Supplementary Information

Inorganic hybrid materials integrating carbon nanotubes with osmium compounds: formation mechanisms, structure and reactivity

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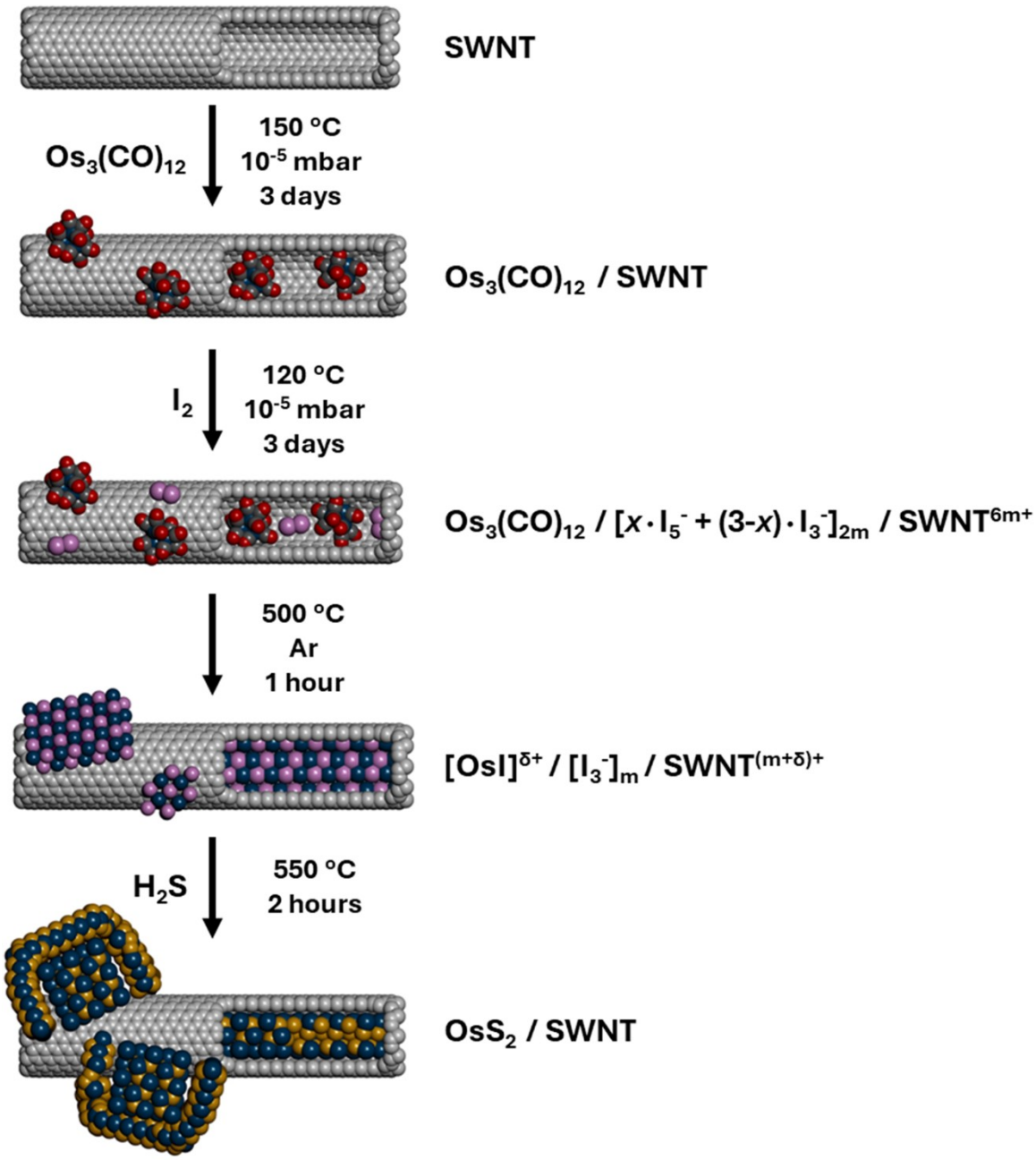

Fig. S1 Schematic diagram showing the synthetic route used to form osmium monoiodide and osmium disulphide using SWNTs.

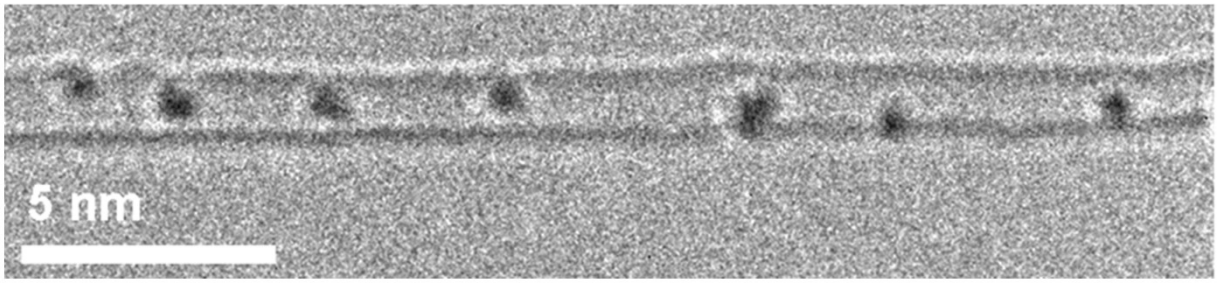

Fig. S2 200 kV HRTEM image of $Os_3(CO)_{12}$ / SWNT showing the clusters engaging in an electron beam-induced ejection (EBIE) process destroying the nanotube sidewall.

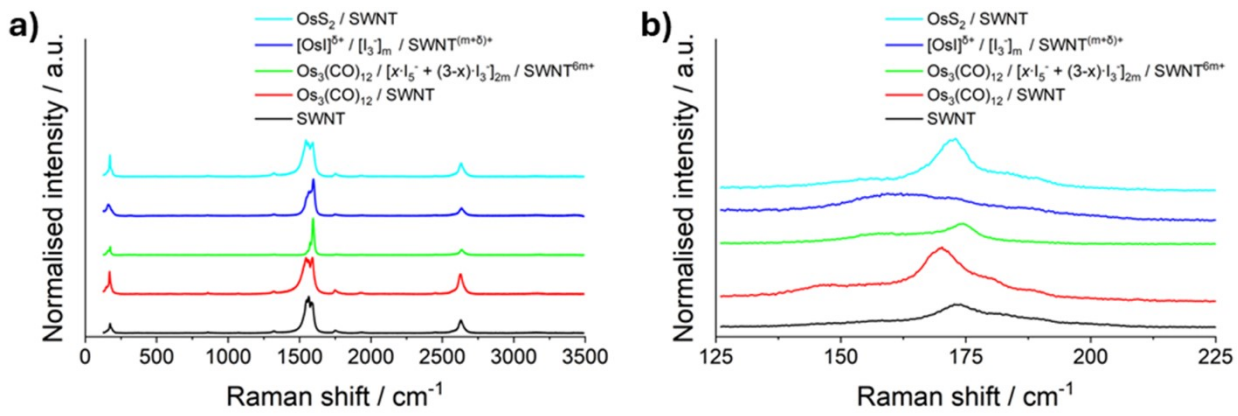

Fig. S3 (a) Comparison of the full 660 nm resonance Raman spectra of metallic nanotubes (b) highlighting the changing positions of the radial breathing modes during stepwise synthesis: empty SWNTs (black), $Os_3(CO)_{12}$ / SWNT (red), $Os_3(CO)_{12}$ / $[x{\cdot}I_5^- + (3\text{-}x){\cdot}I_3^-]_{2m}$ / $SWNT^{6m+}$ (green), $[OsI]^{\delta+}$ / $[I_3^-]_m$ / $SWNT^{(m+\delta)+}$ (blue), and OsS_2 / SWNT (light blue).

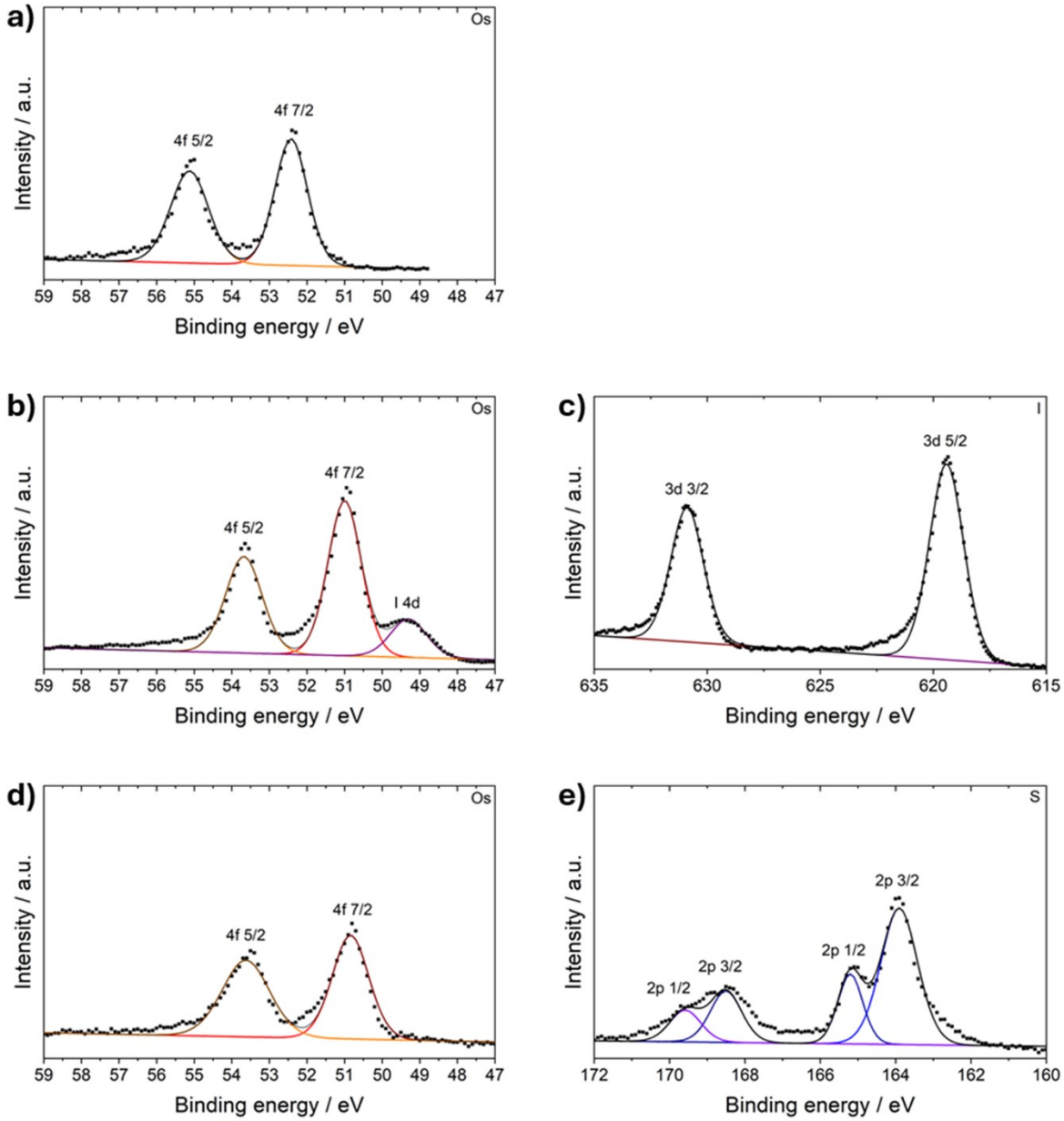

Fig. S4 High-resolution XPS scans of Os *4f*, I *3d*, and S *2p* for (a) $Os_3(CO)_{12}$ / SWNT, (b,c) $[OsI]^{\delta+}$ / $[I_3^-]_m$ / $SWNT^{(m+\delta)+}$ and (d,e) OsS_2 / SWNT in the stepwise synthesis.

Table S1 Binding energies observed in each sample for osmium, iodine and sulphur.

Sample	Os $4f_{7/2}$ / eV	I $3d_{5/2}$ / eV	S $2p_{3/2}$ / eV
$Os_3(CO)_{12}$ / SWNT	52.4	-	-
$[OsI]^{\delta+}$ / $[I_3^-]_m$ / $SWNT^{(m+\delta)+}$	51.0	619.4	-
OsS_2 / SWNT	50.8	-	163.9

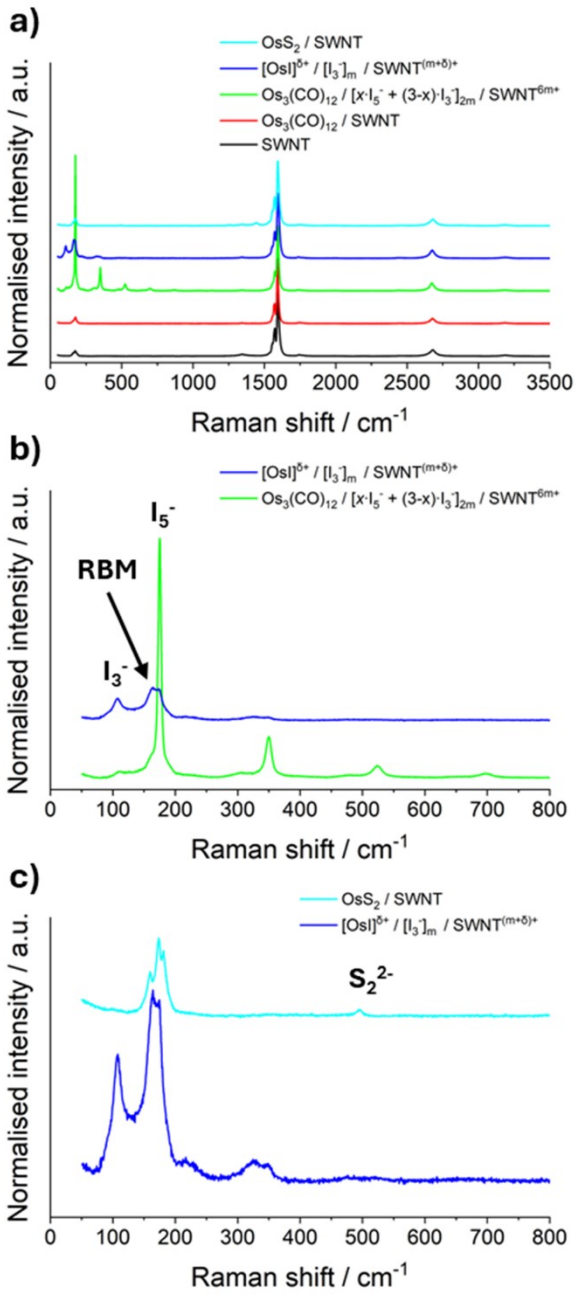

Fig. S5 (a) Comparison of the full 532 nm resonance Raman spectra of semiconducting nanotubes (b) highlighting the changing relative intensities of polyiodide species (I_3^- at 109 cm^{-1}; I_5^- at 175 cm^{-1}, including harmonics at 350, 525 and 700 cm^{-1}) and (c) providing tentative evidence for sulphide species (S_2^{2-} at 496 cm^{-1}) following reaction of OsI with H_2S observed during stepwise synthesis: empty SWNTs (black), $Os_3(CO)_{12}$ / SWNT (red), $Os_3(CO)_{12}$ / $[x{\cdot}I_5^- + (3\text{-}x){\cdot}I_3^-]_{2m}$ / $SWNT^{6m+}$ (green), $[OsI]^{\delta+}$ / $[I_3^-]_m$ / $SWNT^{(m+\delta)+}$ (blue), and OsS_2 / SWNT (light blue).

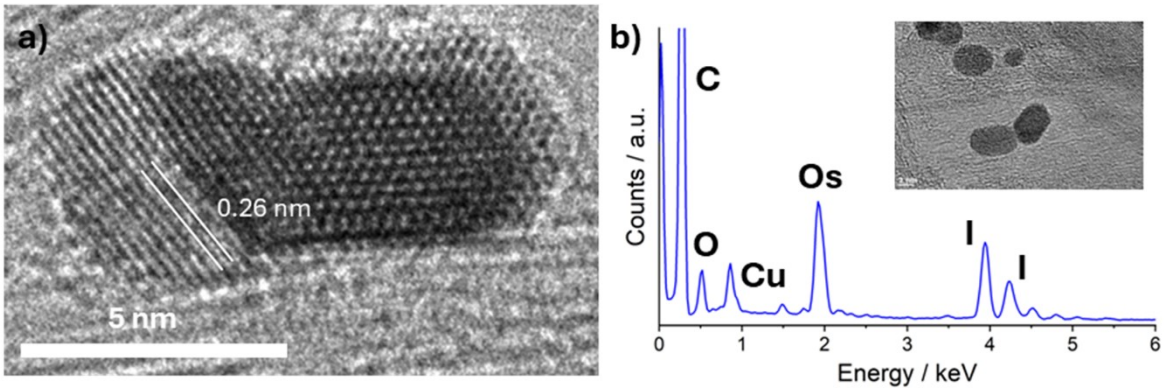

Fig. S6 (a) 80 kV AC-HRTEM image showing two overlapping nanoparticles (the lefthand side shows the same d-spacing as in Fig. 2b, whilst the righthand side shows a hexagonal projection). (b) EDX spectrum of OsI nanoparticles showing the presence of Os and I in a 1: 1.2 stoichiometry. Inset is a TEM image of the area measured over.

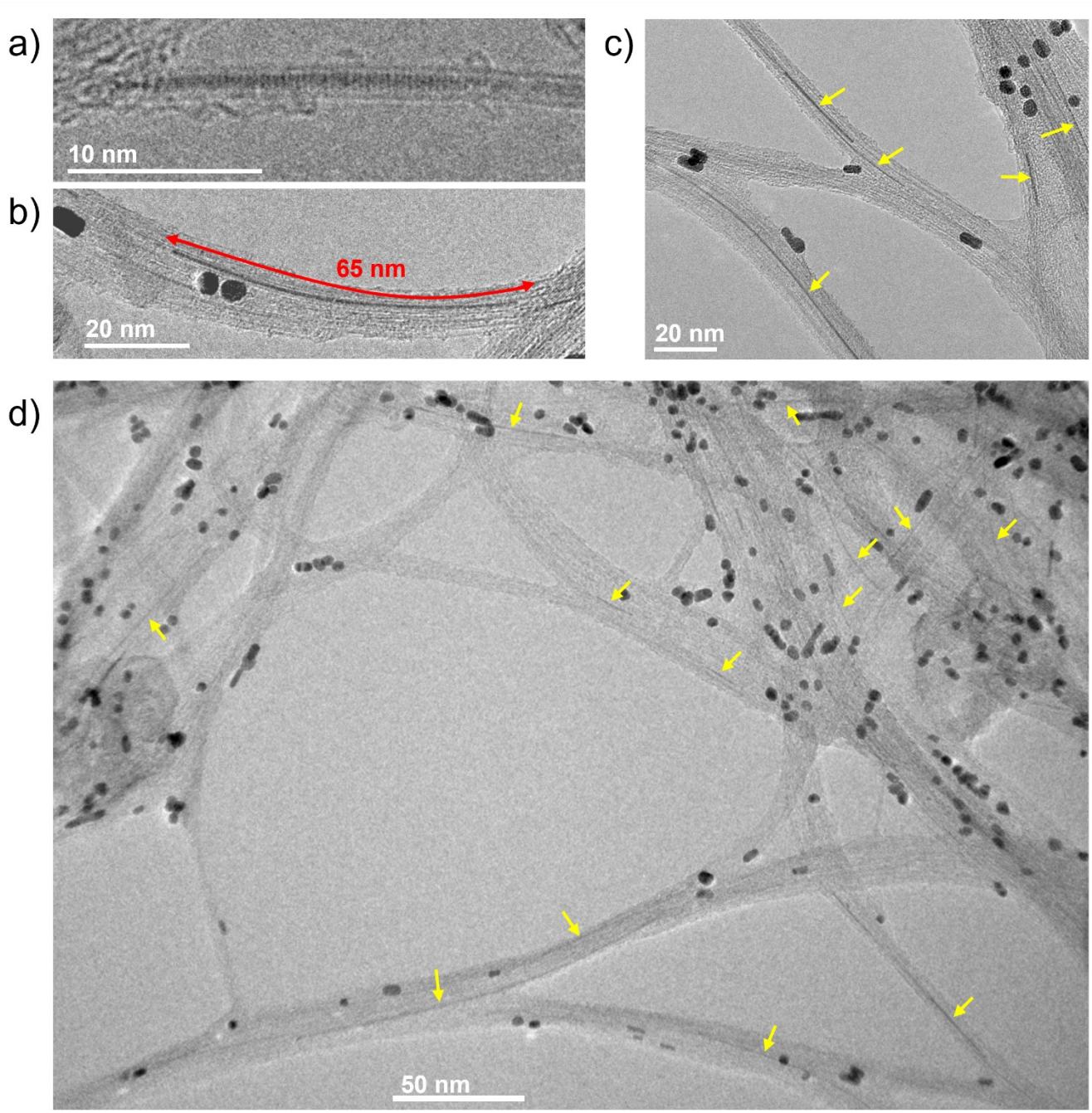

Fig. S7 200 kV TEM images of OsI nanostructures inside and outside SWNTs. (a) A HRTEM image of an OsI nanowire within SWNT, with lattice fringes indicating crystallinity, and (b), (c) and (d) lower-magnification TEM images showing the distribution of lengths of OsI nanowires, typically >20 nm and measuring up to 65 nm, which are found within approximately 1 in 10 nanotubes. Yellow arrows in (c) and (d) indicate the locations of confined OsI nanowires.

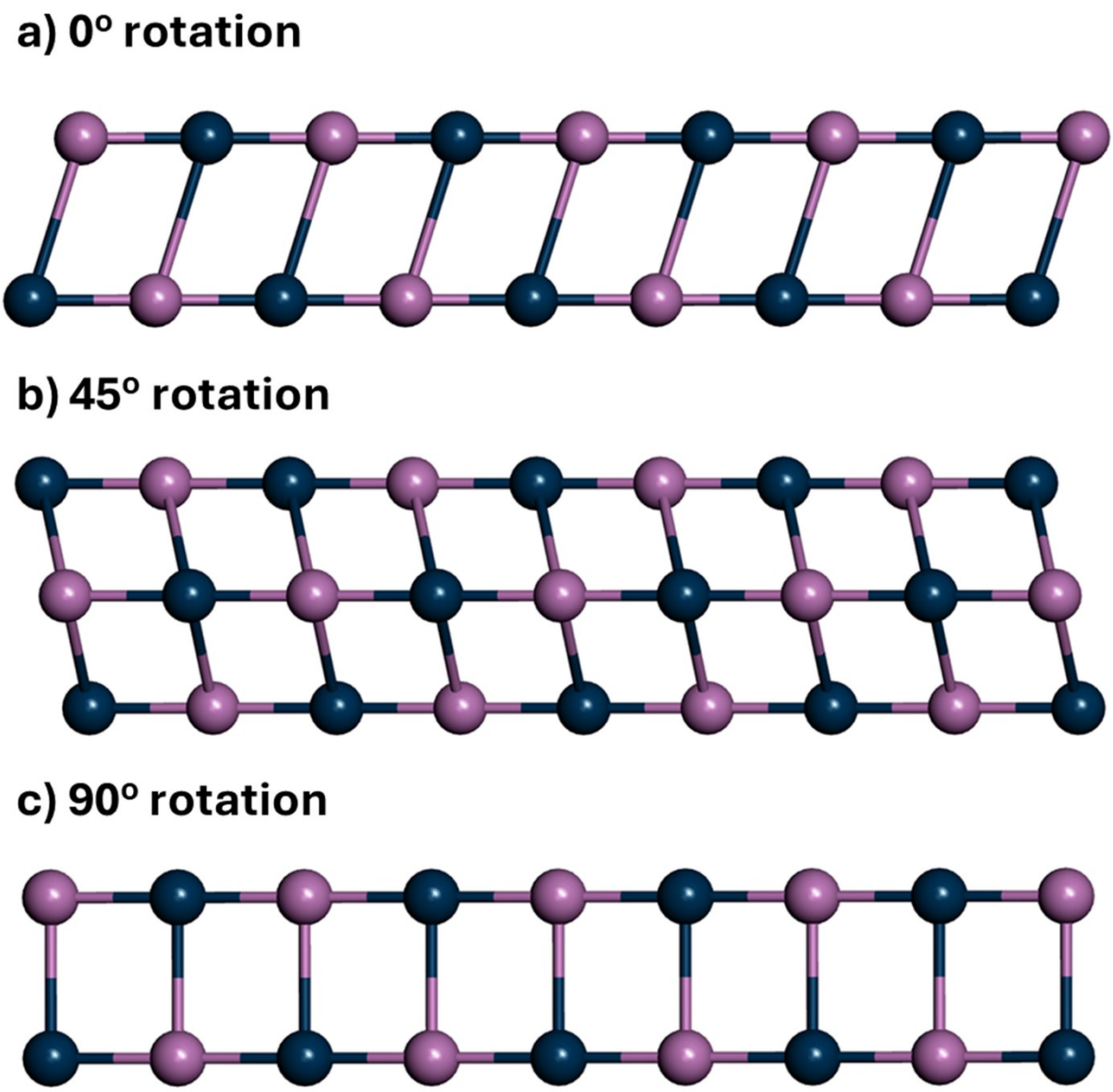

Fig. S8 Structural models of proposed OsI nanowires showing different rotations along the nanowire axis; (a) 0°, (b) 45° and (c) 90° rotation. The osmium and iodide atoms are represented by blue and pink spheres, respectively.

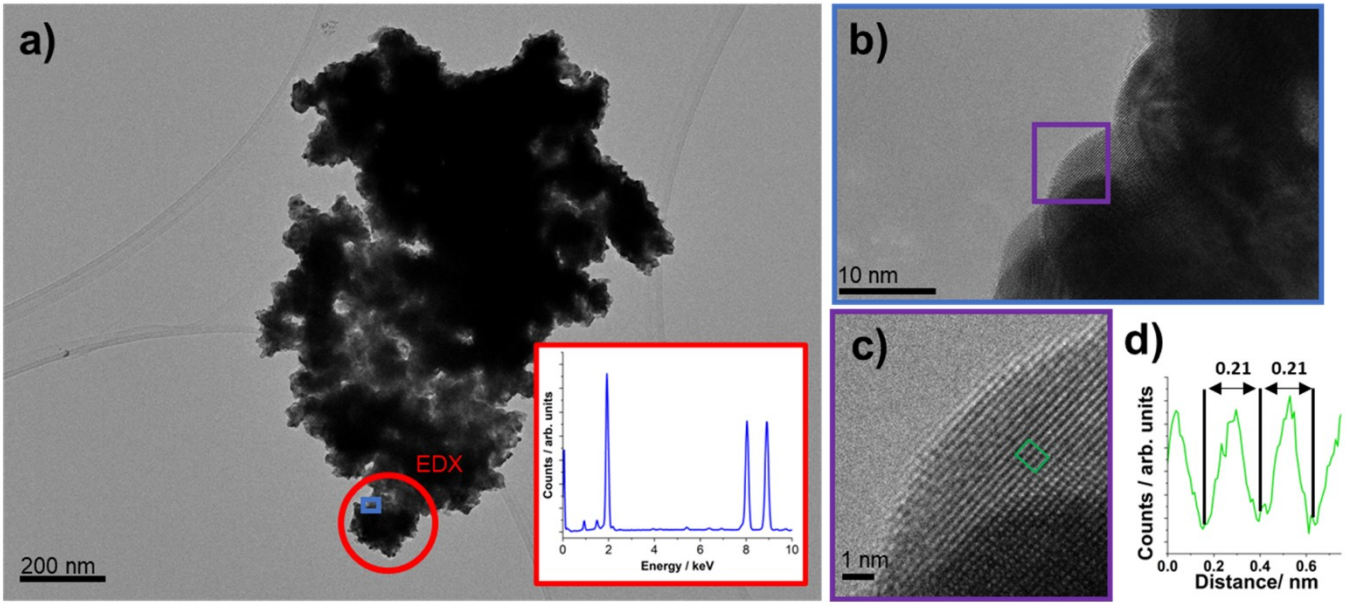

Fig. S9 TEM/EDX analysis of Os nanoparticles produced in a control reaction in the absence of SWNTs. In this reaction, $Os_3(CO)_{12}$ (5 mg) and iodine (10 mg) were sealed in a Pyrex ampoule (10^{-4} mbar) and heated (120 °C, 3 days). The ampoule was then cooled in an ice bath. The following material was then heated under argon (500 °C, 1 hr). The resulting material (> 1 mg) was analysed by TEM and EDX. The afforded product is aggregated Os nanoparticles as seen in TEM images a), b) and c). Inset in a) is an EDX spectrum (obtained from the area denoted with a red circle) with peaks at 1.91 and 8.91 keV consistent with the Lα and M X-ray emissions, respectively, expected for Os. Minor peaks correspond to trace quantities of C and I (Cu is due to the TEM grid). The d-spacings observed in c) and quantified in d) match well with those for Os (011) (see 10.1524/zkri.1937.96.1.497).

Video S1 80 kV TEM image series (10 frames per second) of OsS_2 / SWNT, showing the nanowire rotating and translating within the cavity of the SWNT.