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1 **Vibrational and electronic structures of tin selenide nanowires** 2 **confined inside carbon nanotubes**

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12 **Abstract**

13 We study vibrational and electronic properties of tin selenide (SnSe) nanowires encapsulated in
14 single walled carbon nanotubes (SWCNT) by combining experimental Raman spectroscopy and
15 density functional theory (DFT) calculations at the Heyd-Scuseria-Ernzerhof (HSE) level. The
16 theoretically investigated standalone SnSe nanowires are Sn₄Se₄ with square (2×2) atomic arrange-
17 ment and Sn₆Se₆ with a repeating hexagonal Mo₆S₆-like structure. Raman data support the the-
18 oretical prediction that the square (2×2) nanowires possess specific modes at 151 and 185 cm⁻¹,
19 whereas the hexagonal Sn₆Se₆ structure is characterized by a mode appearing at ~235 cm⁻¹. Cal-
20 culations predict that the (2×2) nanowire has an electronic gap of 1.5 eV and the Sn₆Se₆ nanowire
21 presents a semi-metallic character. Raman spectra of composite SnSe@SWCNT samples show that
22 the radial breathing mode of the nanotubes is strongly suppressed indicating interaction between
23 SWCNT and the encapsulated SnSe nanowire while the Fano asymmetry parameter of the *G* band
24 is increased.

25 **Keywords**

26 carbon nanotubes, tin telluride, Raman spectroscopy, phonons, electrons, *ab-initio* calculations

27 **1 Introduction**

28 Inorganic and organic nanowires and nanostructured materials like nanorods or nanoplates are a
29 topic of utmost importance in many studies of physics, chemistry, biology, and medicine. The me-
30 chanical, electrical, electronic, magnetic, and chemical properties of these nano-objects can differ
31 considerably from those of the parent bulk materials leading to applications for storage devices,
32 electronic chips, photovoltaics, batteries, and therapeutic processes [1-7].

33 In particular, tin selenide, SnSe, is an important binary chalcogenide material which displays re-
34 markable electronic, thermoelectric, and optoelectronic properties depending on its morphology
35 as bulk crystal, thin films, or low-dimensional nanostructures [8]. This material can be applied no-
36 tably for photovoltaics, anodes in rechargeable batteries, supercapacitors, phase-change memory
37 devices, and topological insulators. Bulk tin(II) selenide is a narrow band-gap (IV-VI) semicon-
38 ductor with both indirect and direct band gaps of 0.9 eV and 1.3 eV, respectively. The bulk chalc-
39 ogenide crystal has an accordion-like stacked two-dimensional (2D) structure that gives it low an-
40 harmonicity and low lattice thermal conductivity making it a poor thermal conductor while its ZT
41 factor of merit has a high temperature value of 2.6 [9],[10].

42 Single-walled carbon nanotubes (SWCNT) are low-dimensional allotropes of carbon which have
43 unique mechanical, electronic and optical properties depending on their morphology [11]. As
44 expected for one-dimensional (1D) systems, they present van Hove singularities in the density of
45 states whose energies vary with the diameter and length of the nanotube. Depending on their chi-
46 rality SWCNTs are either metallic or semi-conductors allowing their application in flexible elec-
47 tronic devices, lithium battery anodes, flat panel displays, sensors, supercapacitors, drug delivery,
48 and STM/AFM tips [12,13]. Therefore, binary chalcogenides combined with SWCNTs can give
49 rise to very unusual physical properties in the as-grown composites, but also this can foster drastic
50 changes in the electronic properties of either component. Recently, several binary chalcogenides

51 have been encapsulated in both single-walled and double-walled carbon nanotubes (DWCNT) re-
52 sulting in unique 1D chalcogenide crystalline wires with diameter comparable to a unit cell of the
53 3D crystal [14-17]. Due to their extreme low lateral size and specific atomic arrangement, the phys-
54 ical properties of these confined and atomically constrained nanowires are expected to be signifi-
55 cantly different from those of the corresponding parent bulk materials.

56 Here we present a detailed comparative study of the structural, electronic, and vibrational prop-
57 erties of two original nanostructures of atom-sized SnSe nanowires encapsulated in SWCNTs.

58 Previous high-resolution transmission electron microscopy (HRTEM) investigations have shown
59 that SnSe crystallizes into (2×2) -atom per cross section structure inside SWCNTs, adopting the
60 same atomic arrangement as earlier described 1D (2×2) KI nanocrystals, hereafter referred to as
61 Sn_4Se_4 , embedded in double-walled or single-walled carbon nanotubes [14]. Recently, a novel 1D
62 hexagonal SnSe crystalline form was discovered in SWCNTs [18] with an Mo(S,Se)-type of co-
63 ordination environment [19,20], hereafter referred to as Sn_6Se_6 , comprising three Sn atoms and
64 three Se atoms per constituent layer, which is not observed in any of the other low-dimensional
65 forms of the selenium chalcogenides. Interestingly, Nagata *et al.* [17] reported also similar MoTe
66 nanowires structures in SWNTs. Previous DFT simulations predict a metallic nature of hexagonal
67 MX nanowires with $M=\text{Mo}, \text{W}$ and $W=\text{S}, \text{Se}$ [21,22] but semiconducting properties for the isostruc-
68 tural Cr_6Te_6 compound [21]. Both, theoretical simulations and experiments, confirm the structural
69 stability of the stand-alone Mo(S,Se) nanowires, which were found as effective nanoscale electri-
70 cal connectors between $\text{Mo}(\text{S}, \text{Se})_2$ monolayers [19,20]. In this aspect the physical properties of the
71 isostructural Sn-based nanowires are far from understanding, and our work has been motivated by
72 the following questions:

73 (i) Are the Sn_4Se_4 and Sn_6Se_6 nanowires structurally stable, or can they exist only encapsulated
74 in SWCNTs?

75 (ii) Are the two types of nanowires semiconducting or metallic? While Carter *et al.* previously
76 predicted a gaped band structure for Sn_4Se_4 nanowire using different functional and pseu-

77 dopotentials [16], electronic properties of the then unobserved Sn_6Se_6 1D crystal were not
78 determined.

79 (iii) What are the vibrational modes of both Sn_4Se_4 and Sn_6Se_6 nanowires which could give sig-
80 natures in Raman spectra of SnSe@SWNT composites? This question was not treated up to
81 now.

82 (iv) What is the impact of encapsulation of the SnSe material on the physical properties of the
83 surrounding nanotubes with matching diameter, e. g. metallic or semiconducting character ?

84 We addressed the first problems theoretically by means of extensive DFT calculations of the equi-
85 librium structure, electronic band structure, and vibrational eigenmodes for the two forms of SnSe
86 nanowires. In order to assess the last two questions, we studied experimentally the Raman spec-
87 tra of SnSe@SWCNT composites. Raman spectroscopy has proven to be a very efficient tool for
88 characterizing SWCNTs embedding 1D atom-sized crystalline HgTe and KI nanowires [23,24]. In
89 both cases it has been demonstrated that it is possible to identify several intrinsic vibrational modes
90 of the nanowires superimposed with the Raman spectrum of SWCNTs. By following the same
91 methodology here we study the in-situ dynamics of the embedded SnSe nanocrystals and their in-
92 teractions with the nanotube walls. The radial breathing mode (RBM) and longitudinal vibrational
93 modes (G -band) of the surrounding nanotubes are found to be strongly affected by the presence of
94 the encapsulated material, which leads us to important conclusions concerning the electronic prop-
95 erties of the SnSe@SWCNT composites corroborating the DFT predictions.

96 **2 Experimental methods and calculation details**

97 The SnSe@SWCNT samples were fabricated using infiltration protocols described previously
98 [16,18]. In this set of experiments, commercial SWCNTs from NanoIntegris PureTubes (99%
99 pure, 1.2-1.7 nm diameter, 300 nm to 5 μm length) were used to encapsulate tin selenide. Here,
100 the SWCNTs were washed, dissolved in N - Methyl-2-pyrrolidone (NMP), dried, pre-heated to
101 1173 K to remove solvent and to open the tubes. The nanotubes were filled by the modified high

102 yield molten-phase capillarity technique adapted for SnSe filling. SWCNTs were intimately ground
103 with SnSe (99.995%, Sigma Aldrich), and heated in pure silica quartz tubes sealed under vacuum
104 to 100 K above the melting point of SnSe at around 1233 K.

105 Micro-Raman experiments were performed with Horiba Jobin-Yvon LabRAM HR 800 Vis and
106 Renishaw inVia Reflex Raman microscope spectrometers in single monochromator mode with
107 diffraction gratings of 600 and 1200 grooves/mm, respectively. Laser excitations $\lambda_{\text{exc}} = 633$ and
108 785 nm (1.96 and 1.58 eV) were provided by helium-neon and diode lasers, respectively. Spectra
109 were collected at room temperature in the range between 100 and 3000 cm^{-1} allowing the simulta-
110 neous registration of the spectra of the fillers and the carbon nanotubes. The diameter and power of
111 the laser spot on the sample surface were 2 μm , 200 μW (LabRAM) and 45 μW (Renishaw) respec-
112 tively, for the fully focused laser beam with 50 \times objective magnification. The SnSe@SWCNT sam-
113 ples were generally found to be homogeneous under microscope without the presence of significant
114 amounts of extraneous SnSe amorphous or microcrystalline phase materials. Raman instruments
115 were calibrated against the Stokes Raman signal of pure Si at 520.5 cm^{-1} using a silicon wafer.
116 The spectral resolution was 2 cm^{-1} . In each experiment, several spectra were recorded on different
117 spots in the samples. The Raman spectra of three characteristic composite SnSe@SWCNT sam-
118 ples, # 1, # 2, and # 3 are presented and compared to those of SWCNT pristine samples.

119 The DFT calculations were performed with the Cambridge Serial Total Energy Package (CASTEP)
120 plane wave code [25] by making use of Heyd-Scuseria-Ernzerhof screened Coulomb hybrid
121 exchange-correlation functional HSE06 with 1/4 Hartree-Fock exchange [26] and norm-conserving
122 pseudopotentials for the core electrons. The choice of this functional was motivated by a better
123 geometry optimization of the Sn_6Se_6 nanowire and calculation of the vibrational frequencies with-
124 out imaginaries. It is also reported in the literature that HSE06 yields improved prediction of band
125 gap energy and correct band structure in semiconductors [26]. HSE was also described to be well
126 suited for calculating the phonon frequencies [26-29]. The plane-wave energy cutoff was set mainly
127 at 440 eV (32.34 Ry), and in some cases at 350 and 400 eV. The self-consistent calculations for the
128 1D Sn_4Se_4 and Sn_6Se_6 nanowires were performed on $1 \times 1 \times 2$ and $1 \times 1 \times 6$ Monkhorst-Pack

129 (MP) k-point mesh, respectively. We assessed the chosen DFT scheme by performing test calcula-
130 tions for the bulk tin selenide on a $1 \times 3 \times 3$ MP grid. Electronic convergence threshold for energy
131 was set to be 0.5×10^{-6} eV. The optimization of cell parameters was allowed to proceed by keeping
132 original symmetry with a total energy convergence tolerance of 0.5×10^{-5} eV/atom and until the
133 force on each atom was less than 10 meV/Å. Phonon calculations were carried out at HSE level us-
134 ing exclusively the finite displacement (FD) method in a supercell since the linear response scheme
135 (Density Functional Perturbation Theory, DFPT) was not implemented with hybrid functionals in
136 this DFT code.

137 **3 Results and discussion**

138 Experimental Raman spectra are discussed after the subsection of SnSe nanowires calculations.
139 The spectra were recorded on several pristine and composite SWCNT samples. We sorted among
140 these spectra those of three SnSe@SWCNT composites referred to as # 1, # 2, and # 3. They
141 mainly differ from each other in the low frequency region characteristic of the RBM modes of the
142 SWCNT molecular containers and of possible lines stemming from the SnSe encapsulated crystals.
143 Spectra labelled # 0 are from the pristine SWCNT phase. Fig. 1 shows high-resolution transmission
144 electron microscopy images (HRTEM) of the investigated SnSe filled samples. These images con-
145 firm both the high filling fraction of SnSe in ‘NanoIntegris’ SWCNTs but also the composition of
146 the encapsulated material.

147 **3.1 Predictive calculations for stand-alone SnSe nanowires**

148 This section is devoted to the calculation and analysis of 1D SnSe nanowires. The final relaxed
149 structures are given, and the phonons are calculated after geometry optimization. The Γ -point
150 modes are classified with their different symmetries, and sorted by frequencies. Meanwhile, the
151 electronic band structures of the standalone nanowires are presented and discussed.

152 3.1.1 Relaxed geometries

153 The geometries are entirely based on experimental HRTEM images realized on our samples [16,18]
154 (see right panel in Fig. 1) and were chosen as those of infinite rods along the [001] direction rel-
155 ative to a bulk cubic rocksalt unit cell with 2×2 and $3+3$ SnSe cross sections, corresponding to
156 square NaCl-like and hexagonal MoSe-like coordinations, respectively. The starting crystal pa-
157 rameters of the Sn_4Se_4 nanowire rely on HRTEM measurements by Carter *et al.* [16]. The initial
158 distances in the hexagonal Sn_6Se_6 nanowire were set arbitrarily at values close to those of the lay-
159 ered *Pnma* bulk crystal with a translation period of $c \sim 5 \text{ \AA}$ [30].

160 In order to perform the calculations with a plane wave (PW) basis set, periodic boundary condi-
161 tions were imposed along the *a* and *b* axes of the nanowires with a period of 10 \AA . The geom-
162 etry optimization of the nanowires converges to the two structures shown in Fig. 1. The opti-
163 mized translation period *c* along the nanowire axis is 5.708 \AA and 4.324 \AA for Sn_4Se_4 and Sn_6Se_6
164 nanowires, respectively. Some relevant interatomic distances for the two nanowires are shown in
165 Fig. 1 and are listed in more detail in Table 1. Note that the Sn-Se distances of the Sn_6Se_6 relaxed
166 nanowire match well those found by Slade *et al.* in HRTEM images [18].

167 The rod symmetry elements of the two nanowires consist of a fourfold 4_2 or a sixfold 6_3 screw axis
168 along *c*, of mirror planes *m* parallel to the *ab* and *bc* planes, an inversion center, and glide planes
169 parallel to *ac* and *bc* planes with $1/2$ translation of $c/2$ (Fig. 1). Therefore, the Sn_4Se_4 structure
170 can be described by the rod symmetry group $p4_2/mmc$ (No. 41) with all atoms occupying 4d Wyck-
171 off positions. The Sn_6Se_6 structure can be described as a periodic stack of equilateral Sn_3Se_3 tri-
172 angles. The triangles in the consecutive layers are rotated around the *c*-axis at 180° relative to each
173 other, as shown in Fig. 1(c)-(d). Thus, the periodicity of the Sn_6Se_6 structure corresponds to the
174 doubled interlayer spacing, and the structure is described by the rod symmetry group $p6_3/mmc$ (No.
175 75) with all atoms occupying 6d Wyckoff positions.

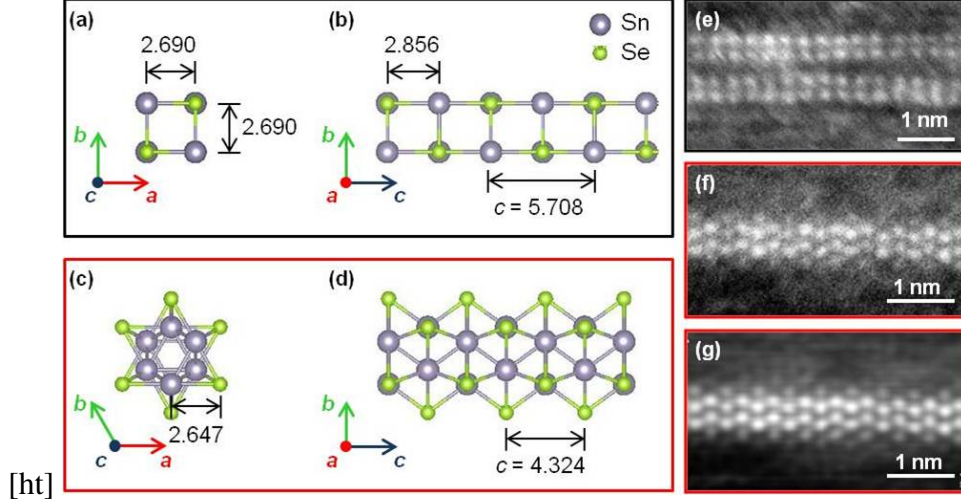


Figure 1: Left panel: Optimized structure of the two SnSe nanowires using the HSE hybrid functional. Vector \mathbf{c} is parallel to the nanowire axis. Vectors \mathbf{a} and \mathbf{b} represent the translation periods of the surrounding superlattice and are parallel to the SnSe layers. All distances are in Angstroms. The 2×2 SnSe crystal of $p4_2/mmc$ symmetry: views along the nanowire axis (a) and parallel to the Sn_2Se_2 layers (b). The hexagonal Sn_6Se_6 crystal of $p6_3/mmc$ symmetry: views along the nanowire axis (c) and parallel to the Sn_3Se_3 layers (d). Right panel: (e) experimental HRTEM annular dark field (ADF) image of a pair of 2×2 SnSe crystals observed in a representative SWCNT sample; (f) and (g) unfiltered and adaptive filtered ADF images of an encapsulated Sn_6Se_6 crystal observed in the same representative SWCNT sample.

176 3.1.2 Normal modes of vibrations

177 The normal modes of vibrations were calculated for the optimized structures at the Γ -point and
 178 along the $\Gamma - Z$ direction for the Sn_4Se_4 nanowire. A one-dimensional acoustic sum rule was im-
 179 posed on the dynamical matrix in order to account for the four zero-frequency modes of a freely
 180 standing nanowire: the three free translations and also the free rotation about the c axis. Since the
 181 unit cells of the Sn_4Se_4 and Sn_6Se_6 nanowires contain 8 and 12 atoms respectively, their corre-
 182 sponding phonon spectra consist of 24 and 36 dispersion branches along the Γ -Z direction. The
 183 normal modes of the Sn_4Se_4 and Sn_6Se_6 nanowire at the Γ -point are classified according to the
 184 irreducible representations of the $4/mmm$ (D_{4h}) and $6/mmm$ (D_{6h}) point groups. The symmetry de-
 185 composition was performed with the aid of SAM software available on the Bilbao Crystallographic
 186 Server [31]. The mechanical representations are:

$$187 \quad \Gamma_{22} = 2A_{1g} + 2A_{2g} + 2B_{1g} + 2B_{2g} + 2E_g + 2A_{2u} + 2B_{2u} + 4E_u \quad (1)$$

Table 1: Optimized structure parameters of Sn₄Se₄ and Sn₆Se₆ standalone nanowires calculated with HSE06 hybrid functional. The bond lengths between atoms belonging to the same Sn₂Se₂ (Sn₃Se₃) plane are denoted as “in”, and those between atoms from neighboring planes – by “out”.

	Sn ₂ Se ₂	Distance (Å)
	Translation period <i>c</i>	5.708
	Sn–Se (in)	2.690
	Sn–Sn (in)	3.698
	Se–Se (in)	3.909
	Sn–Se (out)	2.856
[h]		
	Sn ₆ Se ₆	Distance (Å)
	Translation period <i>c</i>	4.324
	Sn–Se (in)	2.647
	Sn–Sn (in)	2.698
	Se–Se (in)	2.668
	Sn–Se (out)	2.664

188 for the Sn₄Se₄ SnSe nanowire, and

$$\begin{aligned}
 \Gamma_{33} = & 2A_{1g} + 2A_{2g} + 2B_{2g} + 2E_{1g} + 4E_{2g} + 2A_{2u} + 2B_{1u} \\
 & + 2B_{2u} + 4E_{1u} + 2E_{2u}
 \end{aligned}
 \tag{2}$$

190 for the Sn₆Se₆ hexagonal nanowire. The acoustic modes are $A_{2u} + E_u$ and $A_{2u} + E_{1u}$ for the Sn₄Se₄
 191 and Sn₆Se₆ nanowires, respectively. The near-zero-frequency rigid rotations about *c* of the Sn₄Se₄
 192 and Sn₆Se₆ wires correspond to modes of A_{2g} symmetry. The other A_{2g} and B_{2u} modes in the
 193 Sn₄Se₄ nanowire, as well as the A_{2g} , B_{2g} , B_{1u} , B_{2u} , and E_{2u} modes in the Sn₆Se₆ nanowire are op-
 194 tically silent. The remaining even (g) modes are Raman active:

$$\Gamma_{22\text{Raman}} = 2A_{1g} + 2B_{1g} + 2B_{2g} + 2E_g
 \tag{3}$$

$$\Gamma_{33\text{Raman}} = 2A_{1g} + 2E_{1g} + 4E_{2g}
 \tag{4}$$

198 while the rest of the odd (u) modes possess infrared (IR) activity:

$$\Gamma_{22\text{IR}} = A_{2u} + 3E_u \quad (5)$$

$$\Gamma_{33\text{IR}} = A_{2u} + 3E_{1u} \quad (6)$$

Therefore, accounting for the degeneracy of the representations, eight different frequencies are expected in the Raman spectra of both nanowires. The corresponding number of the infrared active modes is four in the two structures. The calculated frequencies of the Γ -point modes are summarized in Table 2.

In Sn_4Se_4 and Sn_6Se_6 nanowires the A_{1g} and the E_g (E_{1g}) vibrations entail comparable types of atomic displacements. The totally symmetric A_{1g} modes are radial breathing-type modes of the Sn and Se sublattices. The E_g (E_{1g}) modes involve atomic motions along the nanowire axis, and can be defined as shearing deformations of the two atomic sublattices. Table 2 gives the calculated Γ -point vibrational frequencies for the standalone Sn_4Se_4 and Sn_6Se_6 nanowires. The modes of the same symmetry are numbered in an ascending order of their frequencies.

3.1.3 Electronic band structures

Fig. 2 presents the electronic band structures, as well as the full and partial density of states (DOS) calculated with the HSE06 functional for the layered SnSe bulk crystal and the Sn_4Se_4 and Sn_6Se_6 -embedded nanowires. Zero energy corresponds to the Fermi energy E_F .

Note that in periodic DFT calculations, the 1D nanowire is placed in the center of a vacuum box of dimensions a, b, c with volume V sufficiently large to neglect inter-wires interactions. In this 3D scheme, the DOS for electrons or phonons of the wire at energy E can be written as:

$$\rho_{3D}(E) = \frac{V}{(2\pi)^3} \int_{-\pi/a}^{\pi/a} \int_{-\pi/b}^{\pi/b} \int_{-\pi/c}^{\pi/c} dk_x dk_y dk_z \delta(E - E(\mathbf{k})) \quad (7)$$

Provided that the interaction between periodic replica of the nanowire is negligible, the band energy function $E(\mathbf{k})$ is practically dispersionless in the xy -plane, i.e. $E(k) \equiv E(k_z)$, where k_z is the

222 1D wavevector along the nanowire axis. In this case the equation (7) is transformed into equivalent
 223 expression for the 1D density of states of the nanowire:

$$224 \quad \rho_{1D}(E) = \frac{c}{2\pi} \int_{-\pi/c}^{\pi/c} dk_z \delta(E - E(k_z)) \quad (8)$$

225 Therefore, the ρ_{1D} values discussed hereafter depend only on translation period c of the wire and
 226 are in principle independent of the vacuum box dimension.

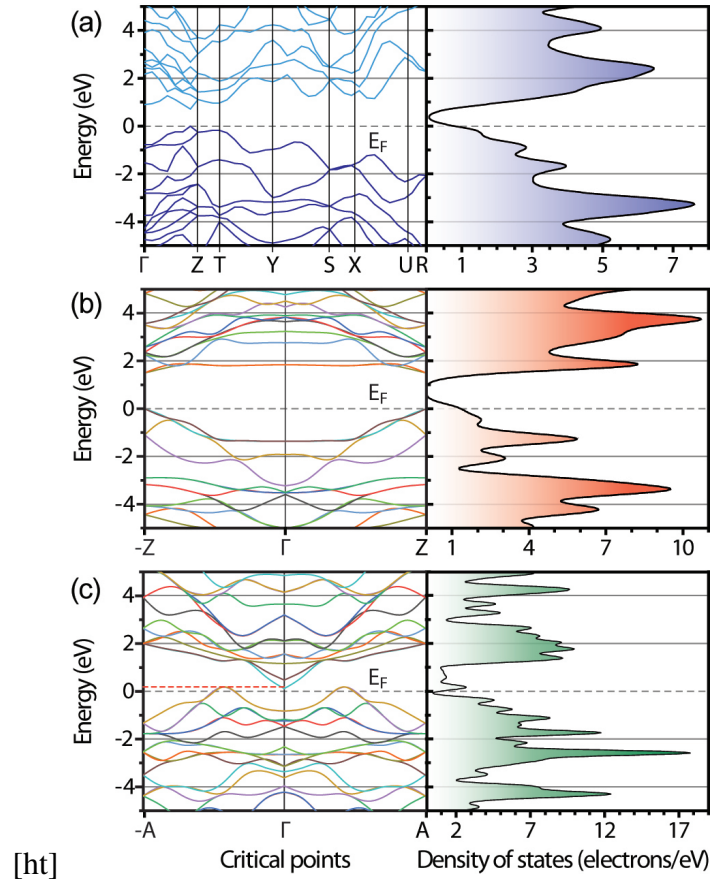


Figure 2: Band structures and density of states of SnSe crystals calculated with DFT at HSE06 level. (a) 3D $Pnma$ crystal; (b) 1D square Sn_4Se_4 nanowire along $-Z\Gamma Z$ direction; (c) 1D hexagonal Sn_6Se_6 nanowire along $-A\Gamma A$ directions with spline interpolation. A semimetallic character is revealed above the Fermi level (dotted line). ΓZ and ΓA paths are oriented along the chain direction. The critical points Z and A lie at the edge of the Brillouin zone with coordinate $(0,0,1/2)$. The electronic configuration of Sn atom is $[\text{Kr}]5s^24d^{10}5p^2$, s and p orbitals hold valence electrons ($n = 5$).

227 The band gap in the layered 3D $Pnma$ crystal is 0.71 eV, a value relatively close to the experimental

228 indirect band gap (0.9 eV) and is in the same range as values reported in previous works [32]. The
229 band structure of the Sn_4Se_4 nanowire clearly evidences a direct band gap of 1.49 eV at Z point
230 which should allow optical and resonant transitions in the near IR at about 830 nm. This bandgap
231 energy is higher than those of the *Pnma* crystal (indirect : 0.9 eV, direct : 1.3 eV) and closer to that
232 found by Carter *et al.* [16] for the same infinite rod (1.36 eV) when using the PW91 functional.
233 These two DFT calculations stress that the infinite Sn_4Se_4 nanorod should present a band gap ex-
234 pansion with respect to the bulk layered form.

235 Here, computations at PBE and HSE levels of theory show that the Sn_6Se_6 nanowire has an almost
236 gapless electronic structure with a small nonzero density of states at the Fermi level. For HSE06
237 the upper valence branch crosses the Fermi level with a valence band maximum (VBM) at 0.18
238 eV above E_F while the conduction band minimum (CBM) is only 0.11 eV above E_F at the Γ point
239 (Fig. 2(c)). These VBM and CBM values indicate an energy overlap of about 70 meV suggesting
240 that the Sn_6Se_6 nanowire is a semimetal. To support this prediction, it should be noticed than Yan
241 *et al.* [33] have observed a semiconductor to semimetal transition in powdered SnSe at a pressure
242 of 9 GPa, which has been also verified by their GGA-PBE band structure calculations. The elec-
243 tronic calculations of Yan *et al.* at 9 GPa in the ΓZ direction ($Z: (0,0,1/2)$) show the same behavior
244 found in the Sn_6Se_6 nanowire: the upper valence band crosses the Fermi level while the lower con-
245 duction band goes down to almost zero energy at Γ point.

246 **3.2 Additional Raman bands upon SnSe encapsulation**

247 Fig. 3 presents the unpolarized micro-Raman spectra of a pristine SWCNT sample # 0 and
248 SnSe@SWCNT sample # 1 between 100 and 3000 cm^{-1} obtained at excitation wavelength 785
249 nm (1.58 eV) for the same power density. In SWCNT spectrum the band of RBM modes is strongly
250 resonant with maximum intensity close to that of the *G* band. The *G* band exhibits an asymmet-
251 ric shape characteristic of metallic nanotubes contribution and has three components at 1556,
252 1571, and 1592-1595 cm^{-1} stemming from both metallic (M) and semiconducting (SC) tubes re-

253 spectively referred to as G^- (LO phonon of M tubes), G^+ (TO phonon of SC tubes), and G^+ (LO
254 phonon of SC tubes) [34,35].

255 Fig. 4 shows that the RBM frequencies of the pristine nanotubes appear between 150 and 180 cm^{-1}
256 with two resolved peaks at 163 and 173 cm^{-1} . The spectra are normalized to the maximum Raman
257 intensity of low frequency lines for clarity.

258 Applying the empirical relationship between the RBM frequency in cm^{-1} and tube diameter d [35],
259 $d(\text{nm}) = 227/\omega_{\text{RBM}}$, we estimate that these peaks are characteristic for SWCNTs of 1.4 nm and
260 1.3 nm diameter, respectively. Thus the experimental Raman results confirm that the commercial
261 nanotubes of 1.2-1.7 nm diameter range chosen for the synthesis of our composites are the dom-
262 inant crystalline structural forms in the samples analyzed here, notwithstanding that other forms
263 may possibly exist but they were not extensively encountered in our study. These diameters can
264 easily accommodate the two types of SnSe 1D nanocrystals discussed in this paper. The estimated
265 diameter of SWCNTs surrounding the SnSe nanowires is:

$$266 \quad d = d(\text{Se-Se}) + 2r_{\text{vdW}}(\text{Se}) + 2r_{\text{vdW}}(\text{C}) \quad (9)$$

267 where r_{vdW} is the van der Waals radius of the atom and $d(\text{Se-Se})$ is the cross-sectional distance
268 between opposite Se atoms. For optimized geometries of Sn_4Se_4 and Sn_6Se_6 crystals we find $d =$
269 1.11 nm and 1.45 nm, respectively. These values correspond well with the diameter estimates from
270 Raman spectra.

271 Strikingly several novel lines appear at low frequencies in the Raman spectra of SnSe@SWCNT
272 samples # 1, # 2 and # 3 for exciting wavelengths 633 and 785 nm, while the absolute intensity of
273 the RBM and G modes either vanishes or strongly diminishes.

274 These additional low-frequency bands are located at 108-109, 126-131, 151, 185, 235 cm^{-1} (see
275 Fig. 3 and Fig. 4). All these bands are absent in the pristine nanotubes spectrum (samples # 0). For
276 sample # 1 the signals of nanotube walls are hardly detected in the region between 140 and 180
277 cm^{-1} and are overlapped by the additional band at 150 cm^{-1} . In sample # 2, the RBM bands are
278 absent.

279 The supplemental lines appearing for the SnSe@SWCNT samples may result from encapsula-
280 tion of SnSe in SWCNTs since their relative intensities do not match those of bulk *Pnma* SnSe or
281 $P\bar{3}m1$ SnSe₂ crystals at 111 cm⁻¹ (*E_g*) and at 187 cm⁻¹ (*A_{1g}*) as shown in Fig. 4, and therefore do
282 not seem characteristic of remnant tin selenide compounds in between and outside the nanotubes
283 walls [36-41]. It can be inferred that these bands are likely to characterize mainly other phases of
284 tin selenide. This assumption is supported by the changes of the RBM and *G* bands of the SWC-
285 NTs in the SnSe@SWCNT nanostructures. The relative intensity of these lines and their moder-
286 ate HWHM indicate that these crystals are well ordered inside the SWCNT walls. The additional
287 strong bands at 185 and 235 cm⁻¹ cannot be ascribed to the SnSe *Pnma* crystal. We found that for
288 633 nm excitation this compound exhibits Raman bands at 32 (*A_g*), 55 (*B_{1g}*), 68 (*A_g*), 106 (*B_{3g}*),
289 129 (*A_g*), 148 (*A_g*), and 179 cm⁻¹ (very weak) in agreement with previous work [36]. They likely
290 characterize intrinsic features of the nanowires embedded in SWCNT because the occurrence of
291 these bands is predicted in SnSe 1D standalone crystals by the vibrational calculations described
292 hereafter. Our interpretation is also conformed by Raman data of MoTe@SWNT samples acquired
293 by Nagata *et al.* [17]. They found in their samples a Raman line at 255 cm⁻¹ that they ascribed to
294 the vibrations of the embedded MoTe nanowires. Similarly to our experiments, their observation
295 was carried out at a laser power of 347 μW using the same equipment and the He-Ne 633 nm laser
296 line. Since Sn₆Se₆ and MoTe nanowires have close structures, their Raman experiment suggests
297 that the SnSe nanowires vibrational Raman lines should lie in the same range of frequencies.

298 **3.3 Analysis of *G* bands**

299 At higher frequencies the *G*⁻, *G*⁺ modes of the SnSe@SWCNT samples are still visible but are
300 considerably reduced in intensity (Fig. 3). The profile of the *G* band remains strongly asymmetric
301 with a shift of the two *G*⁺ components towards higher energies by about 4 cm⁻¹ at 1578, and 1596
302 cm⁻¹, respectively (blueshift). There is an overall diminution of the spectral signal-to-noise ratio
303 in samples # 1 and # 2 and the relative intensity of the *G*⁺ TO line located at 1578 cm⁻¹ is weaker.
304 The relative intensity of the *D* band is enhanced with respect to that of *G* band indicating that more

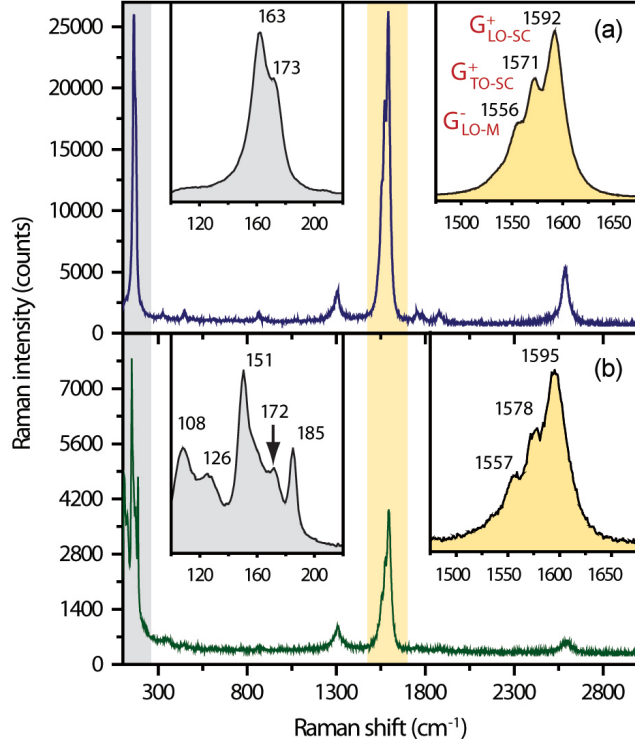


Figure 3: Experimental Raman spectra of pristine SWCNT (NanoIntegris 99% pure sample # 0), a), and SnSe@SWCNT sample # 1, b) recorded between 100 and 3000 cm^{-1} at excitation 1.58 eV (785 nm) and for the same laser power. The insets show sub-band features in the G band for pristine sample and RBM frequency region for the composite.

305 defects are present in the encapsulating nanotube walls. Finally, the second order G' ($2D$) band lo-
 306 cated at 2586 cm^{-1} in pristine SWCNTs shifts towards 2600 cm^{-1} and weakens in relative intensity
 307 in the SnSe@SWCNT samples. The blueshift of the G and G' Raman bands upon encapsulation of
 308 SnSe and the overall intensity damping of the spectrum indicates a p -type doping of the SWCNT
 309 template [42,43].

310 This experimental result is in line with DFT calculations of work functions (WF) carried out on the
 311 SnSe standalone nanowires and presented in the Supporting Information. For Sn_4Se_4 , the bonding
 312 energies of HOMO (4.574 eV) and LUMO (3.385 eV) are lower than the known WF of SWCNT
 313 (~ 4.8 eV) and near the WF of graphene (4.6 eV). The calculated WF of Sn_4Se_4 , which refers to
 314 the Fermi level situated in the middle between HOMO and LUMO, is 3.98 eV. Thus, if there is
 315 a charge transfer between the Sn_4Se_4 and the SWCNT, the CNT should accept electrons, i.e. be-
 316 come n -doped. However, the calculated WF of Sn_6Se_6 is 5.412 eV, significantly larger than that of

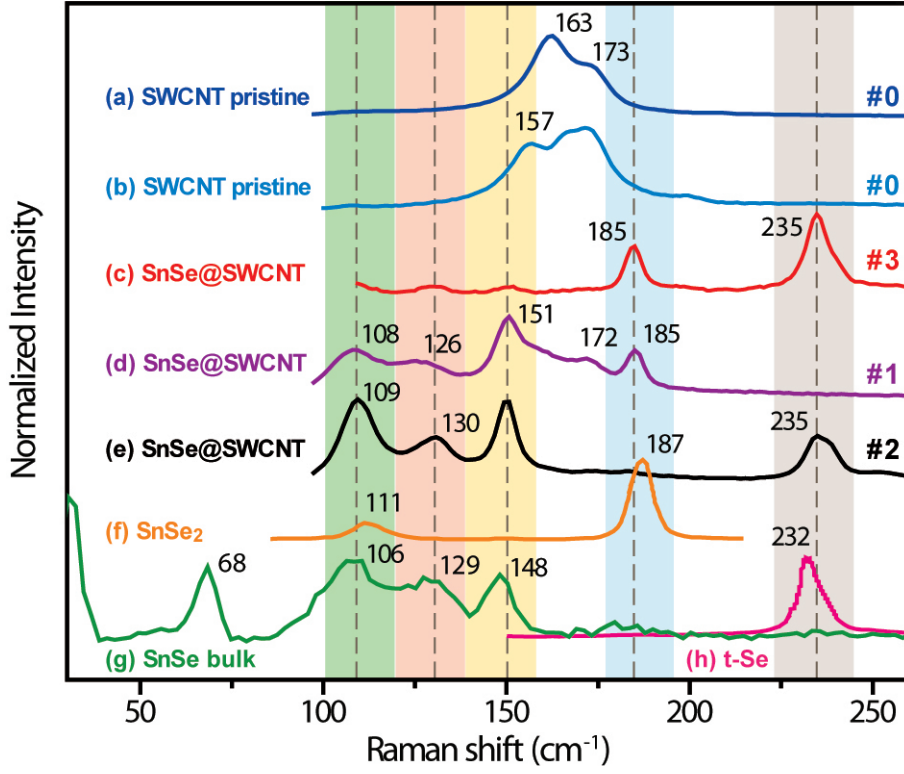


Figure 4: Low frequency Raman spectra of pristine SWCNT, SnSe filled SWCNT, and tin selenide compounds. Pristine SWCNT sample # 0 (NanoIntegris 99% pure) at $\lambda_{exc} = 785$ nm (1.58 eV) (a) and $\lambda_{exc} = 633$ nm (1.96 eV) (b); (c) SnSe@SWCNT (sample # 3) $\lambda_{exc} = 633$ nm ; (d,e) SnSe@SWCNT (samples # 1 # 2), $\lambda_{exc} = 785$ nm ; (f) SnSe₂ $P\bar{3}m1$ crystal, $\lambda_{exc} = 785$ nm; (g) SnSe $Pnma$ crystal $\lambda_{exc} = 633$ nm; (h) for information: trigonal Se $P3_121$ crystal, $\lambda_{exc} = 633$ nm. Spectra (f,h) are taken from literature.

317 SWCNT. Therefore, in this case we can rationalize that the CNT should oppositely give electrons to
 318 the Sn₆Se₆ nanowire, i.e. be *p*-doped. Thus the spectral signatures of a *p*-doping (or hole doping)
 319 of SWCNTs could be fingerprints for presence of Sn₆Se₆ nanowires encapsulated in the nanotubes.
 320 One can anticipate that the experimental shape of the *G* band can be fitted by adding together two
 321 Lorentzian functions for *G*⁺ LO and *G*⁺ TO lines and a Breit-Wigner-Fano (BWF) line shape for
 322 the *G*⁻ LO sub-band [44]. This choice is supported by the fact that the *G*⁻ LO sub-band is sup-
 323 posed to stem from the tangential vibrational modes of metallic SWCNTs [45] and therefore may
 324 acquire a BWF profile. By theoretical predictions Gayen *et al.* [46] also anticipated that a BWF
 325 lineshape might be observed on the *G* band when semiconducting SWNTs are filled with donor

326 atoms. The BWF lineshape writes as:

$$327 \quad I(\omega) = \frac{I_0 [1 + (\omega - \omega_{BWF})/q\Gamma]^2}{1 + [(\omega - \omega_{BWF})/\Gamma]^2} \quad (10)$$

328 where I_0 is the maximum intensity of the line, ω_{BWF} the resonance frequency, Γ the spectral width,
329 and $1/q$ the asymmetry parameter.

330 Fig. 5 shows the experimental Raman spectra fitted with a Breit-Wigner-Fano and two Lorentzians
331 functions obtained for pristine SWCNT (sample # 0), and the two SnSe@SWCNT samples (# 1 and
332 # 2) presented above. Several modifications of the Raman spectra occur upon encapsulation (see
333 Fig. 5):

334 (i) The three components of the tangential G band features undergo both shape and energy changes.
335 The BWF component corresponding to the G^- LO mode of metallic tubes is more asymmetric with
336 an upshift of about 2 cm^{-1} . The Lorentzian components G^+ TO and G^+ LO of semiconducting
337 tubes are upshifted by 3 to 4 cm^{-1} , and their FWHM increases.

338 (ii) The integrated intensity ratio of BWF and highest Lorentzian components (I_{BWF}/I_{G^+LO}) dimin-
339 ishes after encapsulation due to the broadening of the G^+ LO feature.

340 (iii) The asymmetry parameter $|1/q|$ is much higher for encapsulating samples than for the pristine
341 sample indicating that metallicity of tubes is increased in these nanomaterials as expected from the
342 calculated band structures. The value found after fitting for pristine SWCNT is 0.196, close to that
343 of Ref. [44] (0.23) while for samples # 1 and # 2, it increases to 0.380, and 0.306, respectively.

344 The interference part of the BWF profile in eq. 11, i.e. the BWF interference function [47], is ex-
345 pressed as

$$346 \quad I'(\omega) = \frac{2(\omega - \omega_{BWF})/q\Gamma}{1 + [(\omega - \omega_{BWF})/\Gamma]^2} \quad (11)$$

347 It characterizes the interaction between the vibrational mode and a constant continuum of elec-
348 tronic excitations. A plot of this function shows that the electron-phonon interaction between G^-

349 LO and G^+ TO Raman contributions in the encapsulating samples is stronger, showing that metal-
350 licity of these samples is higher than in the pristine carbon nanotubes.

351 In addition, the difference of interference functions between SnSe@ SWCNT and pristine SWCNT
352 samples indicates that a stronger BWF interaction occurs in the former as exemplified by Fig. 5(b)
353 (red contour) whose signal is positive in the range 1540-1565 cm^{-1} and whose maximum is located
354 near the frequency of the BWF component in SWCNT (1555 cm^{-1}) and SnSe@SWCNT samples.

355 As a consequence, the BWF interference does not affect the G^+ LO mode in SnSe@SWCNT but
356 may have a small influence on the frequency of the G^+ TO mode. Overall, the frequency hardening
357 of the G^- band between pristine and encapsulating nanotubes is mainly due to the encapsulated
358 crystals modifying the mechanical properties of the nanotubes walls.

359 In a previous work, CNTs have been decorated by SnSe crystals for applications in Li-battery elec-
360 trodes [48]. In this case there no encapsulation of the chalcogenide. Raman spectra recorded on
361 these hybrids exhibit D and G band profiles different than those we have observed in this work.

362 Aside our HRTEM investigation, this is a hint that the CNTs in our samples are not covered by the
363 chalcogenide.

364 **3.4 Phonons of the encapsulated nanowires**

365 The phonon dispersions and DOS have been calculated at HSE level of theory for the two SnSe
366 standalone nanowires and for the $Pnma$ SnSe crystal for comparison (Fig. 6). Additionally, the par-
367 tial phonon DOS unveils the individual contribution of Sn and Se atoms to the vibrational spec-
368 trum.

369 The partial phonon DOS of the SnSe $Pnma$ crystal shows that the main Sn vibrations occurring be-
370 tween 60-72 cm^{-1} , accompanied by additional modes at 176 and 194 cm^{-1} , with small densities at
371 109 and 210 cm^{-1} . The Se vibrations are mainly centered at 180 and 194 cm^{-1} with smaller densi-
372 ties at 59, 70, 108 and 209 cm^{-1} .

373 The partial DOS of the Sn_4Se_4 nanowire reveal strong differences with the 3D bulk crystal. The
374 DOS exhibit more featured spectra with large contributions at 30, 54, 72, 96, 113, 149, 192 cm^{-1}

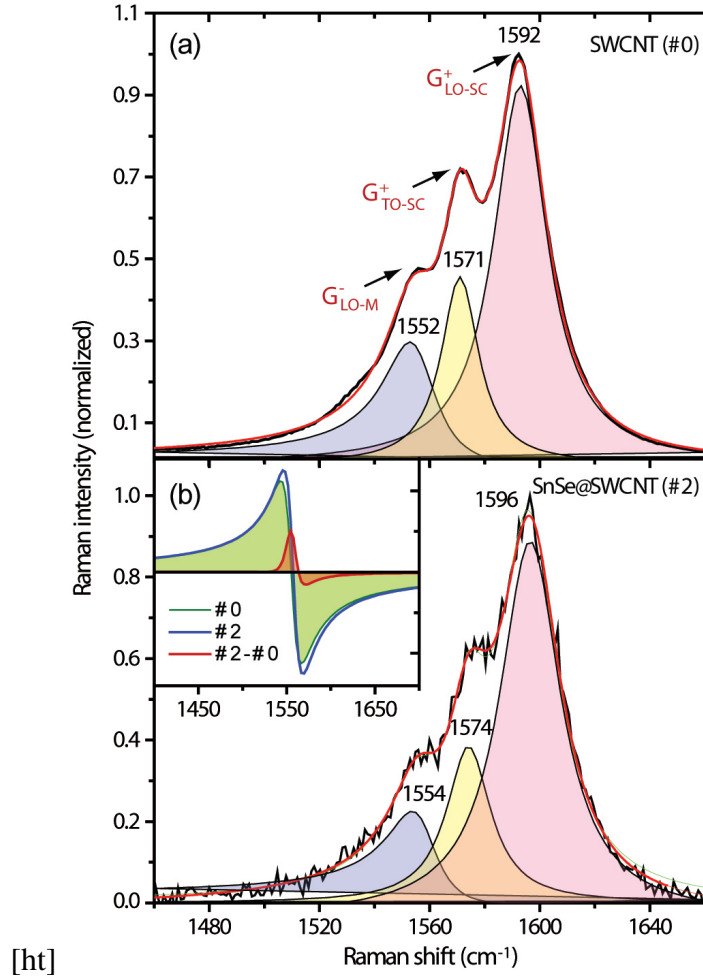


Figure 5: Normalized experimental Raman spectra of pristine and SnSe filled SWCNT fitted with a BWF function (G^- band) and two Lorentzian functions (G^+ TO and G^+ LO bands). (a): pristine SWCNT (NanoIntegraris 99% pure, sample # 0). (b): SnSe@SWCNT (sample # 2). In inset: BWF interference functions for SWCNT (green contour), sample # 2 (solid blue line), and differences of BWF interference functions between sample # 2 and SWCNT (red contour).

375 for the Sn atom, and at 31, 54, 72, 124, 150, 174, 192 cm^{-1} for the Se atom. Therefore, one can
 376 conclude that the phonon DOS of the standalone Sn_4Se_4 nanowire distinguishes from the bulk
 377 crystal with several specific vibrational signatures appearing around 30, 54 and 150 cm^{-1} and pos-
 378 sibly recognizable in the experiment.

379 On the other hand, the vibrational frequencies at Γ point for the Sn_4Se_4 and Sn_6Se_6 1D nanowires
 380 are compiled in Table 2 for the HSE functional. In the case of the Sn_4Se_4 wire, the calculated fre-
 381 quencies are within 7 - 12 cm^{-1} (i.e. either downshifted or upshifted) with respect to the observed
 382 ones in the spectra of the two SnSe@SWCNT samples. The modes computed at 181 and 194 cm^{-1}

383 are pure radial SnSe breathing vibrations related to an experimental line appearing between 185
 384 and 187 cm^{-1} with relatively strong intensity in the Raman spectrum of filled samples.

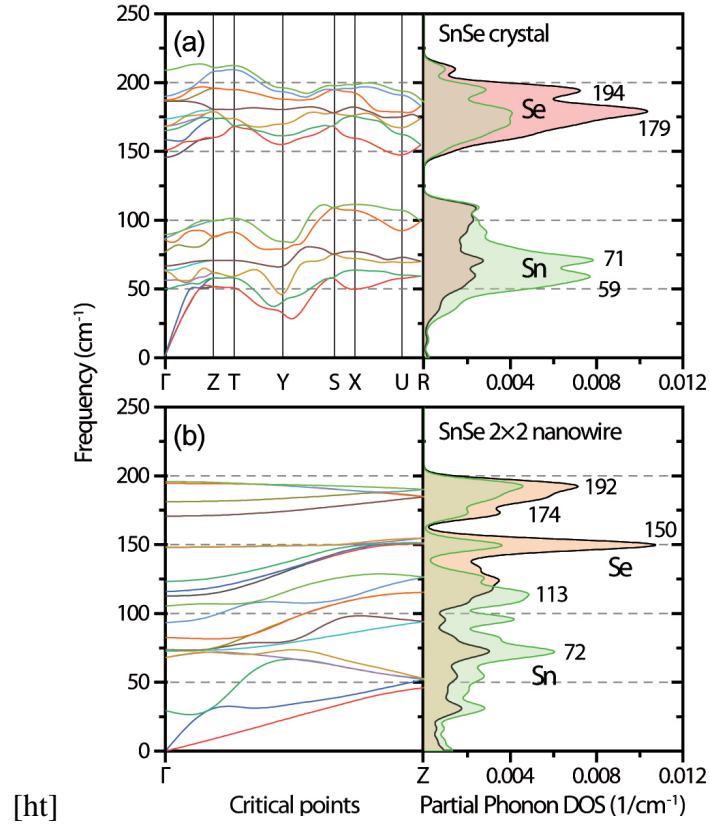


Figure 6: Calculated phonon dispersions and density of states of SnSe crystals: (a) 3D $Pnma$ crystal; (b) 1D $p4_2/mmc$ Sn_4Se_4 crystal with dominating flat bands.

385 The computed phonon DOS ρ_{1D} for the Sn_4Se_4 wire shows several features at 117, 150, 174, and
 386 192 cm^{-1} which are near the additional Raman lines found in experimental spectra (Fig. 6(b)). The
 387 phonon DOS shows that the heavier Sn atoms and the lighter Se atoms contribute mainly to the
 388 acoustic and optical modes, respectively. In particular, the maximum DOS at 150 and 192 cm^{-1}
 389 corresponds to unique flat bands of the phonon dispersion dominated by Se atoms which may lead
 390 to low lattice thermal conductivity in the Sn_4Se_4 nanowire due to the anharmonic scattering of
 391 phonons. Meanwhile the group velocity along Γ -Z direction seems lower in the Sn_4Se_4 nanowire
 392 than in the bulk, consistent with flattening of the phonon dispersion curves in this nanowire. In the
 393 case of the Sn_6Se_6 wire, there is also a very good match between calculated and experimental Ra-
 394 man frequencies at the zone center (Table 2).

Table 2: Calculated Γ -point frequencies (cm^{-1}) for Sn_4Se_4 and Sn_6Se_6 nanowires.

Sn_4Se_4 (2×2)								
A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_g	A_{2u}	B_{1u}	B_{2u}	E_u
	29	73	83	68			93	74
					105			
113				116			123	
	148		148					
								171
181		194						196
Sn_6Se_6								
A_{1g}	A_{2g}	B_{2g}	E_{1g}	E_{2g}	A_{2u}	$B_{1u}+B_{2u}$	E_{1u}	E_{2u}
	22							
	83		83					90
		121		108		112	110	
				135	135		132	
163		186	172	150		162		181
						230		222
246				254				

395 The highest calculated Raman frequencies at the HSE level occur at 194 (B_{1g}) and 254 cm^{-1} (B_{2g})
396 for the Sn_4Se_4 and Sn_6Se_6 wires, respectively, while the highest experimental Raman frequency not
397 assignable to SWCNTs is found at 235 cm^{-1} in the Raman spectrum of one of the SnSe@SWCNT
398 composites. Regarding this band, we note also that phonon calculation of a trigonal-Se crystal with
399 fixed cell parameters using PBE and HSE06 functionals gives a Raman active mode at 227 cm^{-1} ,
400 and 236 cm^{-1} , respectively, close to the experimental value at 235 cm^{-1} (A_1 mode) [49,50]. De-
401 spite that this Raman band observed at 235 cm^{-1} might be the signature of t-Se presence in the
402 samples [51,52], there is no other analytical evidence of this material in the composite or of its for-
403 mation above the melting point of SnSe during the synthesis process. Therefore, we ascribe the 235
404 cm^{-1} line to Sn_6Se_6 embedded nanowires.

405 Finally, the phonon dispersion in the 3D SnSe crystal shows a phonon gap of about 50 cm^{-1} in
406 all directions of the BZ with phonon branches clearly segregated into two groups of frequencies
407 centered at 70 and 180 cm^{-1} (Fig. 6(a)). By comparison, the phonon branches of the 1D Sn_4Se_4
408 nanowire do not extend beyond 200 cm^{-1} with a phonon gap of about 20 cm^{-1} along Γ -Z between
409 150 and 175 cm^{-1} (Fig. 6(b)). While the phonons energies at $q > 0$ in the Sn_6Se_6 nanowire could

410 not be calculated at HSE level with FD method due to limitations stemming from the large size of
 411 the supercell, the $q = 0$ phonons frequencies have been determined and are reported in Table 2.
 412 The absence of negative frequencies in the vibrational calculations and phonon dispersion relations
 413 shows that the standalone 1D nanowires Sn_4Se_4 and Sn_6Se_6 are structurally stable.

414 3.5 Nanotube-nanowire interaction

415 To estimate the nanotube interaction with the encapsulated SnSe crystals we considered the case
 416 of the embedded Sn_6Se_6 nanowire. The cross section of the DFT optimized standalone Sn_6Se_6
 417 crystal is systematically expanded compared to the crystal diameter of $\sim 6.2 \text{ \AA}$ revealed by HRTEM.
 418 In fact, the Sn_6Se_6 crystals can fit into (9,9) tubes of
 419 1.22 nm diameter, which infers for a substantial compressive stress on the Sn_6Se_6 crystal as the Se
 420 distance to the SWCNT wall is $\sim 3.0 \text{ \AA}$, i.e. smaller than the sum of Sn and C van der Waals radii
 421 $\sim 3.5 \text{ \AA}$.

Table 3: Lennard-Jones parameters of $\text{Se} \cdots \text{C}$ interaction. Forces on the Se atom in the composite $\text{SnSe@SWCNT}(9,9)$ and on the Sn_6Se_6 standalone nanowire after optimization (in eV/\AA).

		Cartesian coordinates of forces			Cross-section
		x	y	z	$\sigma \text{ (\AA)}$
	Sn_6Se_6	-0.00044	0	0	7.302
[ht]	Se in (9,9) tube	0.48822	0.02555	-0.00259	
		Lennard-Jones parameters			Distance
		$E \text{ (eV)}$	$r_0 \text{ (\AA)}$	$R_{\min} - R_{\max} \text{ (\AA)}$	$d \text{ (\AA)}$
	$\text{Se} \cdots \text{C}$	0.020	3.52	0.5 – 10	2.98

422 To estimate the nanotube interaction with the encapsulated Sn_6Se_6 crystal, we derived a simple
 423 model involving a Lennard-Jones (LJ) potential for a pair of non-bonded Se and C atoms:

$$424 \quad V(r) = -\epsilon \left[(r_0/r)^{12} - 2(r_0/r)^6 \right] \quad (12)$$

425 where ϵ corresponds to the cohesion energy, and r_0 - to the equilibrium distance between the
 426 atoms, which is usually taken as a sum of their van der Waals radii. Due to the two-body and short-
 427 range nature of LJ interaction, it is sufficient to calculate on a single protruding Se atom the resul-

428 tant force applied by a finite segment of a (9,9) SWCNT (5 unit cells in our case). The as calcu-
429 lated force on Se atoms was compared to that exerted on the Se atom in a Sn₆Se₆ crystal during
430 optimization *in vacuo*. We established that for realistic Se···C interaction parameters (Table 3)
431 the intra-nanowire expansion force obtained from the DFT calculations for the standalone Sn₆Se₆
432 1D crystal is compensated by a repulsive LJ force of 0.488 eV/Å at a distance of ~2.98 Å between
433 the Se atoms and the SWCNT wall. This fact evidences that although Sn₆Se₆ is stable in vacuo,
434 its geometry in encapsulated form is influenced by the pressure exerted from the surrounding
435 SWCNT. On the other hand, the force constant corresponding to the LJ interaction, being of or-
436 der of $72\epsilon/r_0^2 \approx 0.116 \text{ eV/\AA}^2$, is too small to affect significantly the vibrational frequencies of the
437 Sn₆Se₆ crystal, where typical Sn-Se force constants are more than an order of magnitude larger.
438 Therefore, the normal mode analysis based on DFT calculations for the standalone crystal is repre-
439 sentative for the encapsulated crystal, as well.

440 4 Conclusion

441 We have performed a combined experimental and theoretical study of SnSe@SWCNT compos-
442 ites where periodic DFT calculations support the Raman spectra recorded on several samples. At
443 the HSE level of theory, the Sn₄Se₄ 1D crystal exhibits a direct gap larger than that of the 3D crys-
444 tal allowing direct optical excitations in the near infrared. In contrast, the band structure of the 1D
445 hexagonal crystal is typical to that of a semimetal due to the overlap at the Fermi level of the upper
446 valence band and the lower conduction band with small density of states at the Fermi energy. The
447 calculated vibrational frequencies of the two standalone 1D SnSe nanowires are consistent with
448 supplemental Raman lines observed in the Raman spectra of SnSe@SWCNT composites. Addi-
449 tionally, Raman experiments show that the encapsulated SnSe nanowires modify the electronic and
450 vibrational properties of the surrounding SWCNT walls.

451 **Supporting Information**

452 Supporting Information File 1:

453 File Name: snse-nano_SI.pdf

454 File Format: PDF

455 Title: Workfunction and projected electronic density of states of the stand-alone tin selenide
456 nanowires.

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