top. Similarly, there exists no gap or void between the filled metal and the nanotube's inner wall. It may be suggested that the low-melting-point Sn originating from the reduction of tin cation was in a molten liquid state during the growth of carbon nanotubes at the experimental temperature. Although the capillarity for sucking molten metal into a nanotube is argued[15], in this case, we still believe that once the carbon nanotube grows long enough, the molten metal can be sucked into the nanotube under the capillary action.

When examining these nanotubes at high magnification, we observe that a thick layer of amorphous carbon deposited on the surface of the nanotubes. As shown in Fig. 4, the tube walls is poorly graphitized with visible structure defect. The graphitization degree of the as-formed nanotubes is much lower than that prepared by arc-discharge methods, which is similar to the observation of Hsu et al[17]. In our opinion, the reasons may be as follows: the electrolytic conversion of graphite to carbon nanotubes was conducted in relatively low temperature liquid phase(600 − 800 ℃), while the arc-discharge method of preparing carbon nanotube involved evaporating carbon atoms from solid carbon sources at temperature higher than 2 700 ℃. Generally, the higher the reaction temperature is, the more dense and more graphitized carbon nanotubes with relatively few structural defects are generated. The effect of temperature on the carbon nanotubes' graphitic layers structure was easily understood from the viewpoint of their growth mechanism.

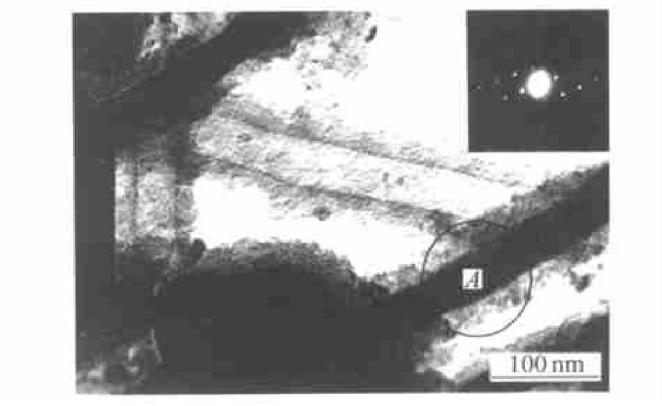

Fig. 4 High magnification image of metal-filled nanotube used for electron diffraction analysis
(Large circled area *A* contains part of full filled nanotube. The upper right inset shows its corresponding SEAD pattern)

Additionally, the nature of the encapsulated materials was investigated by both selected area electron diffraction(SAED) and energy dispersive X-ray spectroscopy(EDS) of the same area. The region used to

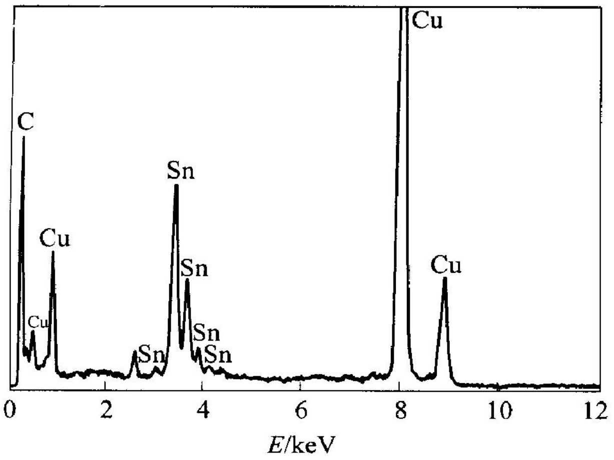

Fig. 5 Corresponding X-ray energy dispersive spectrum(EDS) of metal-filled carbon nanotubes

obtain the spectra is carefully selected and marked in Fig. 4 by *A*. The SAED pattern(upper right inset in Fig. 4) shows that spots due to (200), (101) and (220) planes of β-Sn. The EDS spectrum(Fig. 5) reveals that the presence of carbon and tin, but no evidence of chlorine. The observed carbon peak corresponds to the carbon shell(CNTs) and the Cu signals stem from the copper grid used to support the samples. XRD diffraction pattern further indicated that the encapsulated material is mainly β-Sn with tetragonal structure(space group $I4_1$, $a = 5.831$ Å, $c = 3.182$ Å).

There is a widespread agreement on the role of alkali metals such as Li, Na and K in the growth of carbon nanotubes during the electrolytic process. The alkali metal ion(M^+) intercalates, under the influence of a sufficiently negative electrode potential, into the carbon cathode where it is reduced in situ. The alkali metal then expands the graphite lattice and more strain is put into the lattice as the amount of the metal increases, until the lattice fragments. The carbon based fragments may then enter the molten salts and, without the protection of the graphite lattice, undergo through an inter- and/or intra-fragment recombination process, leading to the formation of various carbon nanoparticles and nanotubes in the electrolyte[16]. The growth mechanism of those Sn-filled carbon nanotubes is not yet well understood. However, several features can be found in our experiments:

1) All the filled metal, whether in the form of nanoparticles or nanorod, are tightly wrapped by the nanotube's wall, that is to say, the nanotube's inner diameter vary with the shape of the filled metal.

2) The salt ratio of $SnCl_2$ to LiCl also affects the formation of Sn-filled nanotubes. Use of pure $SnCl_2$ as the electrolyte generated no nanomaterials, and the salt was reduced to large spherical tin particles with the diameter of 2−4 mm. When the content of $SnCl_2$ was 5.0% in mass fraction in LiCl, we could not observe metal-filled nanotubes in addition to small granular particles and large amorphous carbon fragments in the products. It suggests that the reduction of lithium ions at the surface of graphite cathode plays an important role in the formation of nanostructure.

In order to have a profound understanding of the electrolytic formation of the Sn-filled nanotubes, the dependence of applied current density on the cell voltage between the cathode and an anode of much larger surface area was also investigated in this paper. As shown in Fig. 6, it can be seen that the cell voltage increases with increasing the initial current density in every case. Under the same current density, with the addition of $SnCl_2$(more than 1%, mass fraction) in LiCl, the cell voltage becomes much lower than that in pure LiCl, indicating Sn^{2+} is discharged as free metal in preference to Li^+ at high concentration and the formation of nanotubes is thus inhibited. In our experiment, we found that addition of 5% $SnCl_2$ to LiCl produces only small granular particles embedded in the surface of the cathode.

Based on the above experimental results, a possible growth mechanism of the Sn-filled nanotubes in our experiments is proposed as follows. Under the electrolytic conditions(1.0% $SnCl_2$ in LiCl in mass fraction), as shown in Fig. 6, the presence of Sn^{2+} does not interfere in the process because Li^+ is also reduced electrochemically to the metal and then intercalates into the graphitic layers, which leads to the formation of metastable species Li_xC_y compound. As pointed out by Hsu et al[17], the formation of carbon nanotubes resulted from either the decomposition of Li_xC_y compound or the oxidation of Li_xC_y by chlorine generated at the anode. In our experiments, when a small amount of $SnCl_2$ was introduced into the LiCl electrolyte, Sn^{2+} is reduced to free metal coupled by oxidation of adsorbed Li_xC_y. The reaction process can be illustrated as

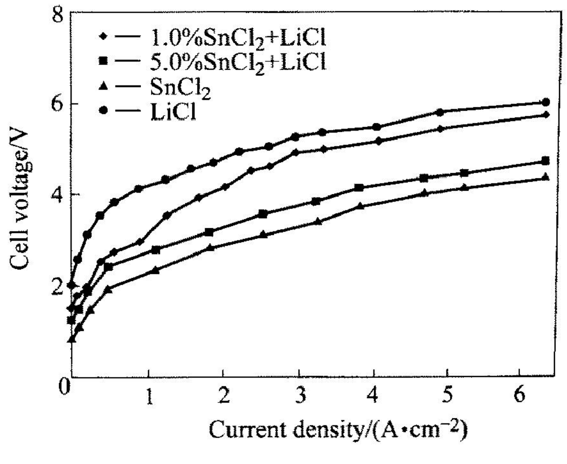

Fig. 6 Variation of cell voltage with applied current density measured in various molten salt ratios of LiCl and $SnCl_2$, respectively

$$Li_xC_y + Sn^{2+} \rightarrow yC_{graphite}(Sn) + xLi^+$$

When tubule carbon resulting from the extraction of lithium is deposited on the surface, Li_xC_y is extruded forming a fresh surface for graphitization, thus propagating tubule growth. The formed carbon tends to wrap tightly around the Sn droplets to reduce the energy. When the reduction process from Sn^{2+} to Sn continues, the growth of the Sn droplets and tubules are strongly coupled. The growing tubules may re-mould the shape of metal droplet, eg from nanoparticles to an elongated structure, and the growing nanoparticles in the nanotubes may change the nanotube from cylindrical to polyhedral. Alternatively, since the low-melting-point Sn is in a liquid state at our experimental temperature, the molten metal can be sucked by capillary action into the open nanotubes and recrystallize into nanoparticles or nanorods during the slow growth. At the same time, it is possible that the Sn droplets, encapsulated in the nanotubes, connect each other due to the metallic liquid flow. The successful connection of many Sn droplets will lead to forming continuous nanowires.

4 CONCLUSIONS

1) The method provides a new way for encapsulating metal materials into the cavity of carbon nanotubes. Sn-filled carbon nanotubes(CNTs) were prepared in situ by electrolysis of graphite in molten LiCl/$SnCl_2$ mixtures. The products contain abundance of carbon nanotubes and most of them are filled with metal nanoparticles or nanorods. The encapsulated Sn tightly wrapped by the nanotube's wall are further confirmed as β-Sn with tetragonal structure.

2) It suggests that reduction of Li^+ at the graphite cathode plays a crucial role in the formation of carbon nanotubes. With the addition of $SnCl_2$ (1.0%, in mass fraction) to the LiCl melts, the growth of nanotubes and the encapsulated metal are strongly coupled by the oxidation of Li_xC_y intercalation compound and the deposition of metal. And also, the capillarity action of the nanotubes may result in the formation of the metal-filled nanotubes during the process.

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