Supporting Information

Structural and Chemical Analysis of Gadolinium Halides encapsulated within WS_2 Nanotubes

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S20 Video5-MD-$GdBr_3$-WS_2 or https://youtu.be/d-8u_snql1c

S21 Video6-MD-GdI_3-WS_2 or https://youtu.be/qVDE1vEXxo8

S22 Video7-MD-$GdCl_3$-WS_2 2 or https://youtu.be/MGoYMfXv4ZE

Scheme S1 Formation of GdX_3 (X=Cl, Br, I) filled WS_2 nanotube

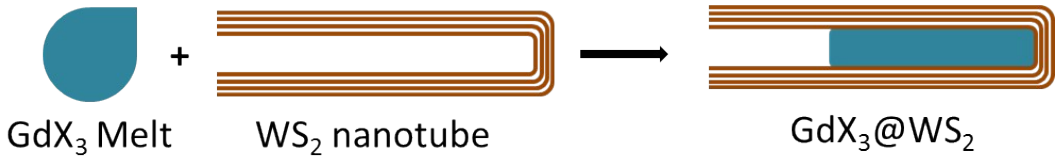


Table S1 Experimental Conditions of the filling of the WS_2 Nanotubes with GdI_3 (Melting Point 926 °C). Temperature at which the filling reaction was carried out: 1000 °C (3° C/min heating and cooling rate).

Sample	WS_2 NTs	GdI_3	Wt Ratio	Reaction Time	Reaction Temperature
1	30 mg	150 mg	1:5	72 h	1000°C
2	30 mg	225 mg	1:7	168 h	1000°C
3	30 mg	300 mg	1:10	168 h	1000°C

Table S2 Experimental Conditions of the filling of the WS_2 Nanotubes with $GdBr_3$ (Melting Point 770 °C). Temperature at which the filling reaction was carried out – 1000 °C (3° C heating and cooling rate).

Sample	WS_2 NTs	$GdBr_3$	Wt Ratio	Reaction Time	Reaction Temperature
1	20 mg	50 mg	1:2.5	168 h	1000°C

2	20 mg	100 mg	1:5	168 h	1000°C
3	20 mg	200 mg	1:10	168 h	1000°C
4	20 mg	300 mg	1:15	168 h	1000°C

Table S3 Experimental Conditions of the filling of the WS_2 Nanotubes with $GdCl_3$ (Melting Point 609 °C). Temperature at which the filling reaction was carried out: 1000 °C (3° C/min heating and cooling rate).

Sample	WS_2 NTs	$GdCl_3$	Wt Ratio	Reaction Time	T
1	20 mg	50 mg	1:2.5	168 h	1000°C
2	20 mg	100 mg	1:5	168 h	1000°C
3	20 mg	200 mg	1:10	168 h	1000°C
4	20 mg	300 mg	1:15	168 h	1000°C

Table S4 EDS elemental quantification of Gd and I in GdI_3@WS_2 NT (Ref: Figure 1c) using Gd-L and I-L peaks.

Element	Atomic%
Gd(M)	25.8
I(L)	74.2

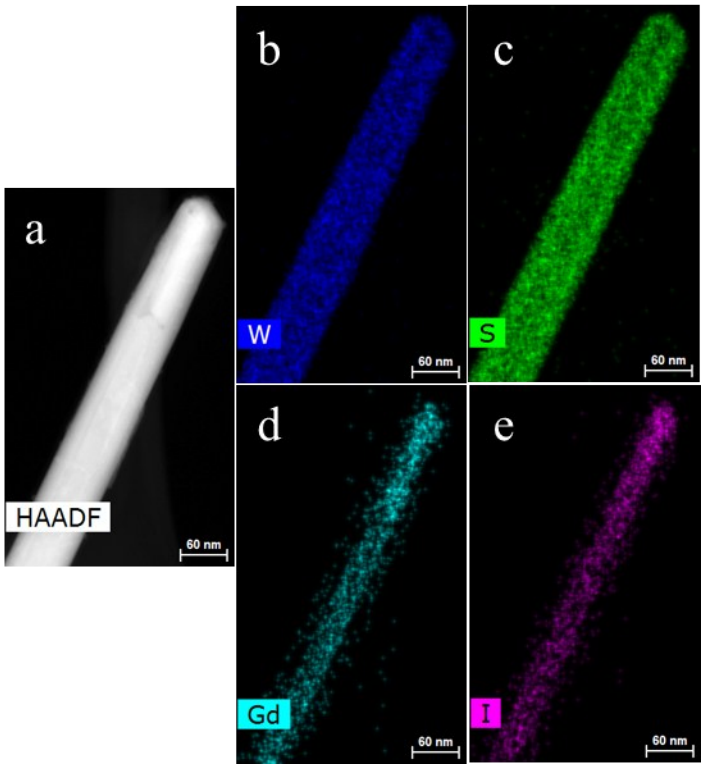


Fig. S1 a) HAADF-STEM image of the GdI_3 filled WS_2 nanotubes and b-e) corresponding EDS elemental maps showing W, S, Gd and I.

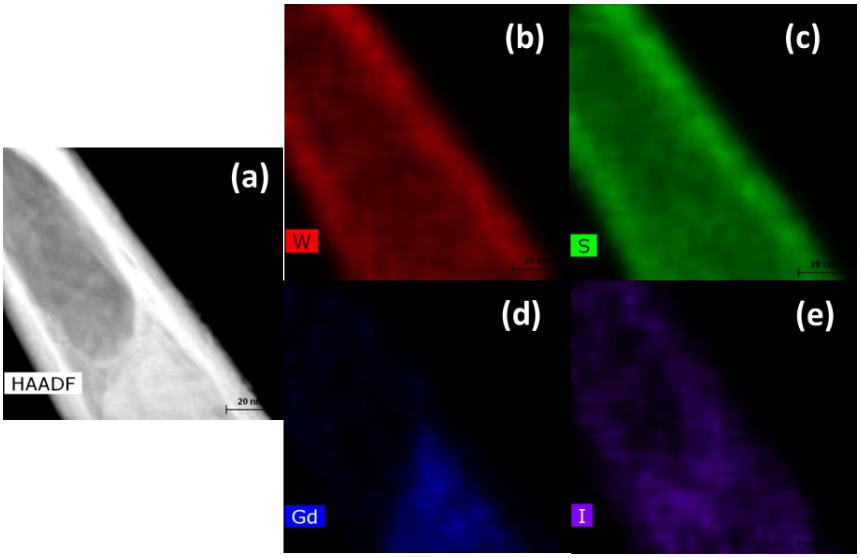


Fig. S2 HAADF-STEM image of the GdI_3 filled WS_2 structure (a) and corresponding EDS elemental maps showing W (b), S (c), Gd (d) and I (e).

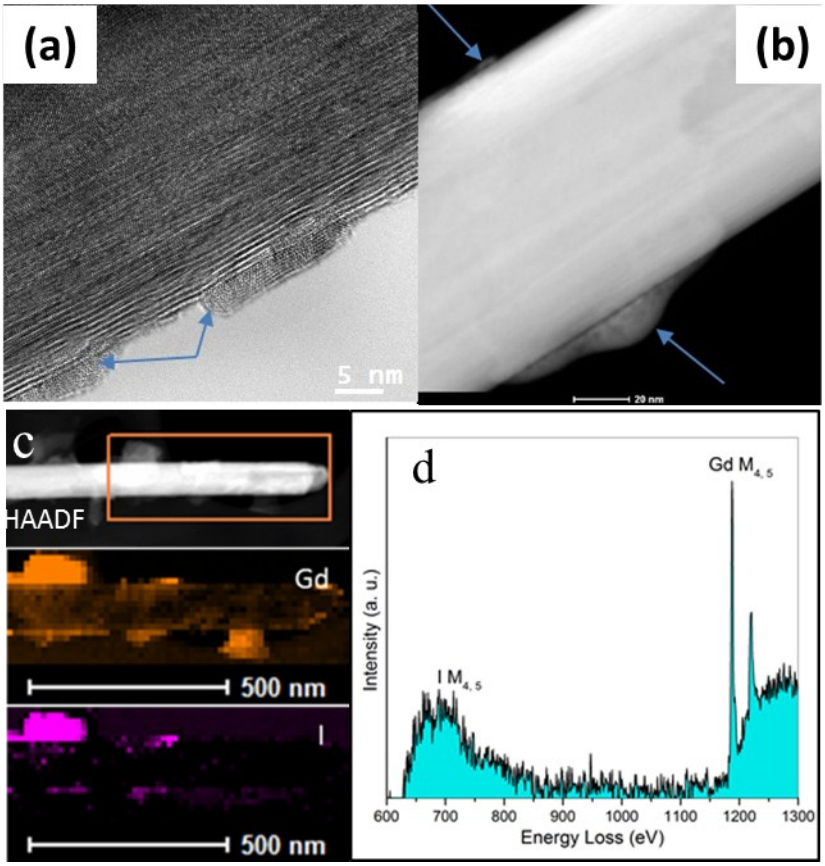


Fig. S3 a) and b) are HRTEM and HAADF-STEM images of GdI_3@WS_2 nanotubes showing the presence of GdI_3 inside the nanotube and on the surface obtained on using 1:10 ratio of WS_2: GdI_3. c) low magnification HAADF-STEM image of GdI_3@WS_2 and the corresponding EELS spectrum images showing Gd and I. d) EELS spectrum.

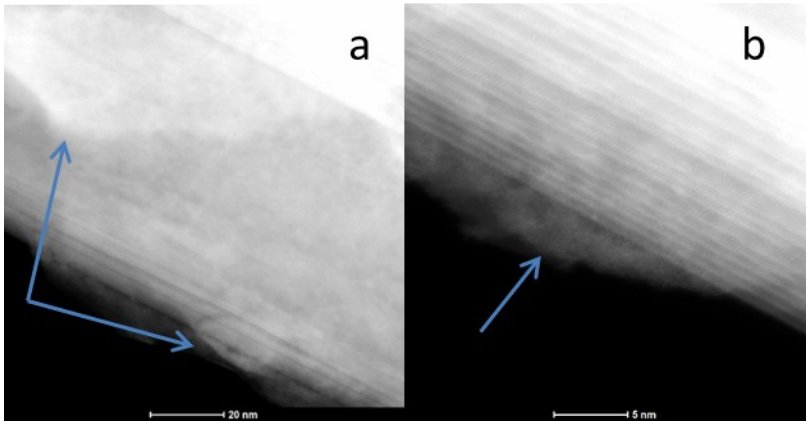


Fig. S4 HAADF-STEM images of $GdBr_3$ filled and coated WS_2 Nanotubes. Arrows show the $GdBr_3$ on the surface of WS_2 nanotube.

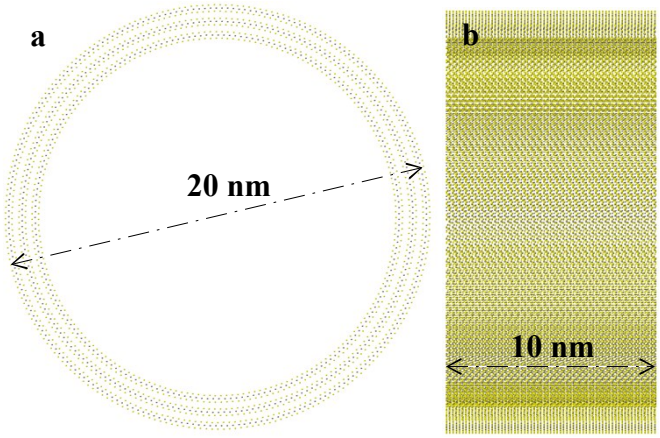
HRTEM Image Simulation

For the HRTEM image simulations, the models of the empty WS_2 nanotube, GdI_3 nanorod and GdI_3@WS_2 composite were created with Crystal Maker v9.2.5. Due to the limit imposed by the modeling software on the maximum number of atoms, only small sections of the nanotubes were considered. In addition, the number of walls of the multiwall WS_2 had to be reduced. The HRTEM micrographs were simulated using a multislice algorithm, QSTEM, developed by Christoph Koch. While the use of this algorithm is not strictly correct - given the dimensions and high atomic weight of the elements considered, the simulated images allowed us to appreciate better the orientation of the metal halide crystals inside the nanotubes. The microscope parameters were: 200 kV, 1 µm of spherical aberration, 0.8 eV of energy resolution, defocus of 100, 50, 0, -50 and -100 nm.

Three models were built and their corresponding HRTEM images simulated: 1) an empty 3-layered WS_2 nanotube, 2) a rhombohedral GdI_3 crystallite, 3) the filled nanotube composite joining models 1) and 2).

1. Empty WS_2 nanotube

A three layered WS_2 nanotube with an external diameter of 20 nm diameter and length of 10 nm was modeled, bearing an interlayer spacing identical to that measured from the micrographs.



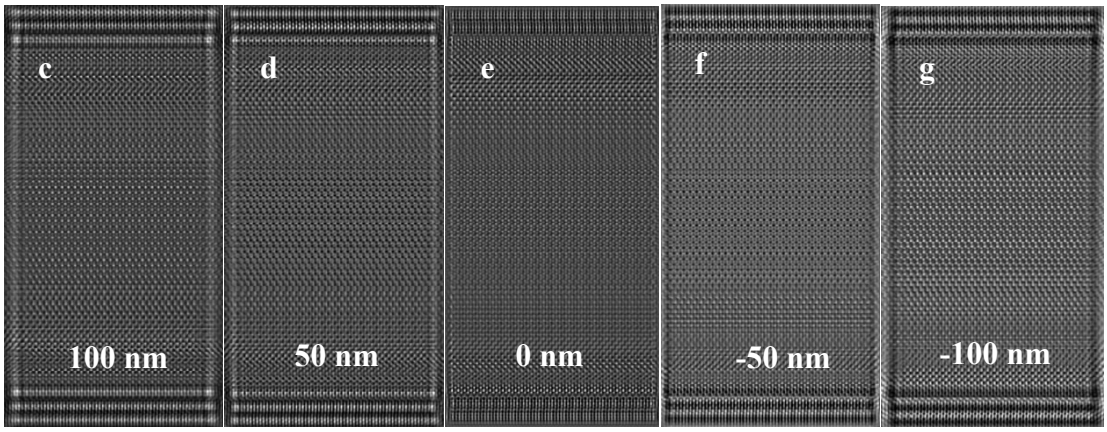


Fig. S5 a) and b) end-on and side-on views of the empty WS_2 nanotube model; c) – g) HRTEM simulated images of b) at different defocus values.

2. GdI_3 crystallite

The GdI_3 crystal, without the nanotube, was modelled with an orientation close to the real crystal as obtained from the FFTs. Zone axis of crystal is $<\bar{3}00>$ with $00\bar{3}$ planes that are oriented perpendicular to the viewer. The crystal is 16 nm in diameter in order to fit inside the 17.6 nm inner diameter WS_2 nanotube.

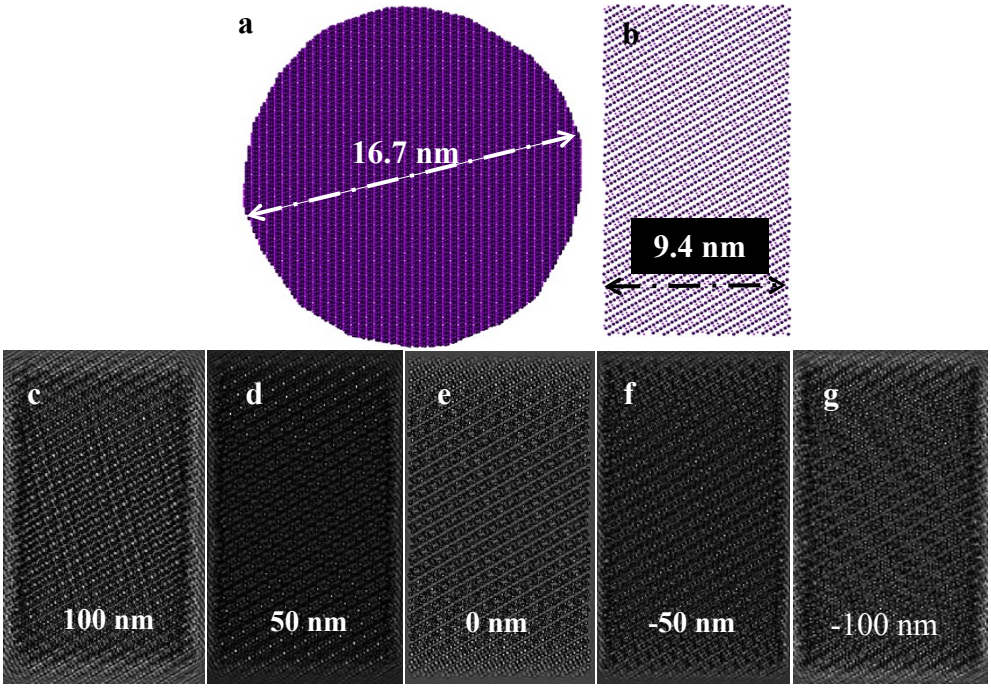


Fig. S6 a) and b) end-on and side-on views of the GdI_3 model; c) – g) HRTEM simulated images of b) at different defocus values.

3. GdI_3@WS_2 composite

The models of the multilayered WS_2 nanotube and the GdI_3 crystal were combined to construct the composite observed experimentally. The simulated HRTEM images confirm that it is easy to identify the filled section of the nanotube and the convex meniscus of the metal halide nanowire.

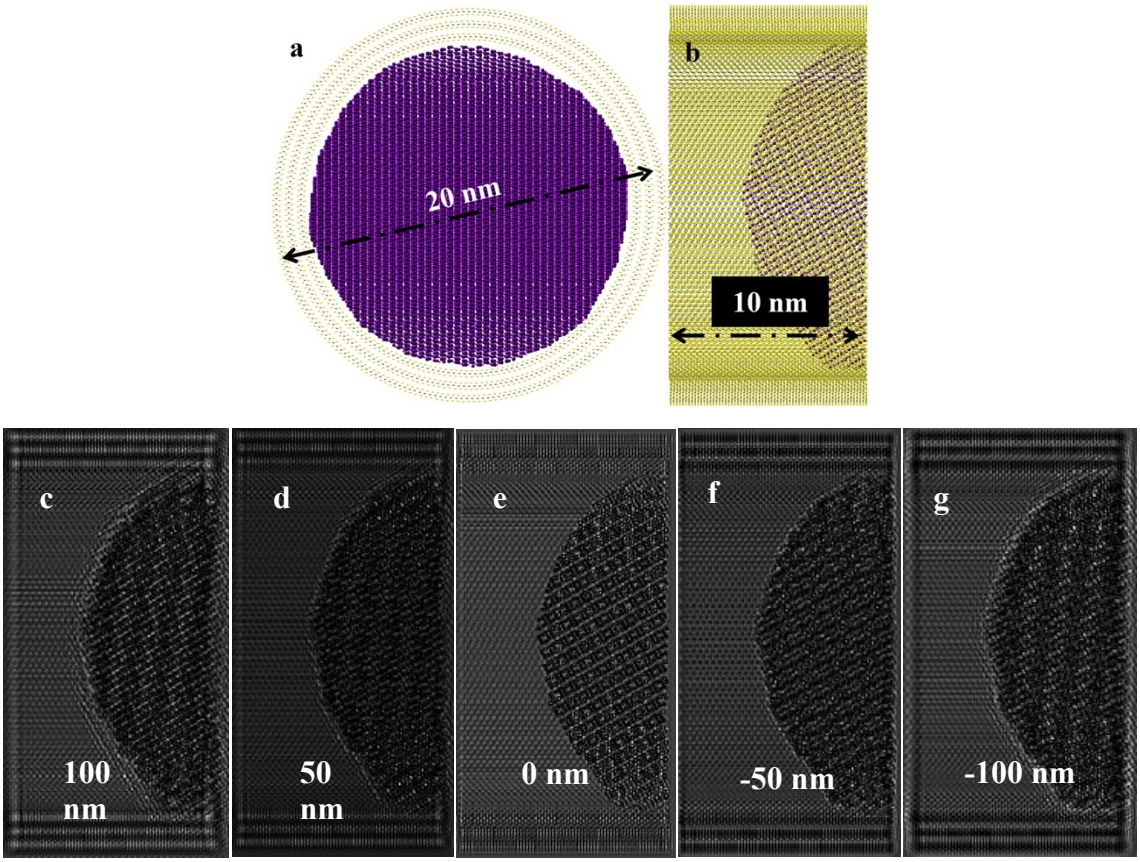


Fig. S7 a) and b) end-on and side-on views of filled nanotube model; c) – g) HRTEM simulated images of b) at different defocus values.

Further to the HRTEM micrographs, electron diffraction patterns were also simulated. For this, the software SIMULATEM was used. Instead of employing the entire model of the tube, flattened cut-sections of the empty and filled nanotube were employed to reproduce the square regions in Figure 4a where the FFTs were taken from. Both the ring-like reflections of the metal disulfide nanotubes and the lower frequency spots assigned to the GdI_3 crystal were obtained.

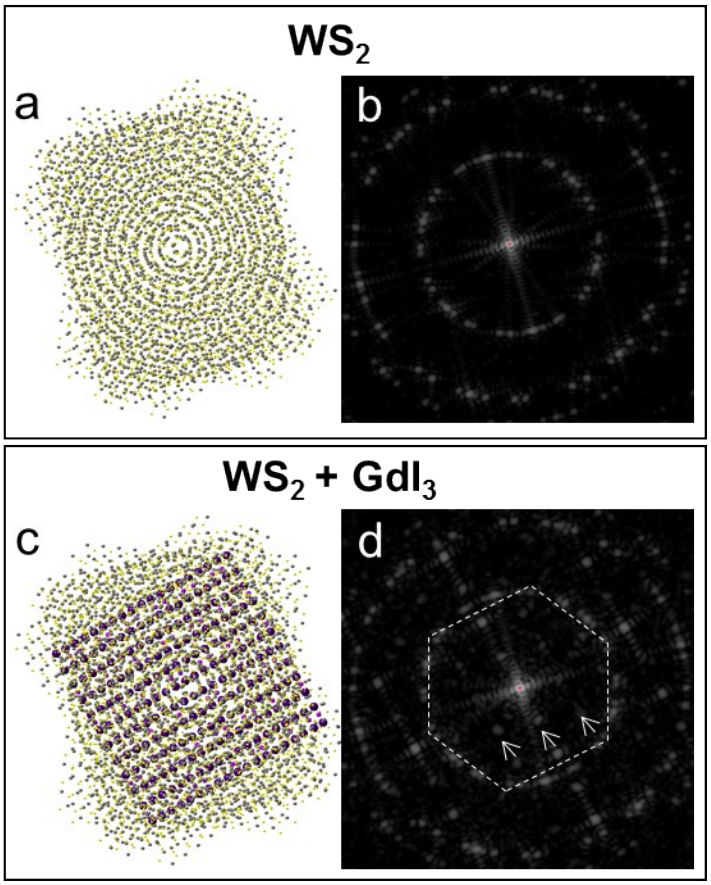


Fig. S8 a) Model for hexagonal WS_2 planes with interlayer stack rotation; b) Simulated ED pattern for a); c) Model for a heterostructure combining various WS_2 rotated monolayers and a GdI_3 crystallite on top; d) Simulated ED pattern for c).

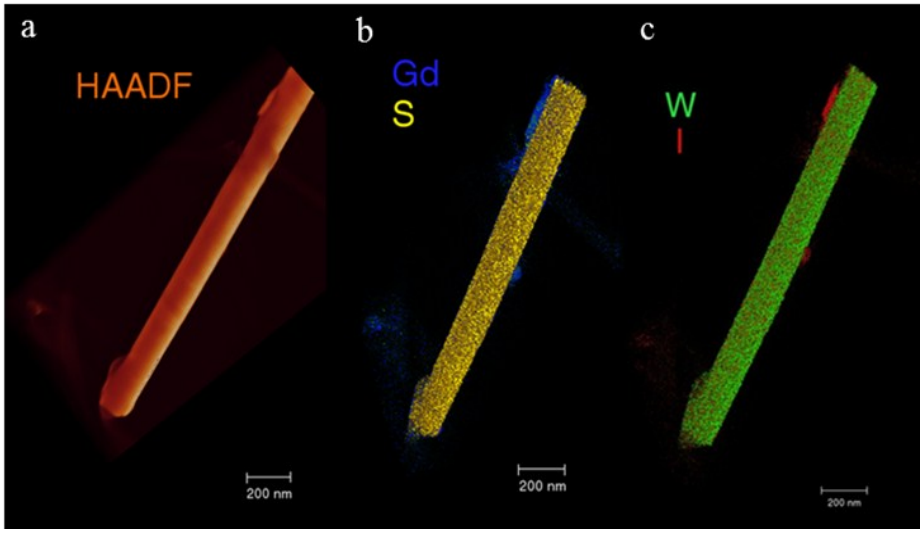


Fig. S9 Tomograms of GdI_3 coated WS_2 nanotube a) HAADF-STEM Image b) Gd (Blue) and S (Yellow) and c) W (green) and I (red).

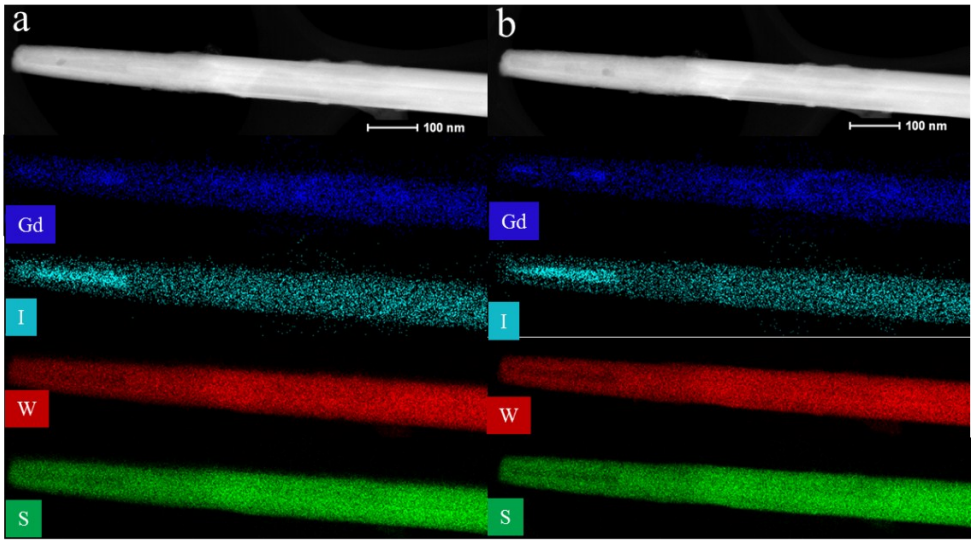


Fig. S10 HAADF-STEM (greyscale) and EDS elemental maps (Gd (blue), I (cyan), W (red), S (green)) of GdI_3 filled WS_2 a) at time 0 and b) after 30 minutes (after). The experiment was done at 80 kV using 0.64 nA probe current and a dose of 0.55 e/Å^{2}s.

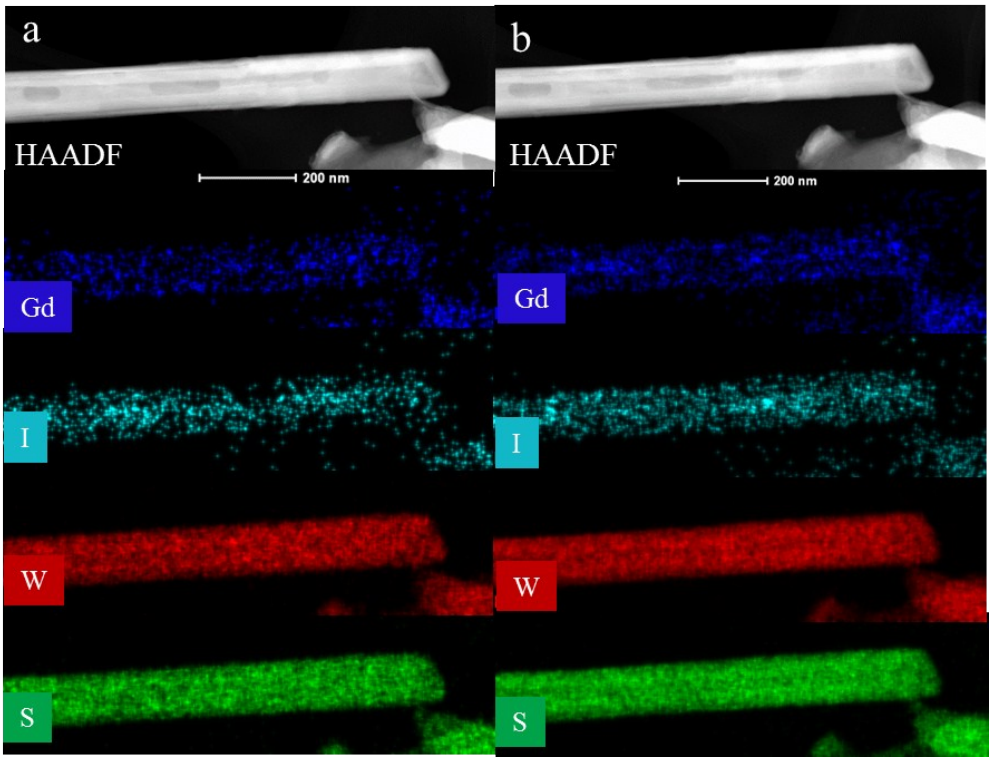


Fig. S11 HAADF images and EDS elemental maps (Gd (blue), I (cyan), W (red), S (green)) of GdI_3 filled WS_2 a) at time 0 and b) after 30 minutes of exposure. The experiment was done at 200 kV using 0.46 nA probe current and a dose of 0.40 e/Å^{2}s.

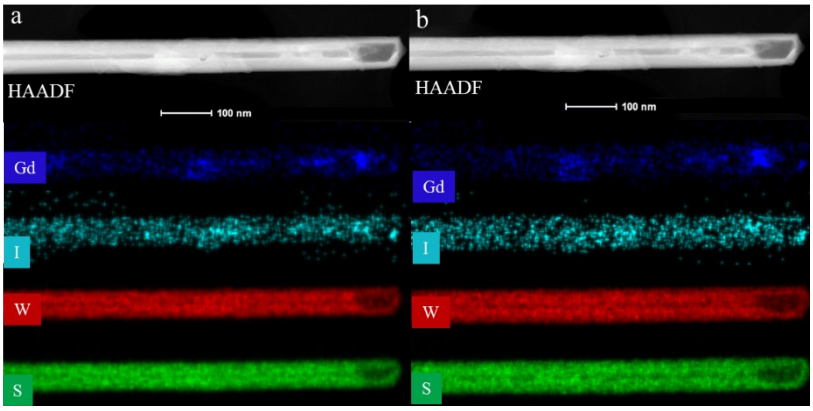


Fig. S12 HAADF-STEM and EDS elemental maps (Gd (blue), I (cyan), W (red), S (green)) of GdI_3 filled WS_2 a) at time 0 and b) after 30 minutes of exposure. The experiment was done at 200 kV using 0.46 nA probe current and a dose of 0.40 e/Å^{2}s.

Molecular Dynamics Simulations

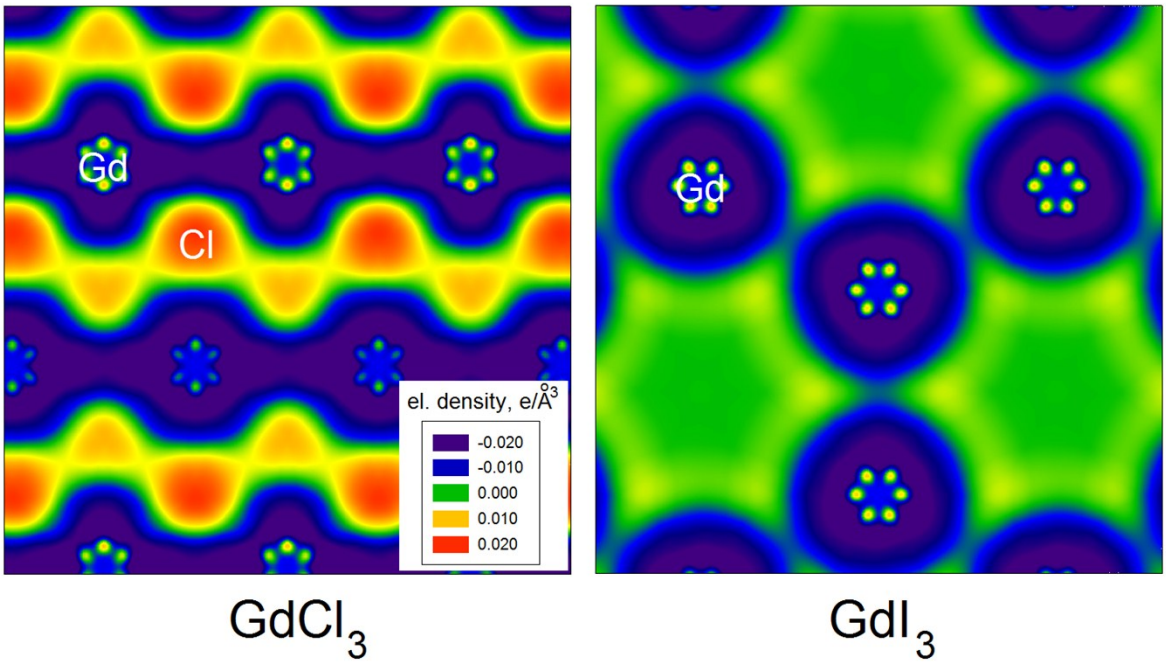


Fig. S13 Electron density redistribution in the layered crystals of $GdCl_3$ and GdI_3 within the intralayer Gd plane. Gd atoms in both trihalides experience an essential lack of valence electron density (only, half-occupied Gd4f-orbitals are visible). The main part of electron density is located in the vicinity of halogen atoms (out of these planes). High ionicity and absence of covalent Gd-Gd bonding is also affirmed by the values of crystal orbital overlap populations (COOP Gd-Gd <0.001-0.01 e, COOP Gd-Cl 0.21 e, COOP Gd-I 0.25 e). The calculations have been performed using DFT pseudopotential approach as implemented in SIESTA software[20] at GGA level and applying single-ζ basis sets with polarization functions.

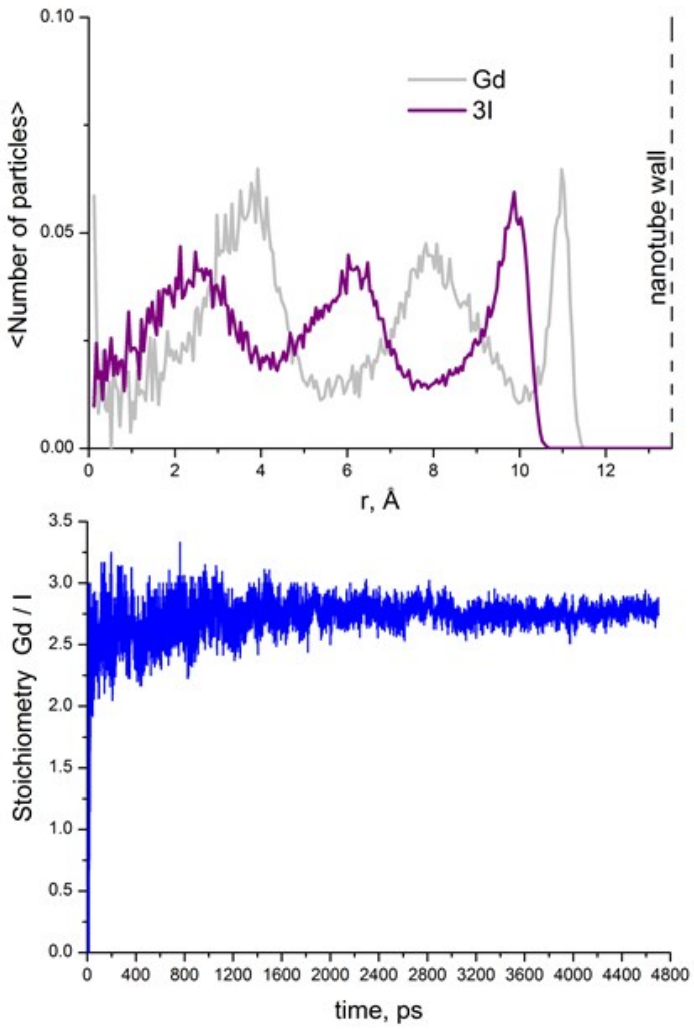


Fig. S14 Radial distribution functions of Gd and I ions within the melt part of GdI_3 penetrated into the cavity of double-walled (30,0)@(42,0) 2H-WS_2 nanotube after MD simulations during 4.8 ns at T = 1300K (*on the top*). Corresponding time modulation in stoichiometry of GdI_3 melt is given below.

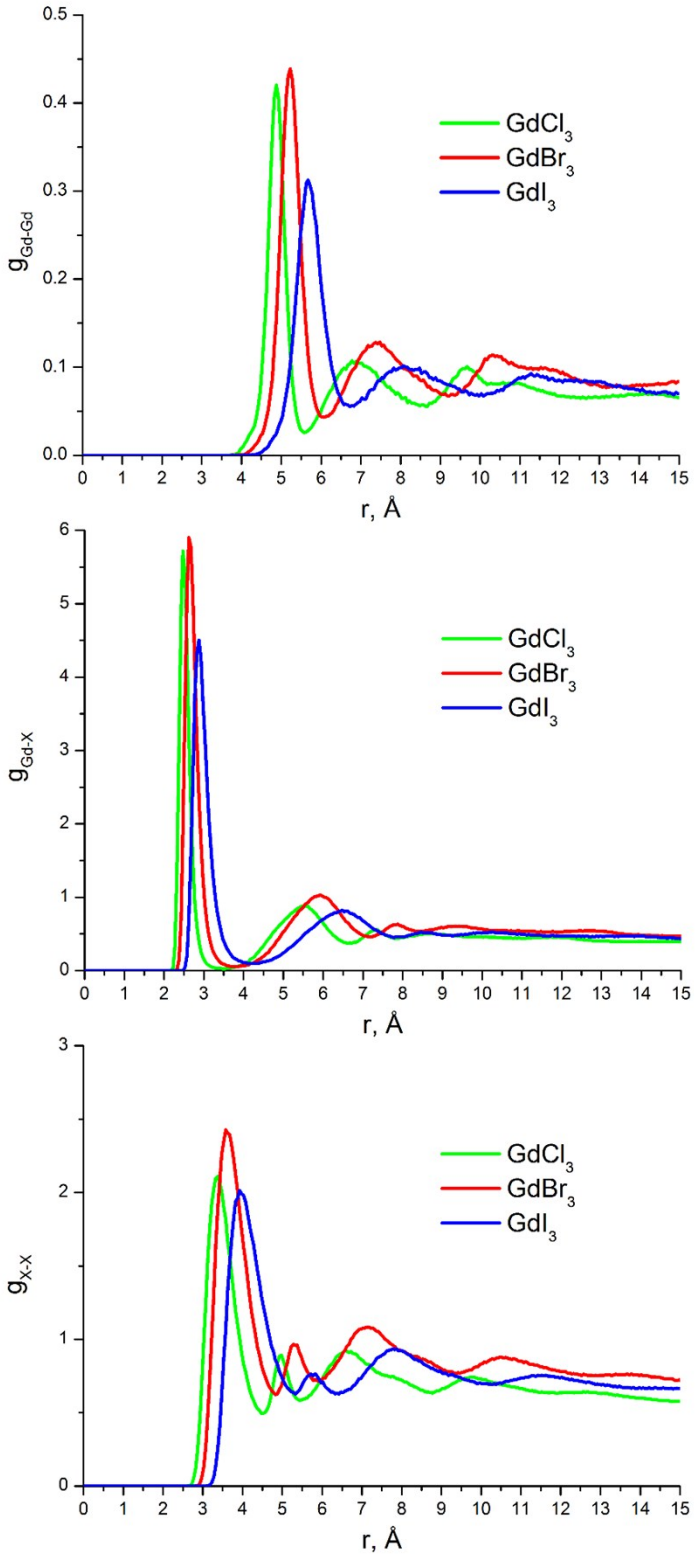


Fig. S15 Pair distribution functions within GdX_3 drops (X = Cl, Br, I) after MD annealing of $(GdX_3)_{1000}$ nanodrops during 2 ns at T = 1300K.

S16 Video1 Tomography of GdI_3 on WS_2 Nanotube

S17 Video2 EDS Tomography 1 - GdI_3@WS_2 Nanotube

S18 Video3 EDS Tomography 2- GdI_3@WS_2 Nanotube-Higher Electron Dose

S19 Video4 MD-$GdCl_3$-WS_2 or https://youtu.be/WpOIybxT_4s

S20 Video5 MD-$GdBr_3$-WS_2 or https://youtu.be/d-8u_snql1c

S21 Video6 MD-GdI_3-WS_2 or https://youtu.be/qVDE1vEXxo8

S22 Video7 MD-$GdCl_3$-WS_2 2 or https://youtu.be/MGoYMfXv4ZE