Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supporting Information: Size-dependent trends in the hydrogen evolution activity and electronic structure of MoS_2 nanotubes

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Supporting figures and tables

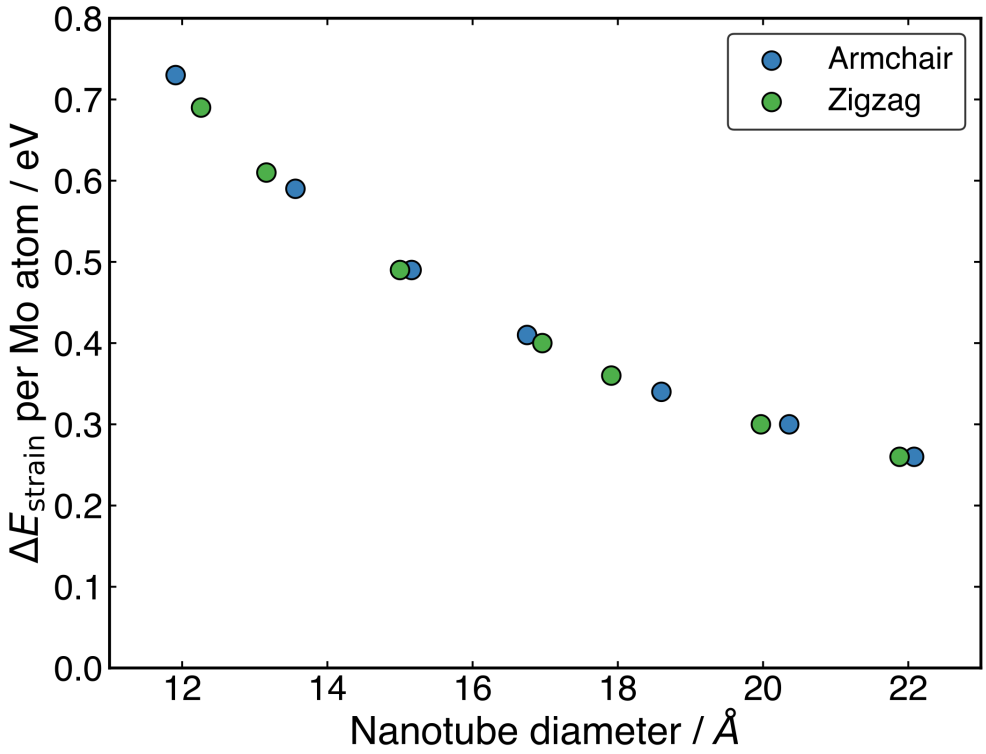

Figure S1: A plot showing the non-linear relation between nanotube diameter and strain energy, ΔE_{strain}, relative to a flat surface of the same size, calculated *via* Equation 1 in the main text.

Table S1: Electronic H adsorption energies, $\Delta E_{\mathrm{H_{ads}}}$, compared between the inside and outside of MoS_2 armchair and zigzag nanotubes of three different sizes.

System	$\Delta E_{\mathrm{H_{ads}}}$ S		$\Delta E_{\mathrm{H_{ads}}}$ Mo	
$(\overrightarrow{n}, \overrightarrow{m})$	Outside	Inside	Outside	Inside
Armchair				
(8, 8)	1.13	1.48	1.31	2.40
(11, 11)	1.41	1.71	1.67	2.50
(14, 14)	1.56	1.81	1.89	2.53
Zigzag				
(14, 0)	1.18	1.51	1.28	2.33
(19, 0)	1.44	1.73	1.64	2.51
(24, 0)	1.56	1.81	1.82	2.59

Table S2: Electron movement from S to neighbouring Mo on H adsorption, calculated *via* Bader charge analysis. The data are presented for all armchair nanotubes of different sizes, and show there is no systematic variance in the charge transfer with system size.

System	Electrons lost by S / e^-	Electrons gained by neighbouring Mo / e^-
(8, 8)	0.24	0.12
(9, 9)	0.24	0.09
(10, 10)	0.23	0.10
(11, 11)	0.20	0.08
(12, 12)	0.17	0.10
(13, 13)	0.22	0.09
(14, 14)	0.18	0.10

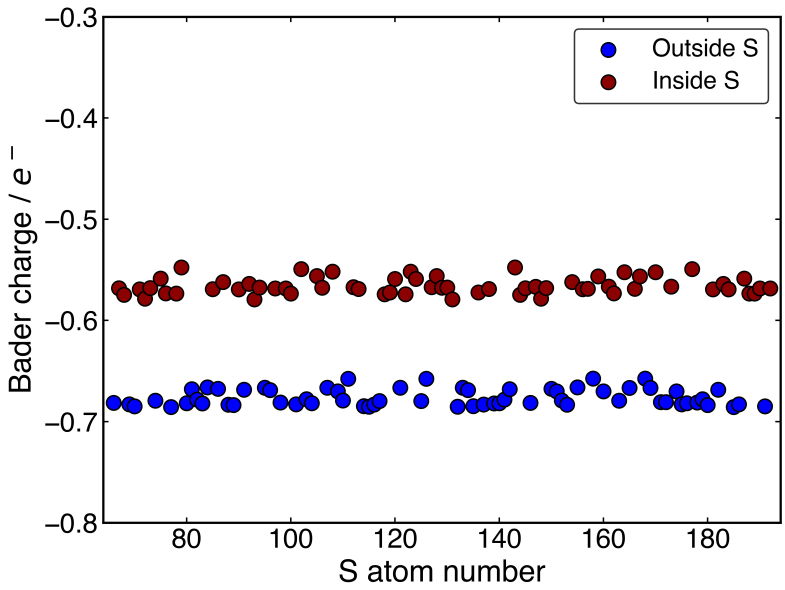

Figure S2: Bader charge on the outside and inside S atoms in an armchair (8, 8) nanotube. The average charge gap between inside and outside is 0.11 e^-.

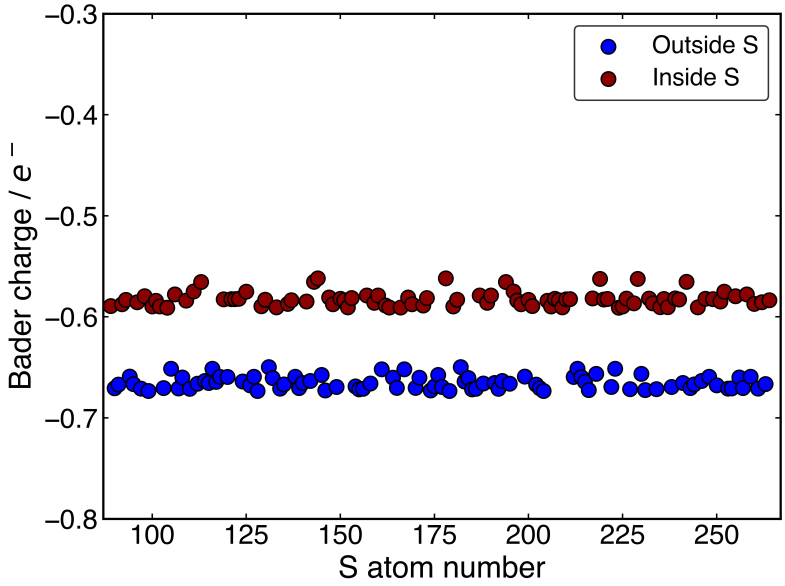

Figure S3: Bader charge on the outside and inside S atoms in an armchair (11, 11) nanotube. The average charge gap between inside and outside is 0.10 e^-.

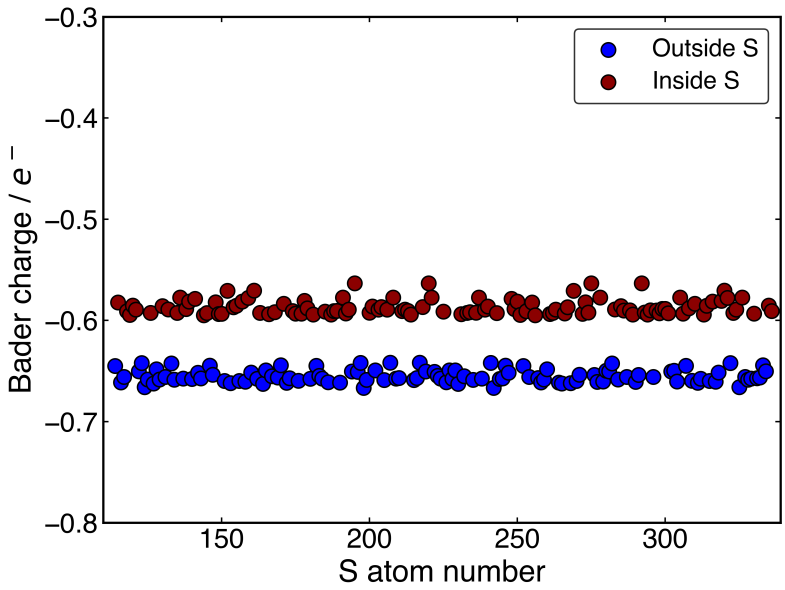

Figure S4: Bader charge on the outside and inside S atoms in an armchair (14, 14) nanotube. The average charge gap between inside and outside is 0.07 e^-.

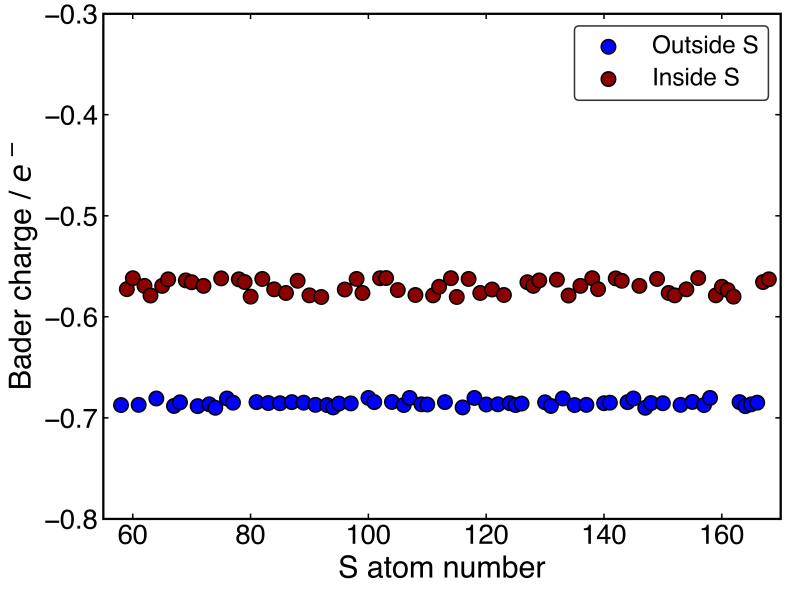

Figure S5: Bader charge on the outside and inside S atoms in a zigzag (14, 0) nanotube. The average charge gap between inside and outside is 0.12 e^-.

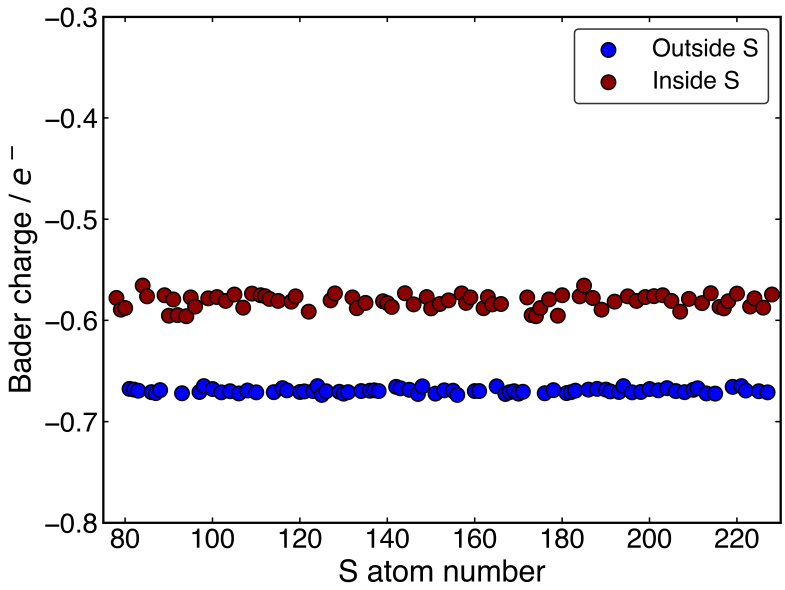

Figure S6: Bader charge on the outside and inside S atoms in a zigzag (19, 0) nanotube. The average charge gap between inside and outside is 0.09 e^-.

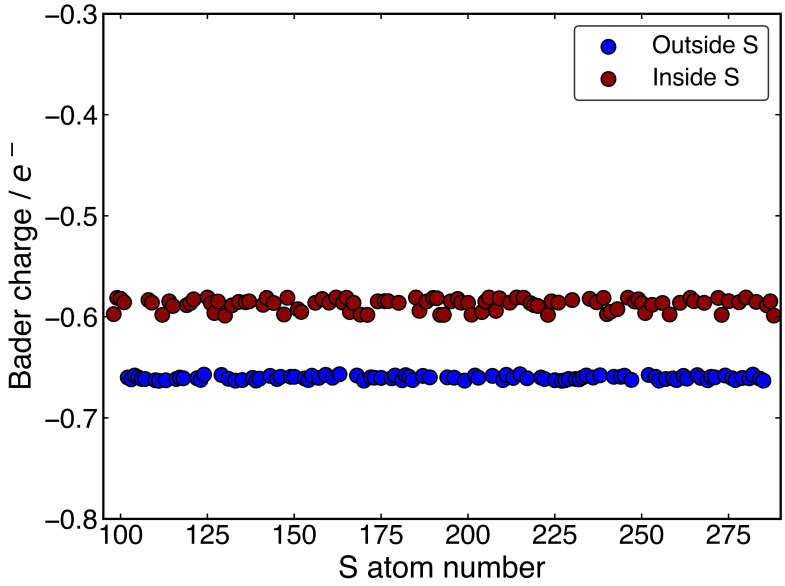

Figure S7: Bader charge on the outside and inside S atoms in a zigzag (24, 0) nanotube. The average charge gap between inside and outside is 0.07 e^-.

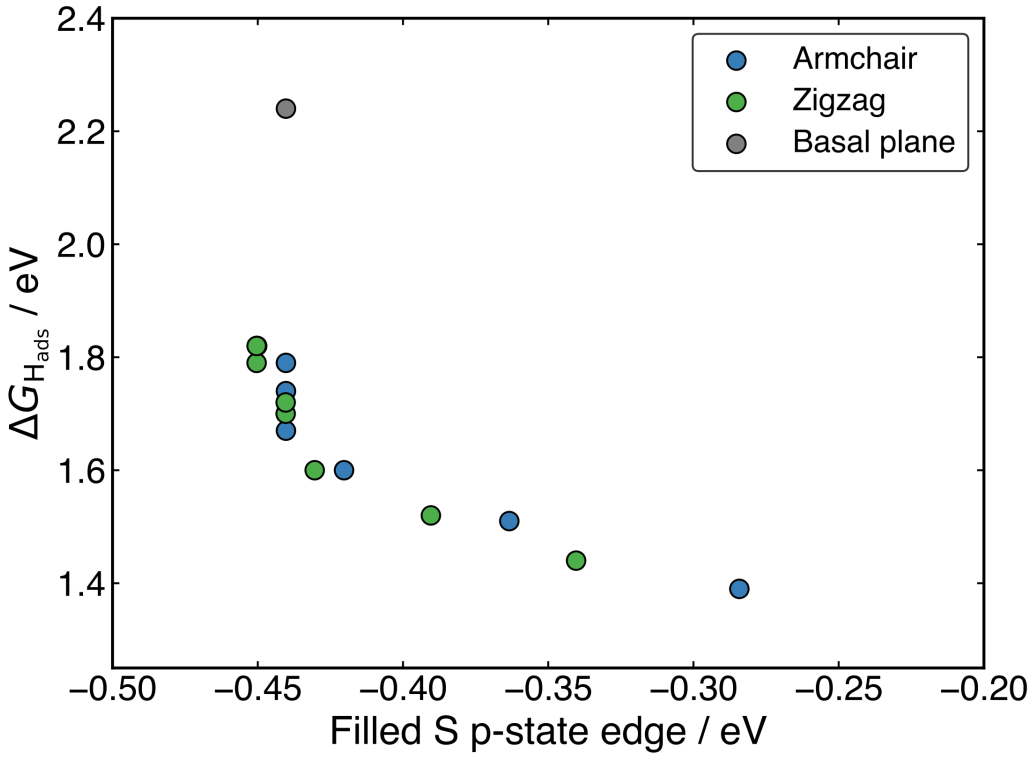

Figure S8: A plot showing that there is no clear linear relation between the energy of the S p-states taken alone and the H adsorption free energy across all nanotube systems studied here and the flat basal plane. This demonstrates that, while the p-state energy is important to determining $\Delta G_{\mathrm{H_{ads}}}$, it is not enough to consider this alone and the Mo d-state energy must also be taken into account.

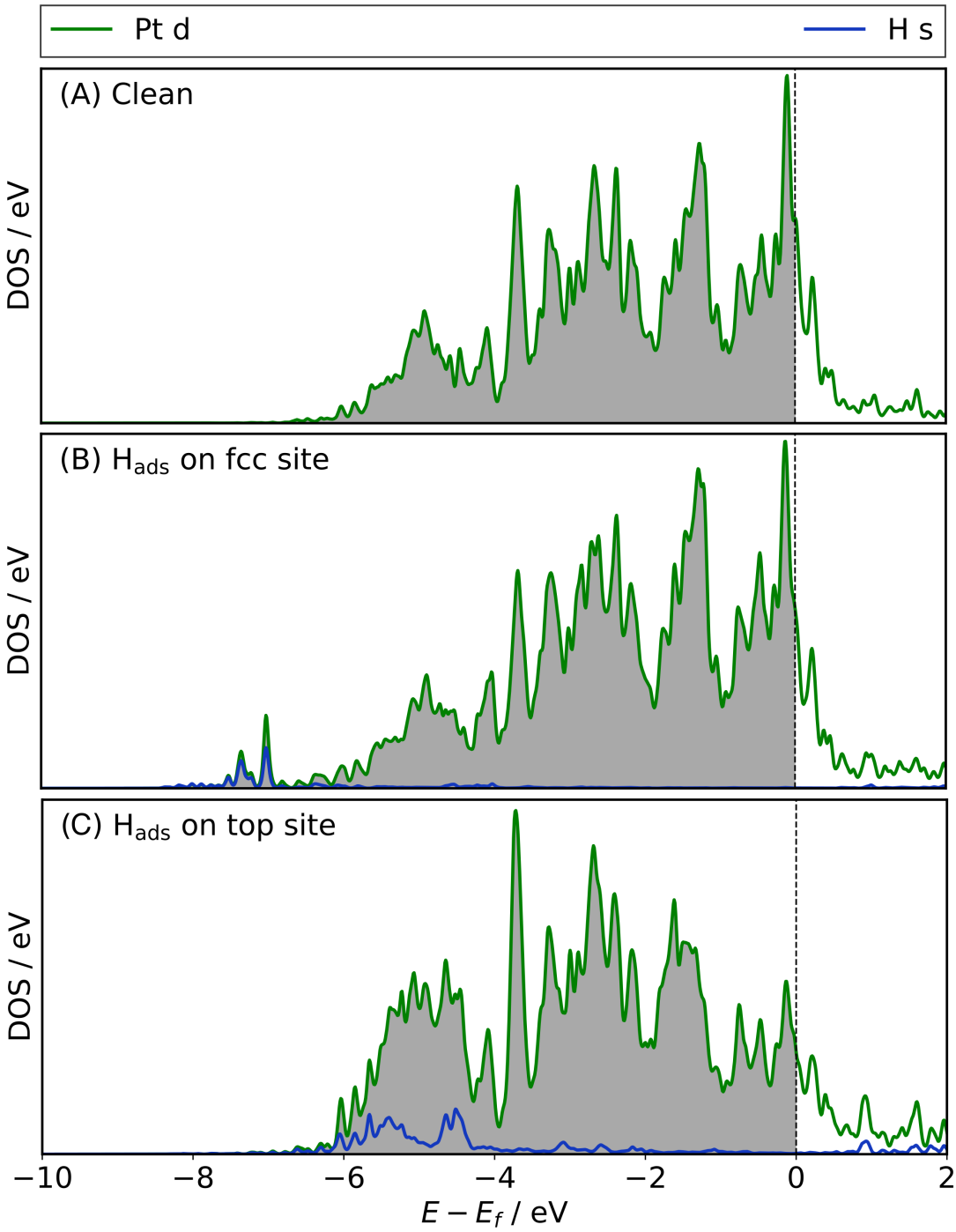

Figure S9: Density of states plots showing Pt(111) as (A) a clean surface, (B) with H adsorbed to the fcc site, and (C) with H adsorbed to the top site. A clear region of broad overlap between the Pt d-states and the H s-states is observed in both H adsorbed cases.

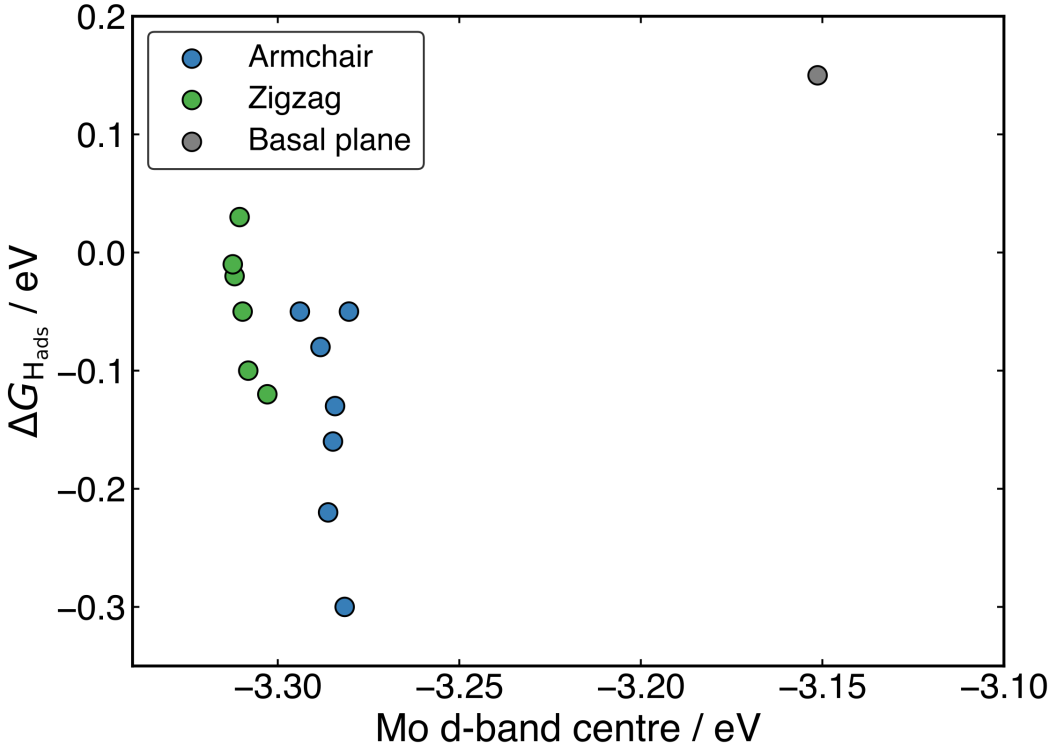

Figure S10: A plot demonstrating the lack of relation between the Mo d-band centre and $\Delta G_{\mathrm{H_{ads}}}$ at the S-vacancy defect site. This demonstrates it is only the energy of the Mo d-states directly involved in bonding, captured by the energy of the d-state edge, which determines $\Delta G_{\mathrm{H_{ads}}}$ at this site.

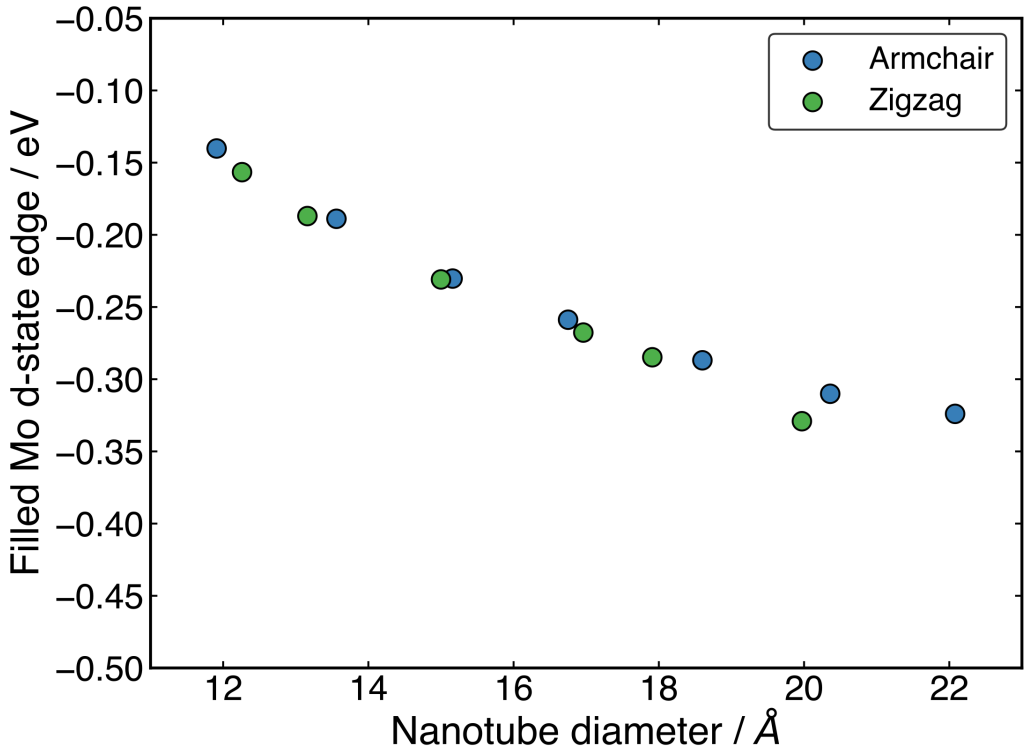

Figure S11: The relation between the Mo d-band edge and nanotube diameter, showing that the change in the d-state energy is controlled by the size of the MoS_2 nanotube.

Density of states plots for pristine materials studied

The following section contains the collection of the density of states plots for each of pristine the materials studied in the main text. They are all organised to show the clean surface and the surface with H adsorbed at the relevant site. In each case, the specific system is noted in the Figure caption.

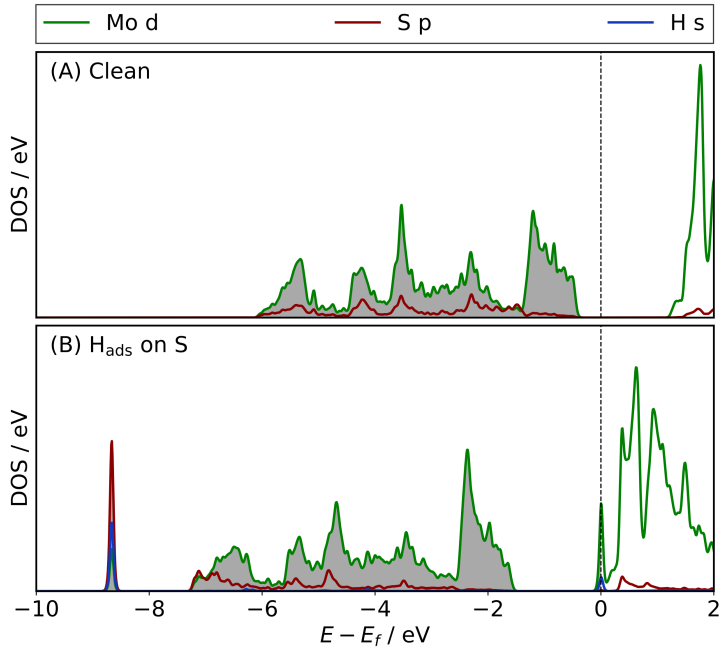

Figure S12: Density of states plots for the flat basal plane as (A) a clean surface, and (B) with H adsorbed to S.

Armchair nanotubes

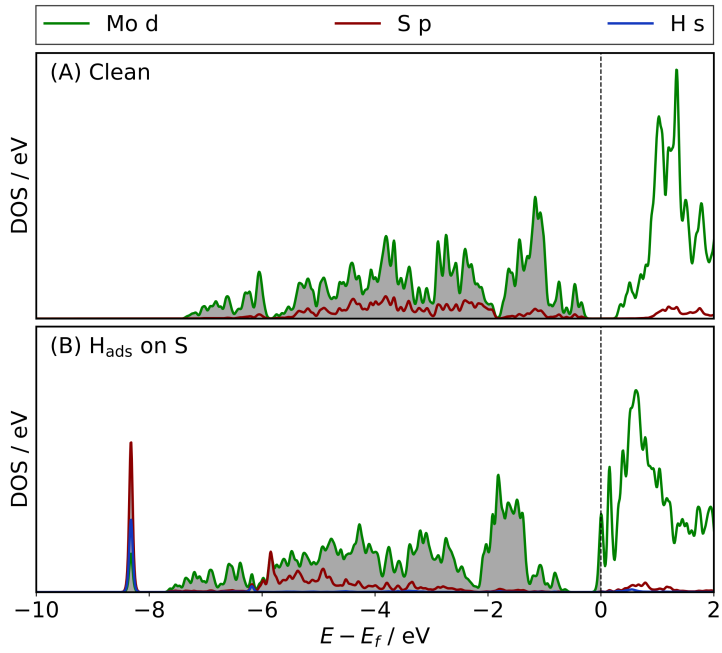

Figure S13: Density of states plots for the (8, 8) armchair nanotube as (A) a clean surface, and (B) with H adsorbed to S.

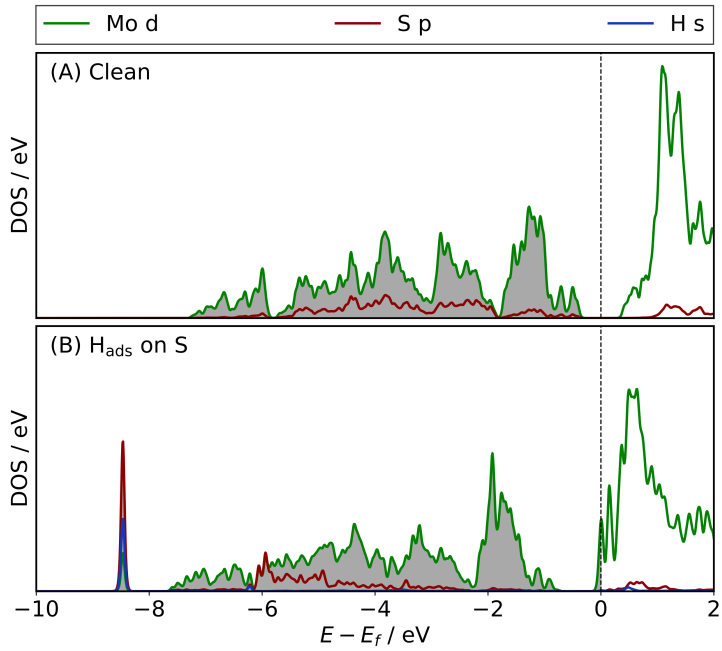

Figure S14: Density of states plots for the (9, 9) armchair nanotube as (A) a clean surface, and (B) with H adsorbed to S.

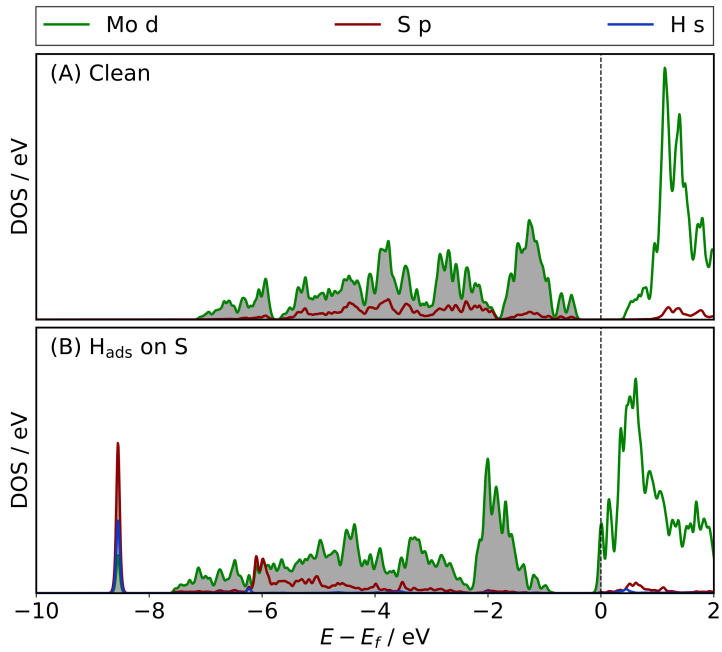

Figure S15: Density of states plots for the (10, 10) armchair nanotube as (A) a clean surface, and (B) with H adsorbed to S.

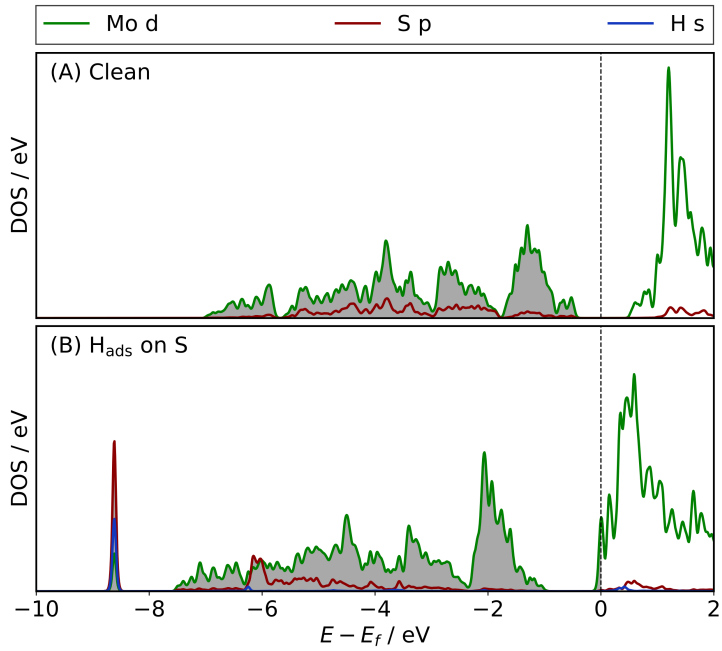

Figure S16: Density of states plots for the (11, 11) armchair nanotube as (A) a clean surface, and (B) with H adsorbed to S.

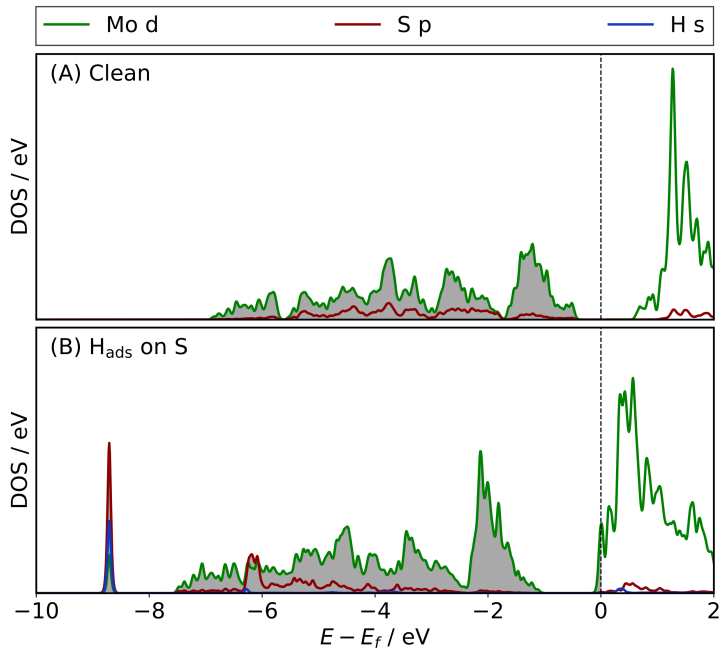

Figure S17: Density of states plots for the (12, 12) armchair nanotube as (A) a clean surface, and (B) with H adsorbed to S.

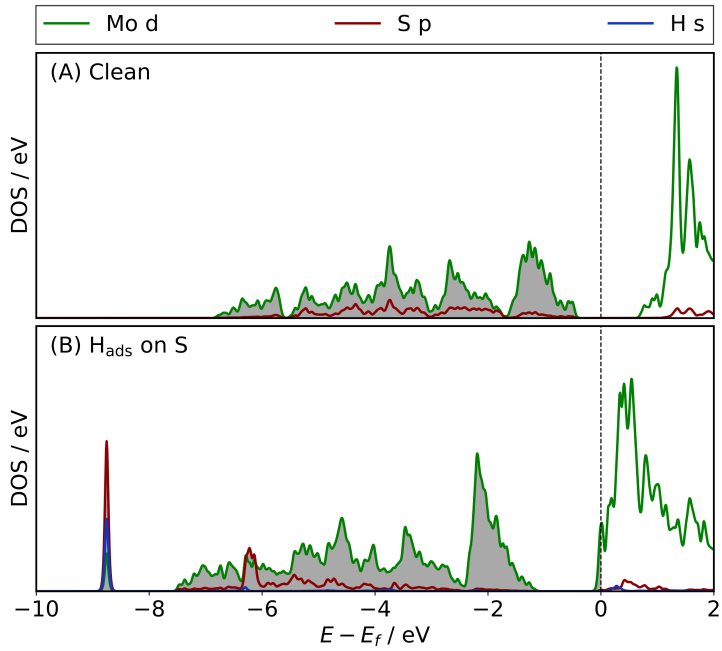

Figure S18: Density of states plots for the (13, 13) armchair nanotube as (A) a clean surface, and (B) with H adsorbed to S.

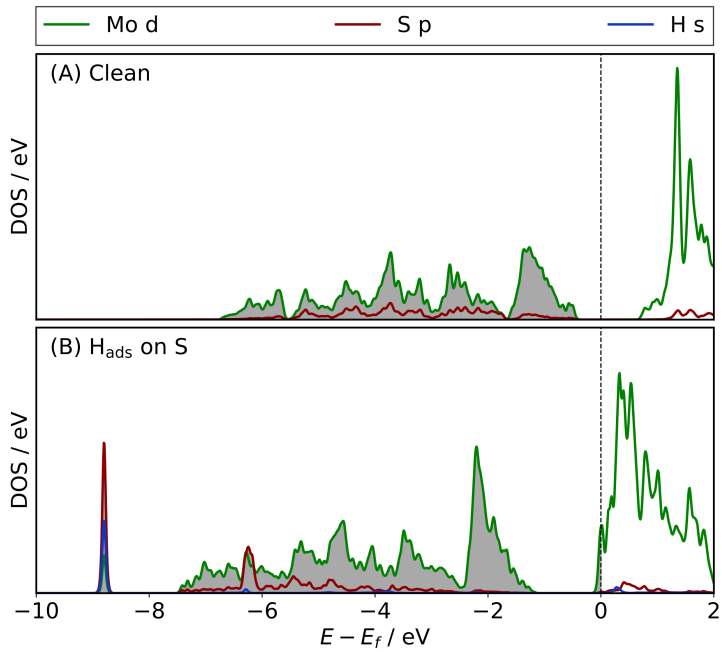

Figure S19: Density of states plots for the (14, 14) armchair nanotube as (A) a clean surface, and (B) with H adsorbed to S.

Zigzag nanotubes

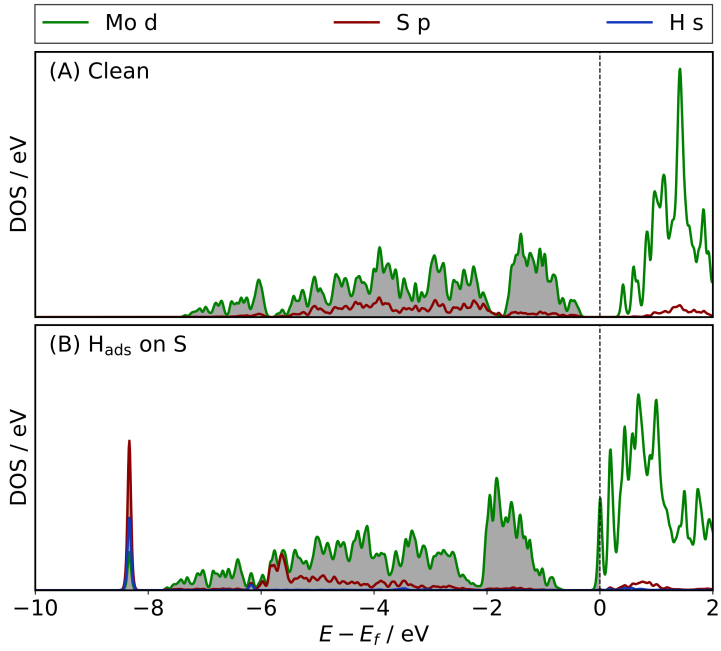

Figure S20: Density of states plots for the (14, 0) zigzag nanotube as (A) a clean surface, and (B) with H adsorbed to S.

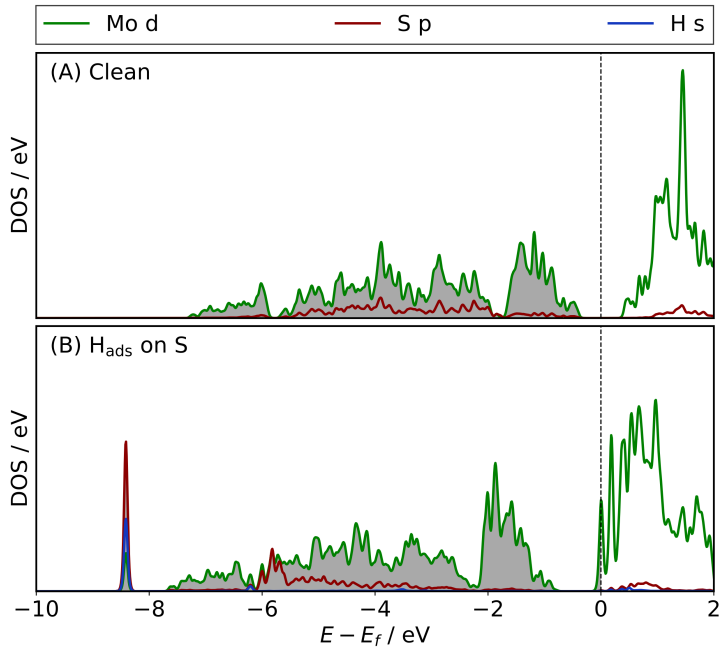

Figure S21: Density of states plots for the (15, 0) zigzag nanotube as (A) a clean surface, and (B) with H adsorbed to S.

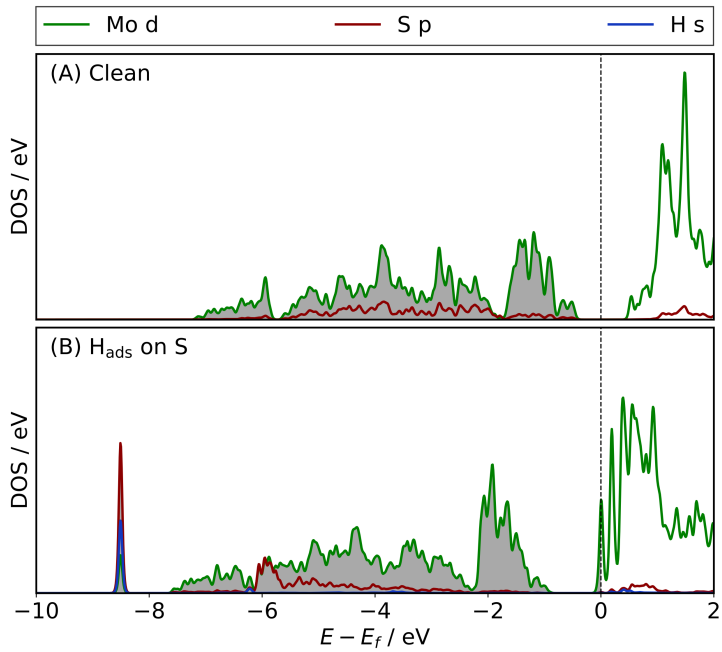

Figure S22: Density of states plots for the (17, 0) zigzag nanotube as (A) a clean surface, and (B) with H adsorbed to S.

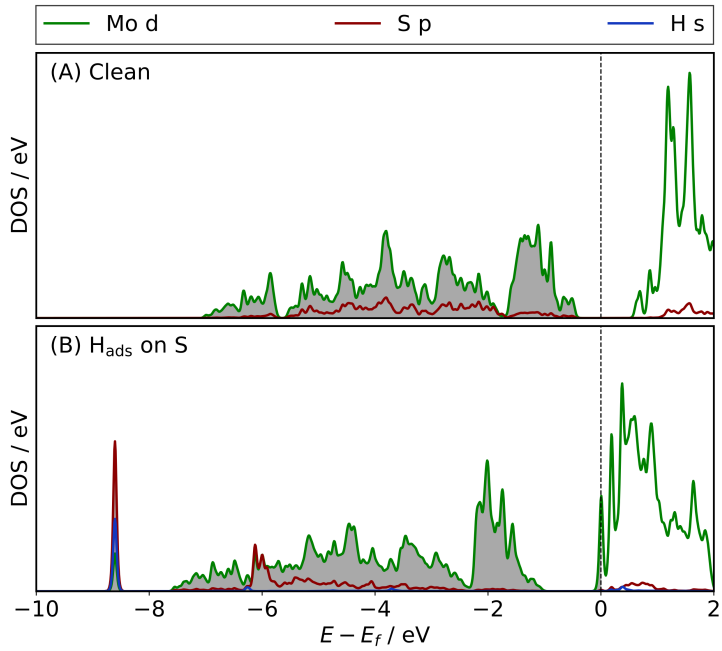

Figure S23: Density of states plots for the (19, 0) zigzag nanotube as (A) a clean surface, and (B) with H adsorbed to S.

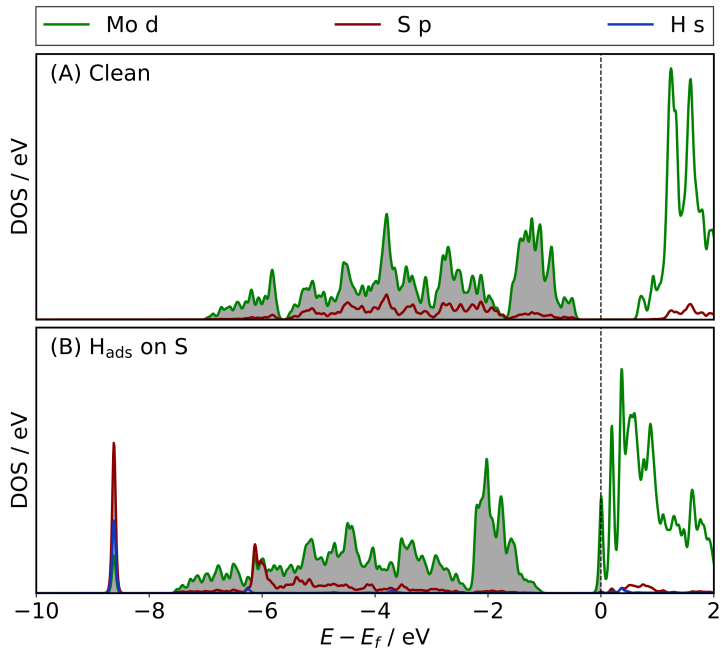

Figure S24: Density of states plots for the (20, 0) zigzag nanotube as (A) a clean surface, and (B) with H adsorbed to S.

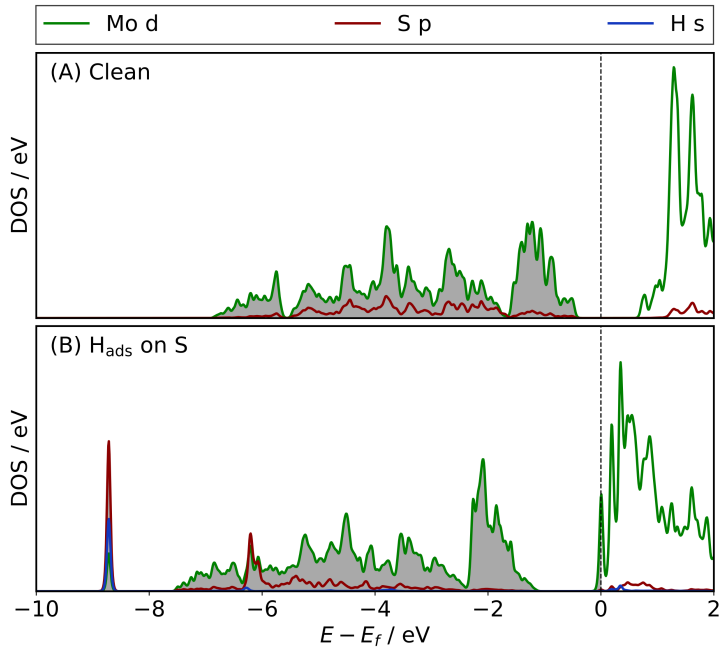

Figure S25: Density of states plots for the (22, 0) zigzag nanotube as (A) a clean surface, and (B) with H adsorbed to S.

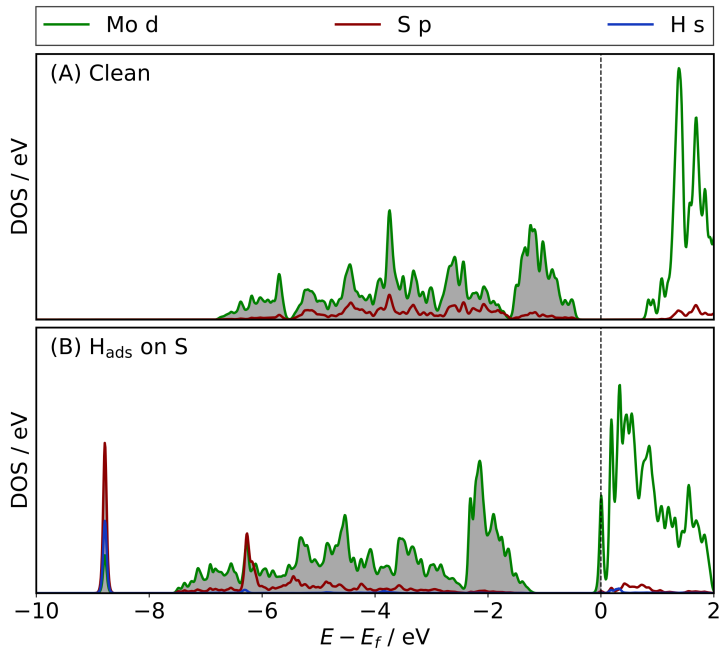

Figure S26: Density of states plots for the (24, 0) zigzag nanotube as (A) a clean surface, and (B) with H adsorbed to S.

Density of states plots for S-vacancy defect materials studied

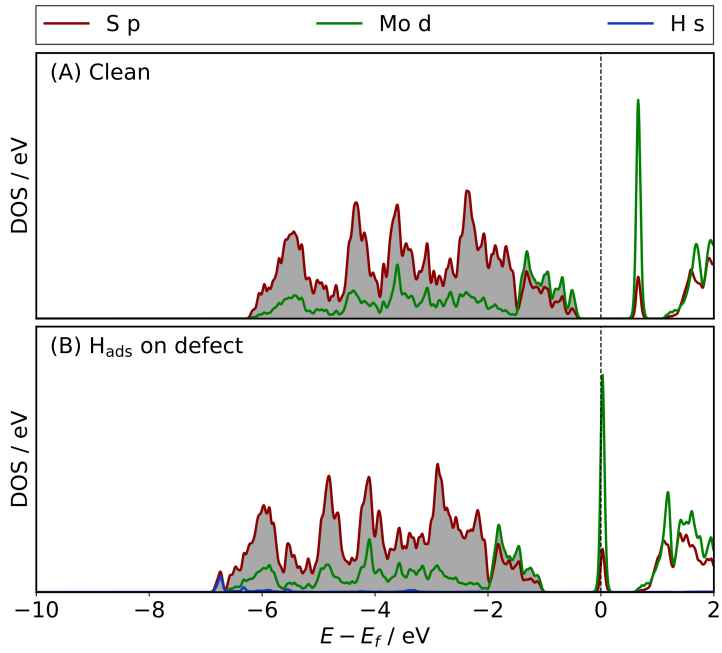

Figure S27: Density of states plots for the S-vacancy site on the flat basal plane as (A) a clean surface, and (B) with H adsorbed to S.

S-vacancy armchair nanotubes

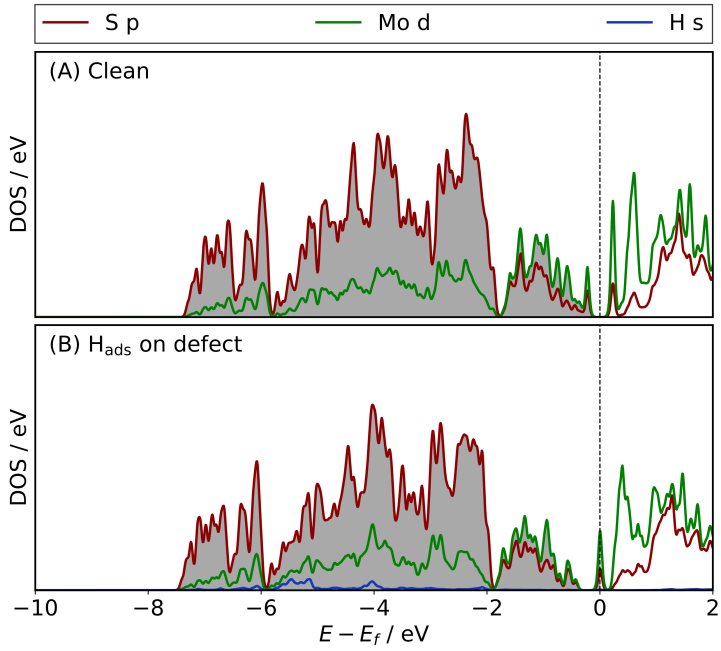

Figure S28: Density of states plots for the S-vacancy defect on the (8, 8) armchair nanotube as (A) a clean surface, and (B) with H adsorbed at the S-vacancy-.

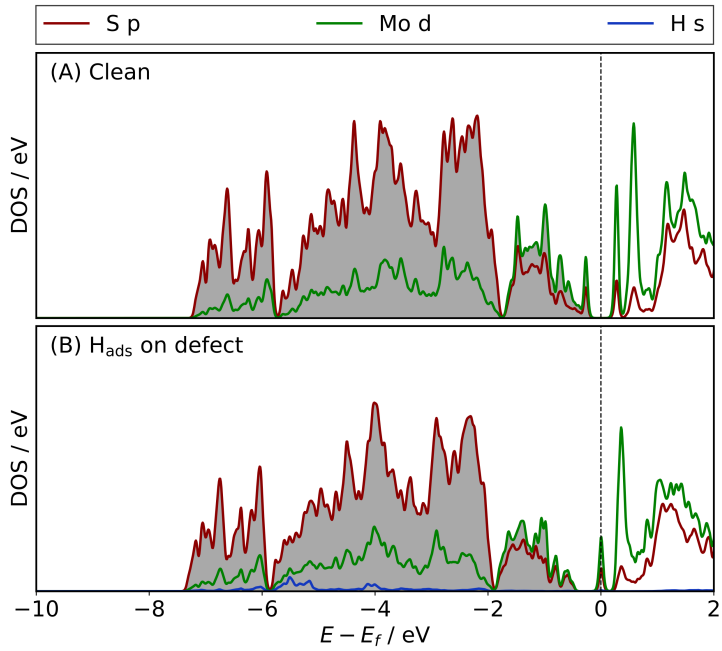

Figure S29: Density of states plots for the S-vacancy defect on the (9, 9) armchair nanotube as (A) a clean surface, and (B) with H adsorbed at the S-vacancy.

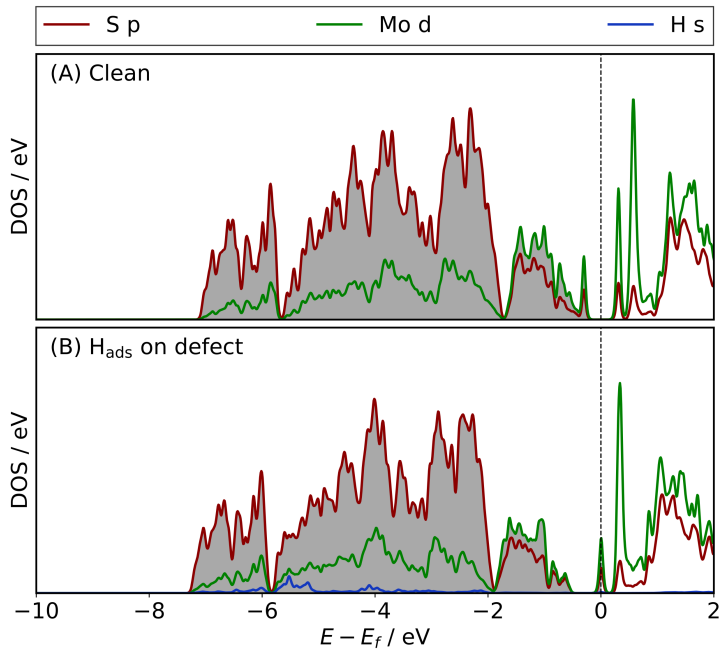

Figure S30: Density of states plots for the S-vacancy defect on the (10, 10) armchair nanotube as (A) a clean surface, and (B) with H adsorbed at the S-vacancy.

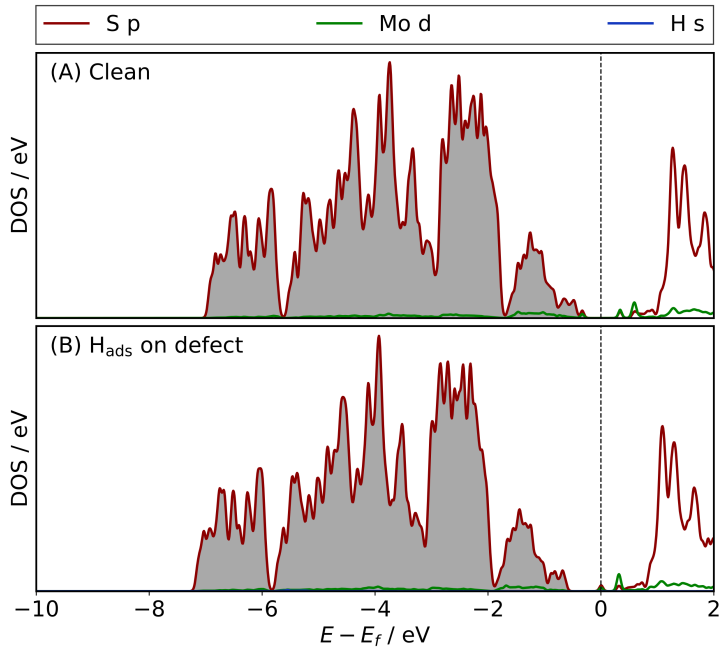

Figure S31: Density of states plots for the S-vacancy defect on the (11, 11) armchair nanotube as (A) a clean surface, and (B) with H adsorbed at the S-vacancy.

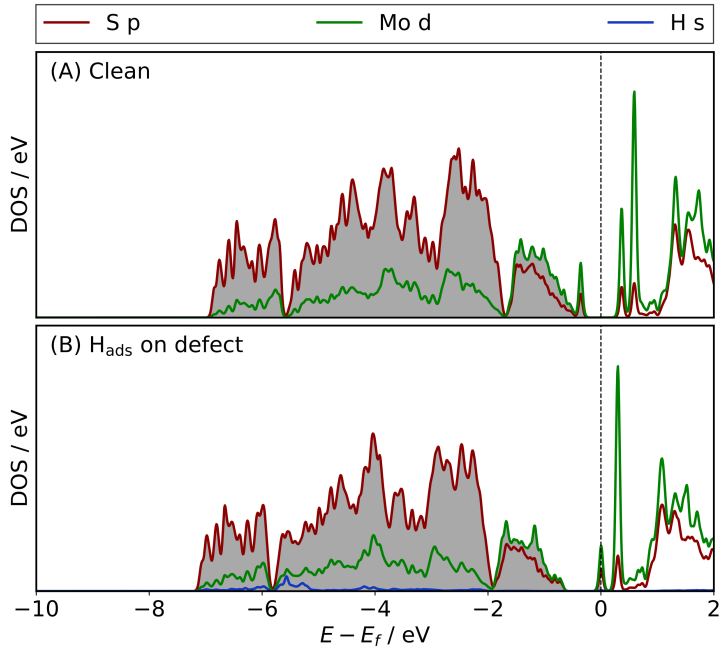

Figure S32: Density of states plots for the S-vacancy defect on the (12, 12) armchair nanotube as (A) a clean surface, and (B) with H adsorbed at the S-vacancy.

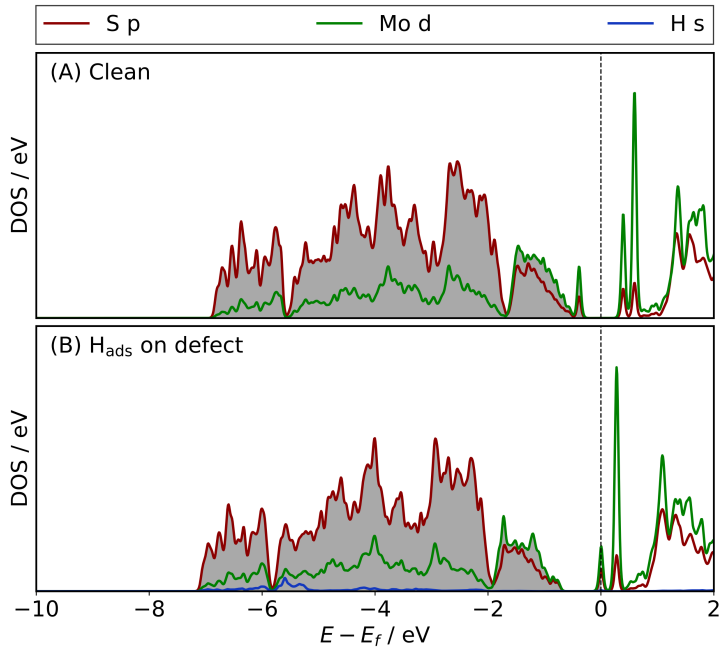

Figure S33: Density of states plots for the S-vacancy defect on the (13, 13) armchair nanotube as (A) a clean surface, and (B) with H adsorbed at the S-vacancy.

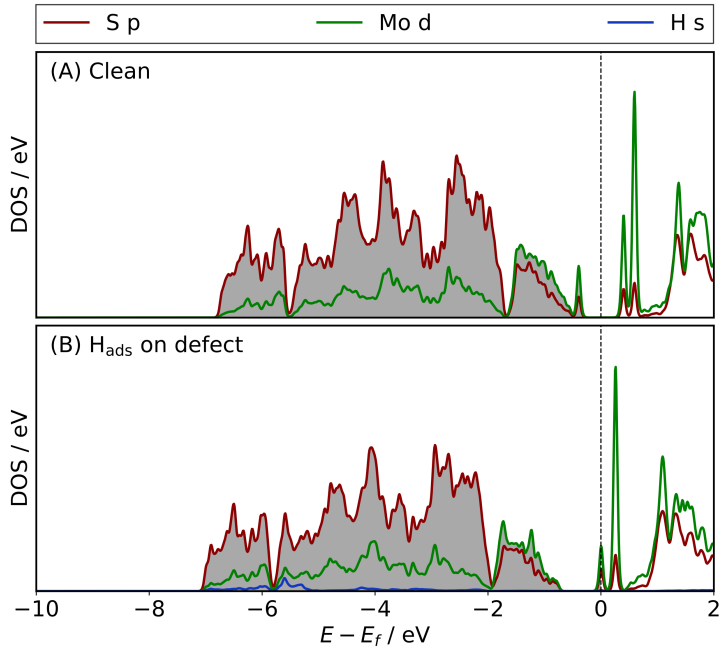

Figure S34: Density of states plots for the S-vacancy defect on the (14, 14) armchair nanotube as (A) a clean surface, and (B) with H adsorbed at the S-vacancy.

S-vacancy zigzag nanotubes

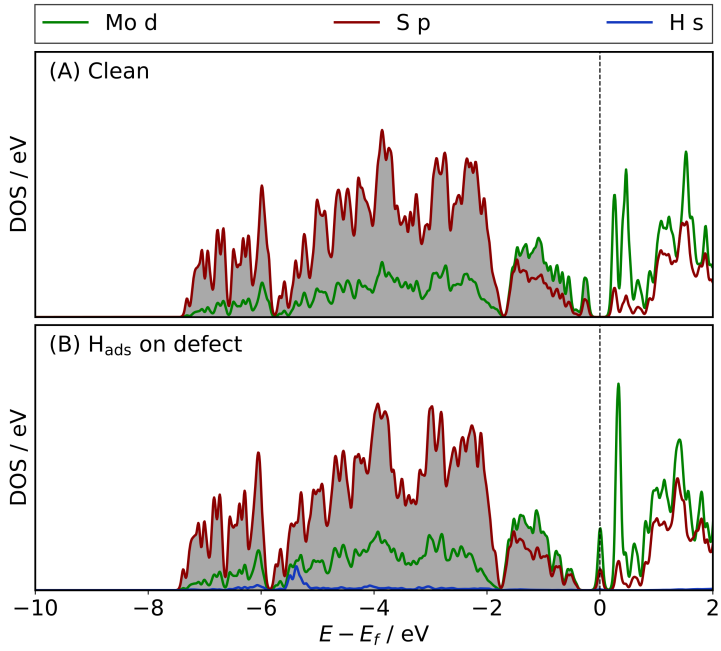

Figure S35: Density of states plots for the S-vacancy defect on the (14, 0) zigzag nanotube as (A) a clean surface, and (B) with H adsorbed at the S-vacancy.

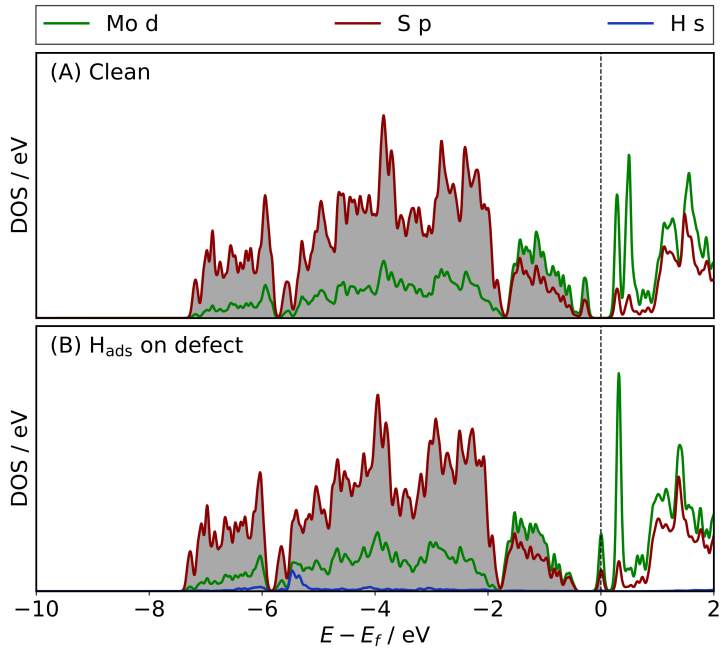

Figure S36: Density of states plots for the S-vacancy defect on the (15, 0) zigzag nanotube as (A) a clean surface, and (B) with H adsorbed at the S-vacancy.

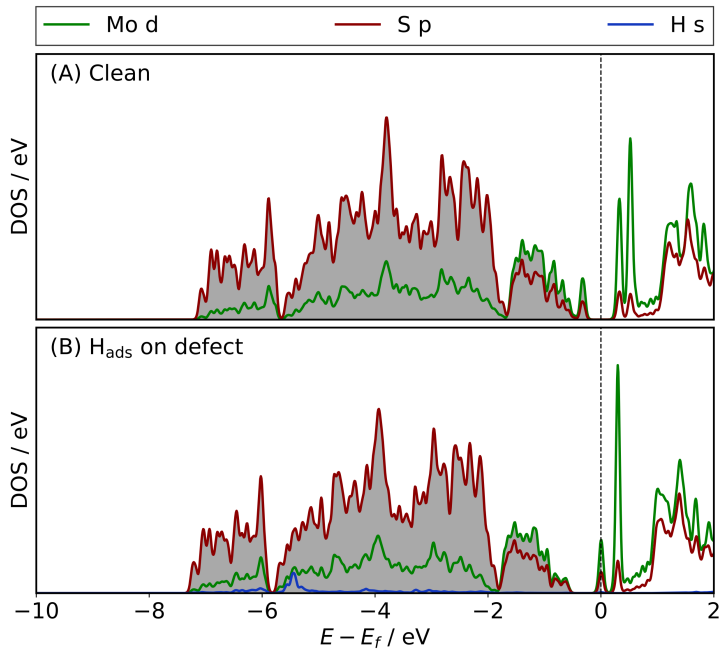

Figure S37: Density of states plots for the S-vacancy defect on the (17, 0) zigzag nanotube as (A) a clean surface, and (B) with H adsorbed at the S-vacancy.

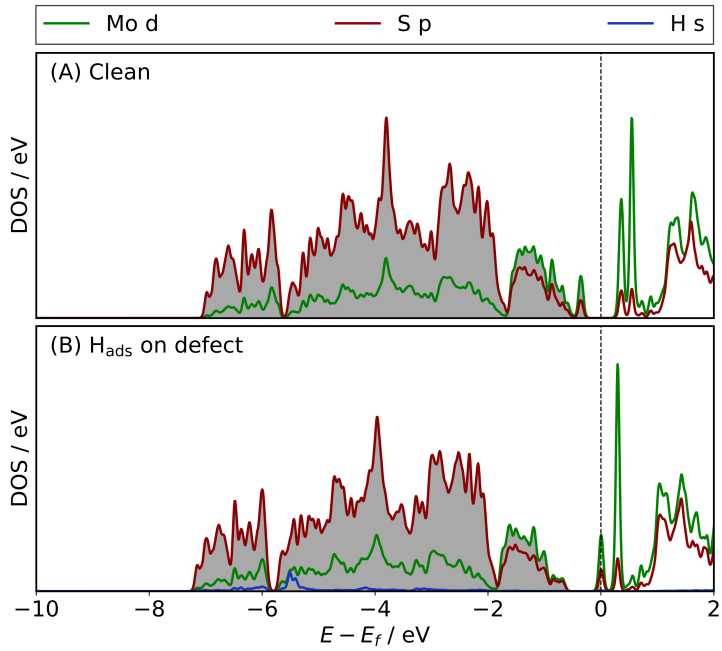

Figure S38: Density of states plots for the S-vacancy defect on the (19, 0) zigzag nanotube as (A) a clean surface, and (B) with H adsorbed at the S-vacancy.

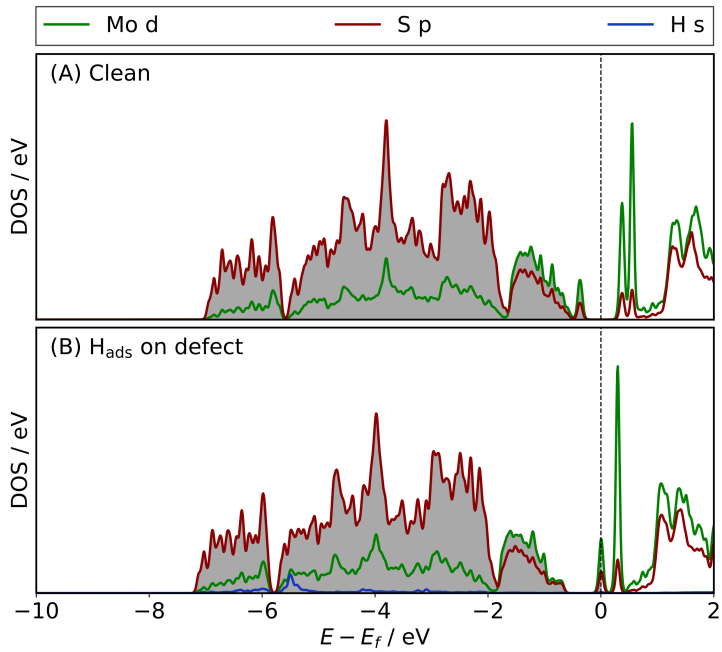

Figure S39: Density of states plots for the S-vacancy defect on the (20, 0) zigzag nanotube as (A) a clean surface, and (B) with H adsorbed at the S-vacancy.

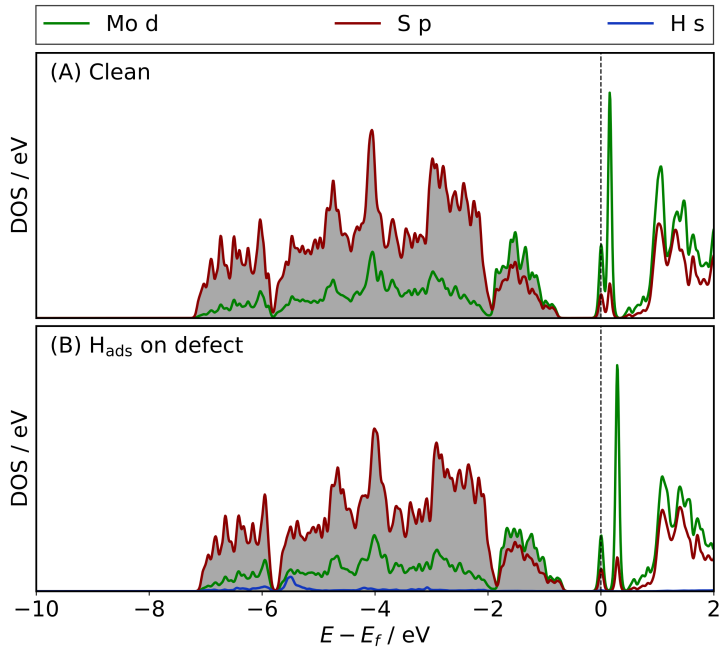

Figure S40: Density of states plots for the S-vacancy defect on the (22, 0) zigzag nanotube as (A) a clean surface, and (B) with H adsorbed at the S-vacancy.

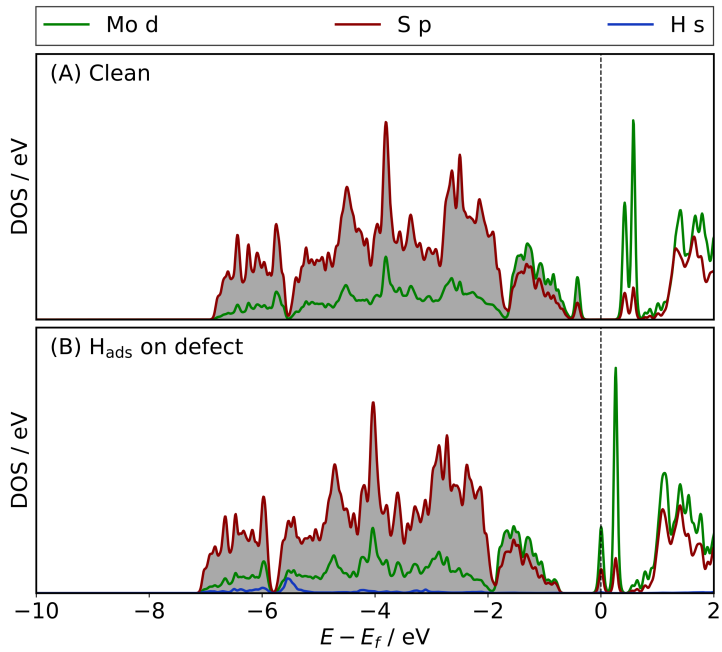

Figure S41: Density of states plots for the S-vacancy defect on the (24, 0) zigzag nanotube as (A) a clean surface, and (B) with H adsorbed at the S-vacancy.