

Supporting Information

Carbon Nanotubes Encapsulating Superconducting Single-Crystalline Tin Nanowires

Luboš Jankovič,¹ Dimitrios Gournis,^{1,2*} Pantelis N. Trikalitis,^{3*} Imad Arfaoui,² Tristan Cren,⁴ Petra Rudolf,^{2*} Marie-Hélène Sage,² Thomas T.M. Palstra,² Bart Kooi,⁵ Jeff De Hosson,⁵ Michael A. Karakassides,¹ Konstantinos Dimos,¹ Alikei Moukarika,⁶ and Thomas Bakas⁶

¹ Department of Materials Science and Engineering, University of Ioannina, 45110 Ioannina, Greece. E-mail: dgourni@cc.uoi.gr

² Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands. E-mail: p.rudolf@rug.nl

³ Department of Chemistry, University of Crete, 71409 Heraklion, Greece. E-mail: ptrikal@chemistry.uoc.gr

⁴ Institut des Nanosciences de Paris, 140, rue Lourmel, 75015 Paris, France

⁵ Department of Applied Physics, Materials Science Centre and the Netherlands Institute for Metals Research, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands.

⁶ Department of Physics, University of Ioannina, 45110 Ioannina, Greece

I. Materials and Methods

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I. Materials and Methods

Carbon nanotubes were synthesized by catalytic decomposition of acetylene over tin-dioxide catalyst (Aldrich, 99.9%) in a fixed-bed flow reactor at a temperature of 700°C. In a typical run, about 100 mg of the catalyst powders were placed in a alumina boat within a quartz tube, with an inner diameter of 2.2 cm and length of 90 cm, located in a resistance furnace. The sample was heated up to 700°C at nitrogen atmosphere. At this temperature acetylene as a carbon precursor was admixed with the carrier gas (N₂) at a flow rate of 10 cm³/min and 90 cm³/min, respectively. Sixty minutes later, the C₂H₂ gas flow was stopped, the ceramic boat was cooled down to room temperature in the nitrogen atmosphere, and the deposited materials were finally collected.

Transmission electron micrographs were obtained with a JEOL 2100F instrument equipped with field-emission gun and operating at 200 kV. TEM samples were prepared by gently grinding the powders and then casting on holey carbon grid. The images are typical and representative of the samples under observation.

The magnetization was measured using a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer in temperature range from 2 to 6 K with applied magnetic fields up to 1 T. The powder samples were contained in transparent gelatine capsules. The background of Fig. 4b consists of both a paramagnetic component coming from impurities in Sn-CNT and a diamagnetic signal coming from the gelatine capsule and the core contribution to the susceptibility.

II. Powder X-ray Diffraction (XRD)

X-ray powder diffraction data were collected on a D8 Advance Bruker diffractometer by using $\text{CuK}\alpha$ (36 kV, 36 mA) radiation and a secondary beam graphite monochromator. The patterns were recorded in the 2-theta (2θ) range from 2° to 80° , in step of 0.02 and counting time 2s per step. The X-ray diffraction (XRD) pattern of the final product, named Sn-CNT, is shown in Figure S1. The pattern shows the presence of β -Sn (JCPDS 4-0673) and SnO_2 (JCPDS 41-1445) phases in the final product.

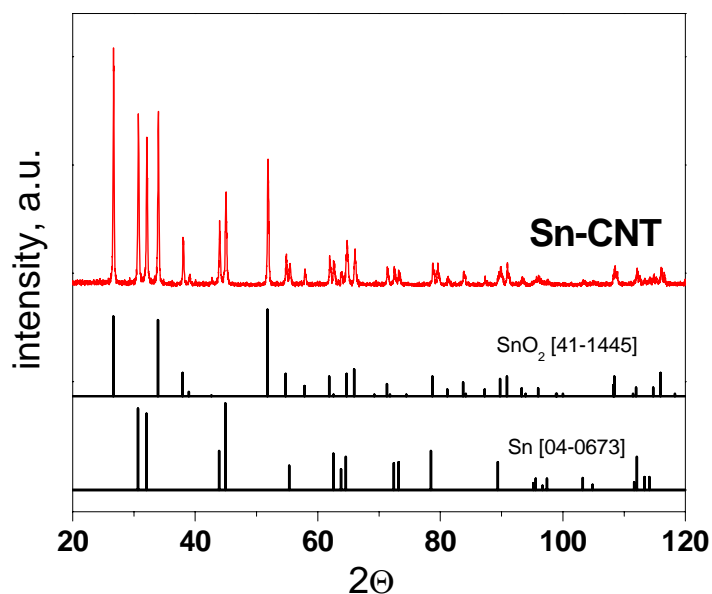


Figure S1

III. ^{119}Sn -Mössbauer spectroscopy

^{119}Sn -Mössbauer spectroscopy served as powerful and complementary to XRD technique in order to identify and characterize the Sn local environment and formal oxidation state in Sn-CNT powder. Mössbauer measurements were carried out using a constant acceleration spectrometer with $\text{Ba}^{119}\text{SnO}_3$ source maintained at room temperature. A Pd filter was used to eliminate the 25.2 keV X-ray radiation. A liquid helium/nitrogen cryostat (MD306 Oxford Instruments) was used to control the measuring

temperature at 80K. Suitable computer programs were used to fit the experimental spectra using Lorentzian line shapes.

In the Mössbauer spectrum (Figure S2), obtained at 80 K, two quadrupole doublets observed indicating the presence of two Sn containing phases. Analysis of the corresponding spectra shows that these phases are β -Sn and SnO₂ (Table S1)¹. Their quantitative relative ratio can accurately be measured from the corresponding Mössbauer spectral areas. Accordingly, the {SnO₂ : β -Sn} percent ratio was found to be 0.59.

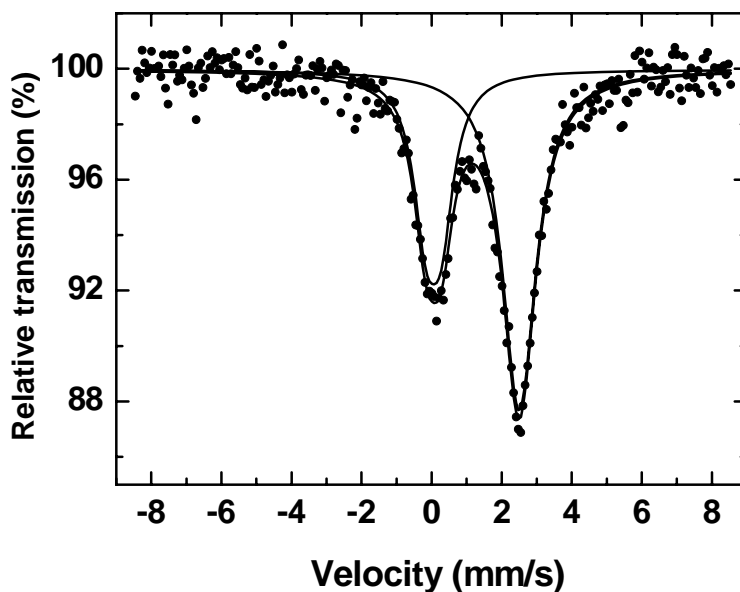


Figure S2

Table S1

Mössbauer effect spectral data at 80 K.

Sample	IS (mm/s)	GA/2 (mm/s)	QS (mm/s)	Area (%)
Sn -CNT	0.05	0.42	0.45	37
	2.50	0.58	0.00	63

The estimated errors on the Mössbauer parameters are ± 2 on the last significant digit for isomer shift (IS) and quadrupole splitting (QS) and ± 5 for half width at half maximum (GA/2) and for the spectral area.

IV. Raman Spectroscopy

A very powerful method for the characterisation of CNTs is Raman spectroscopy, as it has been reported for both single-wall (SWNTs) and multi-wall carbon nanotubes (MWCNTs)^{2,3}. Raman spectra were recorded with a Micro-Raman system RM 1000 RENISHAW using a laser excitation line at 532 nm (Nd-YAG). A 0.5 to 1 mW was used with 1 μm focus spot in order to avoid photodecomposition of the samples.

Figure S3 shows the Raman spectrum of the as-grown CNTs on SnO_2 powder. The spectrum is characteristic for the respective nanotubes; it does not change significantly if the laser spot is scanned over the sample. In the Raman-shift range 1200–1800 cm^{-1} , two peaks are observed at 1350 and 1595 cm^{-1} corresponding to graphite D- and G-bands, respectively. The G-band corresponds to the tangential stretching (E_{2g}) mode of highly oriented pyrolytic graphite (HOPG) and can be used to assess the degree of crystallinity/graphitisation, while the D-band at 1354 cm^{-1} originates from disorder in the sp^2 -hybridized carbon atoms, characteristic for lattice distortions in the curved graphene sheets and/or tube ends^{3,4}. The relative intensity of D and G bands (I_D/I_G), reveals the degree of disorder and it was found to be 0.86. This value is similar to those reported ($I_D/I_G = 0.85\text{--}1.3$) in the literature for CNTs prepared using acetylene⁵.

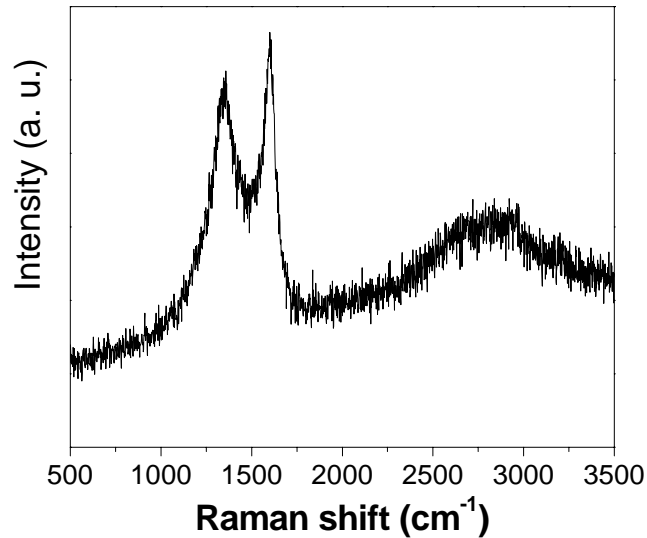


Figure S3

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