The Role of Valence Electron Concentration in Tuning the Structure, Stability, and Electronic Properties of $Mo_6S_{9-x}I_x$ Nanowires

J. Karthikeyan,[†] Vijay Kumar,[‡,¶] and P. Murugan[*,†]

Functional Materials Division, CSIR-Central Electrochemical Research Institute, Karaikudi - 630003, Tamil Nadu, India, and Dr. Vijay Kumar Foundation, 1969 Sector 4, Gurgaon 122 001, Haryana, India

E-mail: murugan@cecri.res.in

Phone: +91-4565-241443. Fax: +91-4565-227779

[*]To whom correspondence should be addressed

[†]Functional Materials Division, CSIR-Central Electrochemical Research Institute, Karaikudi - 630003, Tamil Nadu, India

[‡]Dr. Vijay Kumar Foundation, 1969 Sector 4, Gurgaon 122 001, Haryana, India

[¶]Center for Informatics, School of Natural Sciences, Shiv Nadar University, NH91, Tehsil Dadri, Gautam Budh Nagar 201 314, Uttar Pradesh, India

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Table. S 1: Various atomic models (A, B, ...) of $Mo_6S_{9-x}I_x$ NWs that were explored for a given x by distributing S and I atoms in different ways. O_1 and O_2 represent two Mo_6 octahedra in the unit cell while P_1 and P_2 represent the prism sites formed in between the octahedra. Here, S&I means that the Mo_3 triangle is decorated with both S and I atoms without preserving C_{3v} symmetry. Starting with the configuration of Mo_6S_9 with all the sites occupied by S atoms, three S atoms were replaced by I atoms symmetrically either on bridge positions or on the faces of the octahedra every time when x is increased by 1.5. The occupancies of S or I atoms at various sites for different values of x, the optimized lattice constant along the NW axis, c (Å), the energy of a given nw with respect to the lowest energy configuration, ΔE (eV) are given. * mark represents the models proposed in earlier theoretical work.

x	0.0	1.5		3.0								4.5					6.0					7.5		9.0
Model	A	A	B	A	B*	C	D	E	F	G	H	A*	B	C	D	E	A*	B	C	D	E	A	B	A
P_1	S	S	S	I	S	S	S	S	S	S&I	S&I	S	S	I	I	I	S	I	S	I	I	S	I	I
O_1	S	S	I	S	S	S	I	S	S	S&I	S&I	I	I	I	S	I	I	I	I	I	I	I	I	I
	S	S	S	S	I	I	I	S	S	S&I	S&I	I	S	I	S	S	I	S	S	S	I	I	S	I
P_2	S	I	S	I	S	S	S	I	I	S&I	S&I	S	I	S	I	S	S	I	I	S	I	I	I	I
O_2	S	S	S	S	I	S	S	I	S	S&I	S&I	S	S	S	S	I	I	I	I	I	S	I	I	I
	S	S	S	S	S	I	S	S	I	S&I	S&I	I	I	S	I	S	I	S	I	I	S	I	I	I
c (Å)	13.1	10.0	11.9	9.3	12.6	11.3	11.9	10.8	11.8	11.3	12.2	12.4	12.3	11.1	10.6	11.1	13.7	11.3	11.3	11.6	11.3	11.6	11.6	13.5
Δ E (eV)	0	0	1.29	0	1.92	3.06	3.17	1.26	2.69	3.32	3.61	3.01	1.57	1.99	0	1.69	4.42	0.98	1.21	1.84	0	1.90	0	0

Table. S 2: Average Mo-Mo bond length at P_1, O_1, P_2 and O_2 sites of the lowest energy $Mo_6S_{9-x}I_x$ NWs for various x. $\angle P_1$ and $\angle P_2$ are the average $\angle$Mo-I-Mo bridging angles in P_1 and P_2 sites, respectively.

x	0.0	1.5	3.0	9.0
P_1(Å)	4.08	3.08	2.76	3.87
O_1(Å)	2.75/3.24/2.75	2.80	2.76	2.61
$\angle P_1$ (°)	124	77	61	84
P_2(Å)	4.07	2.85	2.85	5.07
O_2(Å)	2.70	2.83	2.73	2.61
$\angle P_2$(°)	124	59	61	119

Table. S 3: Average Mo-Mo bond length in P_1, O_1, P_2, O_2, P_3, O_3, P_4 and O_4 sites in the supercell of the lowest energy model of $Mo_6S_{9-x}I_x$ NWs with $x = 4.5$, 6.0, and 7.5. $\angle P_1$, $\angle P_2$, $\angle P_3$ and $\angle P_4$ are the average $\angle$Mo-I-Mo on the bridging sites of the prisms P_1, P_2, P_3, and P_4 between the octahedra, respectively.

x	4.5	6.0	7.5
P_1	I	I	I
O_1	I	I	I
P_2	I	I	I
O_2	S	S	I
P_3	I	I	I
O_3	S	I	S
P_4	I	I	I
O_4	S	S	I
c (Å)	10.0	10.6	11.6
P_1	3.33	3.43	4.54
O_1	2.63	2.63	2.69
P_2	3.46	3.44	3.65
O_2	2.75	2.71	2.69
P_3	3.06	3.47	3.39
O_3	2.78	2.63	2.66
P_4	3.11	3.44	3.37
O_4	2.76	2.71	2.69
$\angle P_1(^\circ)$	63	74	72
$\angle P_2(^\circ)$	75	74	103
$\angle P_3(^\circ)$	60	74	79
$\angle P_4(^\circ)$	67	74	73

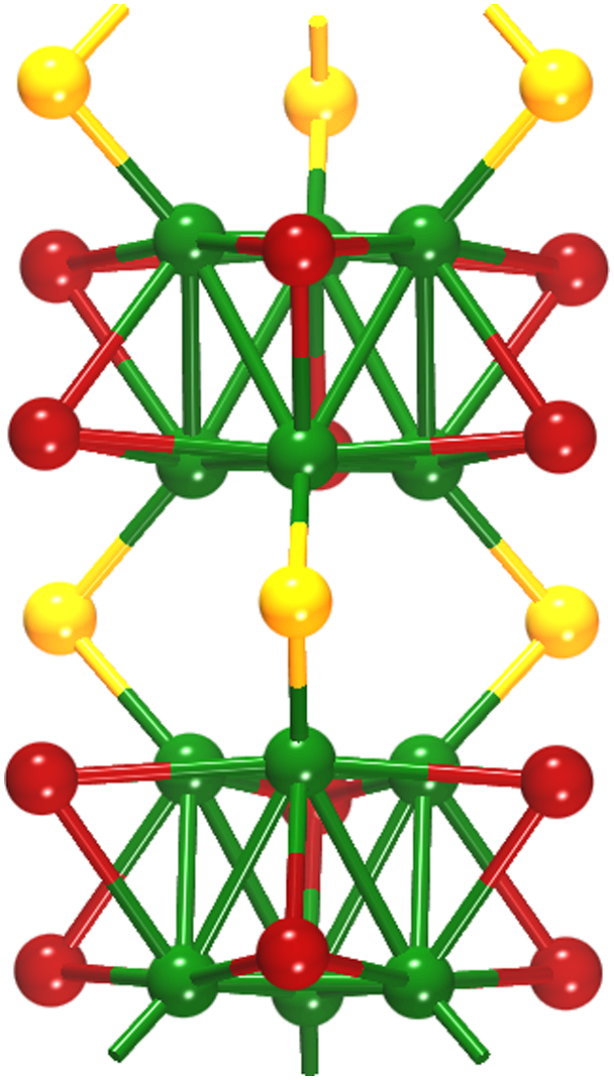

Figure. S 1: Atomic structure of $Mo_6S_3I_6$ NW proposed in earlier reports. Green, yellow, and dark red balls correspond to Mo, S, and I atoms, respectively.

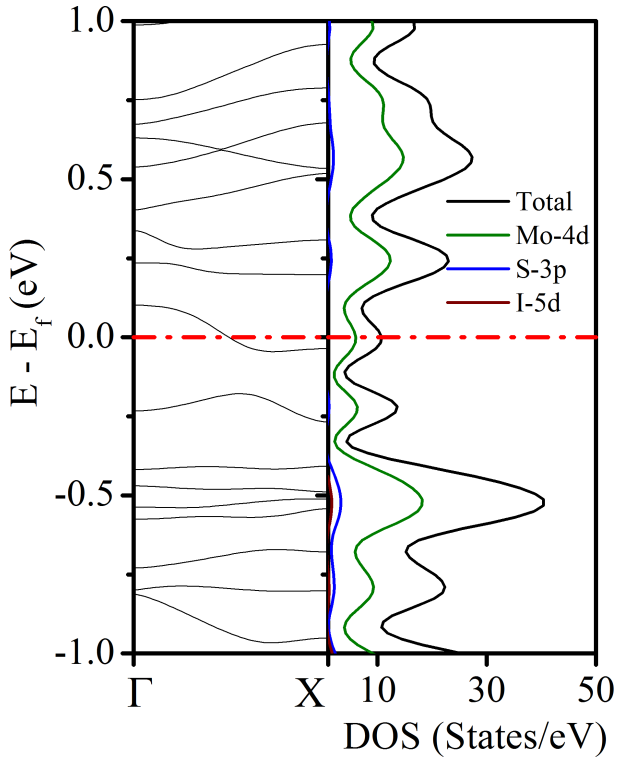

Figure. S 2: Electronic structure of $Mo_6S_{7.5}I_{1.5}$ NW. The horizontal dashed line shows the E_f.

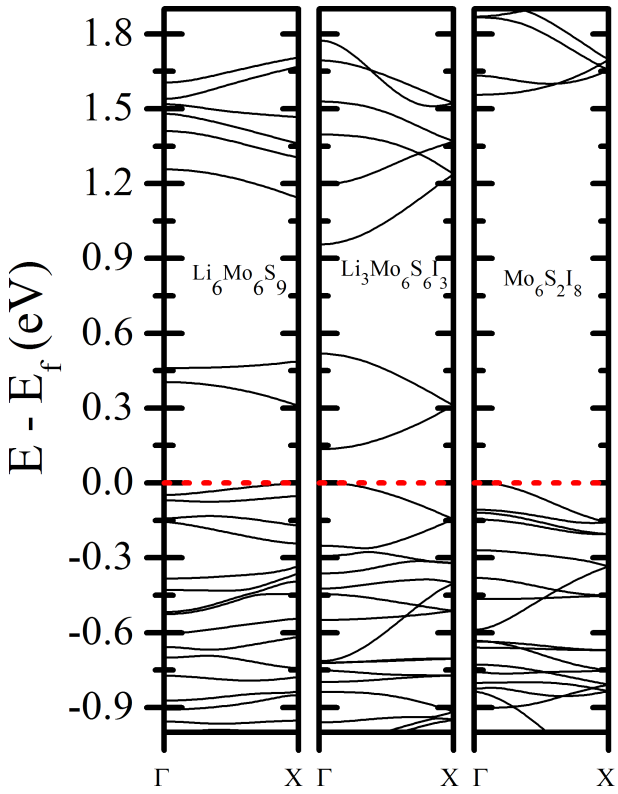

Figure. S 3: Band Structure of $Li_6Mo_6S_9$, $Li_3Mo_6S_6I_3$, and $Mo_6S_2I_8$ NWs. The horizontal dashed line shows the E_f. The composition of the NWs is written in the respective panels.