

27 February 1998

Chemical Physics Letters 284 (1998) 177-183

CHEMICAL PHYSICS LETTERS

# Electrochemical formation of novel nanowires and their dynamic effects

W.K. Hsu <sup>a</sup>, M. Terrones <sup>a</sup>, H. Terrones <sup>b</sup>, N. Grobert <sup>a</sup>, A.I. Kirkland <sup>c,d</sup>, J.P. Hare <sup>a</sup>, K. Prassides <sup>a</sup>, P.D. Townsend <sup>a</sup>, H.W. Kroto <sup>a</sup>, D.R.M. Walton <sup>a</sup>

<sup>a</sup> School of Chemistry, Physics and Environmental Sciences, University of Sussex, Brighton BN1 9QJ, UK
<sup>b</sup> Instituto de Física, UNAM, Apartado Postal 20-364, México, D.F. 01000, México
<sup>c</sup> Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB5 8UR, UK

<sup>d</sup> JEOL House, Silvercourt, Watchmead, Welwyn Garden City, Herts AL7 1LT, UK

Received 11 September 1997

### Abstract

Novel and uniform  $\beta$ -Sn nanowires surrounded by graphitic material (fully filled tubes; 40–50% of the overall material, length  $\leq 2 \mu$ m;  $\leq 100 \text{ nm o.d.}$ ) are produced by passage of a current between graphite rods immersed in molten mixtures of LiCl and SnCl<sub>2</sub> under argon at 600°C. Prolonged electron beam irradiation (under HRTEM) of the nanowires leads to axial growth, re-orientations and allied dynamic transformations. The technique may be applied to other soft metals in order to generate filled nanotubes. © 1998 Elsevier Science B.V.

## 1. Introduction

Following the bulk production of carbon nanotubes by the arc discharge technique [1], the suggestion was made that it might be possible to introduce metals into the inner core of the nanotubes. Such a proposal followed logically from the successful preparation of fullerenes containing endohedral metals [2,3], and indeed elements such as Pb, Bi, Cs, S and Se were first introduced by heating these substances with open-ended nanotubes [4–6] (sometimes in the presence of oxygen). Capillarity, wetting, and surface tension play an important role in the process. Generally, only low surface tension substances can be introduced into nanotubes [6] in this way.

In subsequent arc discharge experiments, where the graphite anode was drilled and packed with a metal, the formation of nanotubes and polyhedral particles both containing encapsulated metals and

carbides was achieved [7-12]. A problem arises however because the nanotubes are only partly filled. This fact may be disadvantageous in the context of nanoscale applications (e.g., conductivity). Recently, Loisseau and Pascard found optimal conditions for a more-or-less complete encapsulation of Se, S, Sb and Ge using arc discharge techniques in some of the nanotubes generated [13], and it was concluded that elements with incomplete electronic shells stood the best chance of being encapsulated [14]. At present, it has proved possible to 'partly' encapsulate: LaC<sub>2</sub> [15], YC<sub>2</sub> [8,16], LaC<sub>2</sub> [17], CeC<sub>2</sub> [12,17], Gd<sub>2</sub>C<sub>3</sub> [14,18], TiC [14,19], V<sub>4</sub>C<sub>3</sub> [20], ZrC [20], TaC [12,15], HfC [21], Fe<sub>3</sub>C [14], Ni<sub>3</sub>C [14] and other carbides of Cr [14], Dy [14] and Yb [14]. Only a few metals such as Mn, Co and Cu, and semiconducting elements such as Se, Ge and Sb have been inserted into nanotubes without carbide formation.

Chemical techniques have also been used to pre-

pare partly encapsulated materials. In particular, carbon nanotubes were oxidatively opened by boiling aqueous nitric acid, then filled with metal oxides (e.g., NiO,  $UO_2$ ) [22] and metals (e.g., Pd) [23] by wetting techniques.

Additionally, carbon nanotubes react with metal oxides above 1200°C to yield carbide nanorods [24] (i.e., filaments consisting of pure metal carbides which are not encapsulated, e.g., TiC, NbC, Fe<sub>3</sub>C, SiC and BC<sub>x</sub>). Ajayan and co-workers reported that it is also possible to coat carbon nanotubes externally with a single layer of metal oxide (e.g.,  $V_2O_5$ ) in addition to inserting the oxides into the core [25]. In this Letter, the production and characterisation of  $\beta$ -Sn fully-filled nanotubes via a condensed phase (electrolysis) technique is described.

#### 2. Experimental

The apparatus consists of a quartz tube (length 40 cm, o.d. 5 cm) with a gas in/out-let and electrical connectors in the end flanges. The anode is a crucible made by drilling a 3 cm diameter hole to a depth of 7 cm in a cylindrical block of high-purity graphite (o.d. 4 cm, 10 cm long; Le Carbone, Portslade, UK) [26]. This cell was supported inside the quartz tube by suitably positioned carbon rods, and was filled with a mixture of ionic salts (1% SnCl<sub>2</sub> plus 99% LiCl by weight, total mass ~ 42 g). The cell was then heated to ~  $600^{\circ}$ C under an argon flow (100-150 Torr) in a vertical furnace surrounding the quartz tube. When the salt mixture melted, the cathode (3 mm diameter carbon rod) was immersed to a depth of 1 cm in the electrolyte. A direct current ( $\sim 3 \text{ A}, \sim 3-4 \text{ V}$ ) was then passed through the system for 2 min. During this process the initially white ionic salt mixture darkened. After cooling, the solidified melt was dissolved in distilled water, and insoluble nanoscale materials were extracted as a suspension by adding toluene. The toluene layer was separated, concentrated by rotary evaporation, and the residual solid was sonicated in acetone for 20 min. Samples were dispersed on a 400 mesh holey carbon support (copper grid). HRTEM observations were made at 400 and 200 keV on JEOL 4000FX and 2010-EX microscopes, respectively. A video recorder was attached to the microscope in order to

record dynamic behavior in real time. ED-X (energy-dispersive X-ray analysis), EELS (electron energy loss spectroscopy), electron diffraction simulations and X-ray diffraction (XRD) analyses were also performed in order to determine the structure and composition of the encapsulated materials.

## 3. Results and discussion

Previous electrolysis experiments, performed using only LiCl as electrolyte, produced mainly nanotubes (30–35 nm o.d.; 5–7 nm i.d.) [27], some containing encapsulated materials (possibly lithium carbide or lithium chloride). Use of pure SnCl<sub>2</sub> as electrolyte produced no nanomaterials; the salt was reduced to large spherical particles of pure Sn (~ 2–4 mm diameter), found at the bottom of the crucible. However, when mixtures of SnCl<sub>2</sub> (0.5–1%) and LiCl (99–99.5%) were used as electrolyte, carbon nanotubes filled with  $\beta$ -Sn (nanowires) were generated in high yield (40–50% of extracted material; see Fig. 1).



Fig. 1. TEM image of  $\beta$ -Sn filled nanotubes (nanowires); external diameter ~ 30–50 nm. Some tube tips partly filled.

ED-X measurements on the nanowires showed clear signals for carbon and tin, and no traces of chlorine. Electron and X-ray powder diffraction studies confirmed that the encapsulated material was  $\beta$ -Sn (tetragonal structure with space group I4<sub>1</sub>, a = 5.832 Å and c = 3.182 Å) (Fig. 2). TEM observations showed that most of the tubes were almost

completely filled (Fig. 1). The Sn crystals exhibit different orientations with respect to the tube axis, therefore we believe that there is little epitaxial relationship between the graphitic walls and the encapsulated metal. This phenomenon may be due to the reluctance of tin to form carbides. EELS results reveal the absence of sp<sup>3</sup> bonding in carbon forming



Fig. 2. (a) Simulated electron diffraction pattern of a HRTEM image (right-hand side) of encapsulated tin exhibiting almost a square lattice (*d*-spacing =  $2.79 \times 2.90 \text{ Å}^2$ ); (b) X-ray powder diffraction patterns (experimental and simulated) of the  $\beta$ -Sn nanowires. Unidentified (starred) peaks may be due to SnO<sub>2</sub> or to a novel lithium carbide phase.

the nanotube. The tube walls consist of graphitic sheets and occasionally disordered domains; small areas of roughly aligned graphite can also be observed (Figs. 3 and 4). These domains encapsulate completely the Sn metal, rendering the wires impervious to oxygen (e.g., one week's treatment with concentrated sulphuric acid at room temperature, resulted in no oxygen or sulphur signals).

While analysing the nanowires under HRTEM (400 keV under normal observation conditions), it was observed that the encapsulated Sn exhibited

dynamic transformations, including: (1) crystal reorientations of Sn; (2) in situ growth and crystal translation; and (3) generation of polycrystalline phases within the metal after prolonged electron irradiation. In this respect, structural changes (dislocation and re-arrangement) of graphitic [28,29] and metallic [30-33] systems under electron irradiation have been observed previously.

After ~ 1–3 min irradiation (400 keV) of the  $\beta$ -Sn nanowires, tin crystals appear to change as indicated by the difference in the lattice pattern



Fig. 3. HRTEM images of a tin nanowire interconnected to a globule (left-hand side): (a) square lattice is observed at right-hand side; (b) after irradiation square lattice disappears, generating one-dimensional fringes (see right-hand side).

shown in Fig. 4, in which the two-dimensional array image is superceded by a one-dimensional system. In the almost square lattice (2-dimensional region), the spacings correspond to 2.79 Å (distance between (01) planes) and 2.91 Å (distance between the (200) planes). The spacing observed in the one-dimensional array is ~ 2.79 Å. Diffraction pattern simulations of  $\beta$ -Sn in the (011) zone axis, reproduces the latter observations. The lattice changes witnessed here (at distinct times) may be due to a dynamic phenomenon caused by the electron beam, resulting in differences in thickness and orientation along the metal nanowire.

A striking phenomenon, associated with the encapsulated tin, is the observation of a mobile phase at moderately high irradiation energies (400 keV). The encapsulated tin moves within the confines of the walls of the carbon tube and the motion has been recorded in situ by monitoring successive images over 2h in a VCR attached to a Jeol 4000FX elec-

tron microscope. One sequence shows that tin moves intermittently and approaches a fixed particle (possibly tin; see Fig. 5): (1) the tin first moves  $\sim 10$  nm in 5s after 1 min irradiation (Fig. 5a and b); (2) 20-30 s later a further movement of ~10-15 nm occurs within 6s (Fig. 5b and c); (3) after a further 10s the tin moves an additional 10 nm in 40s (Fig. 5c and d); and (4) finally arrives at the end of the tube, having moved 40 nm overall (Fig. 5e). Usually, these encapsulated tubes were connected to a tin globule at one end. This globule behaves as a reservoir providing material to fill the tube. It is possible that a temperature rise occurs upon irradiating the sample and that a simultaneous thermal expansion accompanied by a pressure change favours movement and growth of the nanowire. This sequence of events can be regarded as a nanothermometer.

We have also observed that the initial 'single' crystalline domains of encapsulated tin change into a disordered polycrystalline form after  $\sim 25$  min of



Fig. 4. Close-up image sequence of the irradiating single nanowire from Fig. 3: (a) original square lattice from the bottom left-hand side together with a one-dimensional array at the top right (Fourier transforms of these areas are shown above the HRTEM image); (b) transformation into one-dimensional fringe arrangement, in which the square lattice is eliminated after 2-3 min irradiation (Fourier transforms from bottom left and top right areas of the HRTEM image are displayed above).



Fig. 5. Image sequence, recorded in a VCR attached to the electron microscope, in which tin approaches a fixed particle (arrowed) inside a partly filled nanowire: (a) initial observation; (b) displacement after 60 s; (c) tin reaches the particle (80 s); (d) particle consumed by tin (90 s); (e) tin reaches end of tube (150 s; for reference see starred arrow).

electron irradiation at 400 keV (in situ measurements) perhaps due to atomic displacement effects and/or radiation enhanced diffusion.

#### 4. Conclusions

The production of  $\beta$ -Sn nanowires when SnCl<sub>2</sub> is present as a minor constituent in bulk LiCl, may be due to the fact that the electronegativity of tin is much smaller than that of lithium. As a consequence, SnCl<sub>2</sub> readily dissociates to yield molten tin which partly coats the carbon cathode. Subsequently, lithium moves to the cathode and reacts with carbon forming many embryos which can continually trap the tin. Under high-energy electron irradiation the tin tubular crystals are subjected to re-orientations and displacements caused by thermal expansion of the material and small epitaxial interaction between the graphitic walls and the encapsulated tin. Note that in the arc discharge method, the encapsulated material inside carbon nanotubes is usually a metal carbide. However, in our condensed phase experiment we did not see any tin carbide (which is consistent with the reluctance of tin to form carbides).

The novel technique presented in this account may be applicable to other metals (with high surface tension and low melting point) and their associated (low melting) salts, thus generating metallic nanowires (fully-filled nanotubes) with potential applications in nano-engineering.

#### Acknowledgements

We thank the ORS scheme (WKH, MT), Conacyt-México (MT, HT), DGAPA-UNAM IN-107-296 (HT), BOC-Gases UK (MT), The Royal Society and EPSRC for financial support (UK). We also grateful to L. Rendón, J.A. Flores, S. Seraphin, J. Jiao, J. Thorpe, D.P. Randall and S. Tehuacanero for HRTEM assistance and useful discussions.

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