Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

First Principles Modeling of Mo_6S_9 Nanowire *via* Condensation of Mo_4S_6 Clusters and Effect of Iodine Doping on Structural and Electronic Properties

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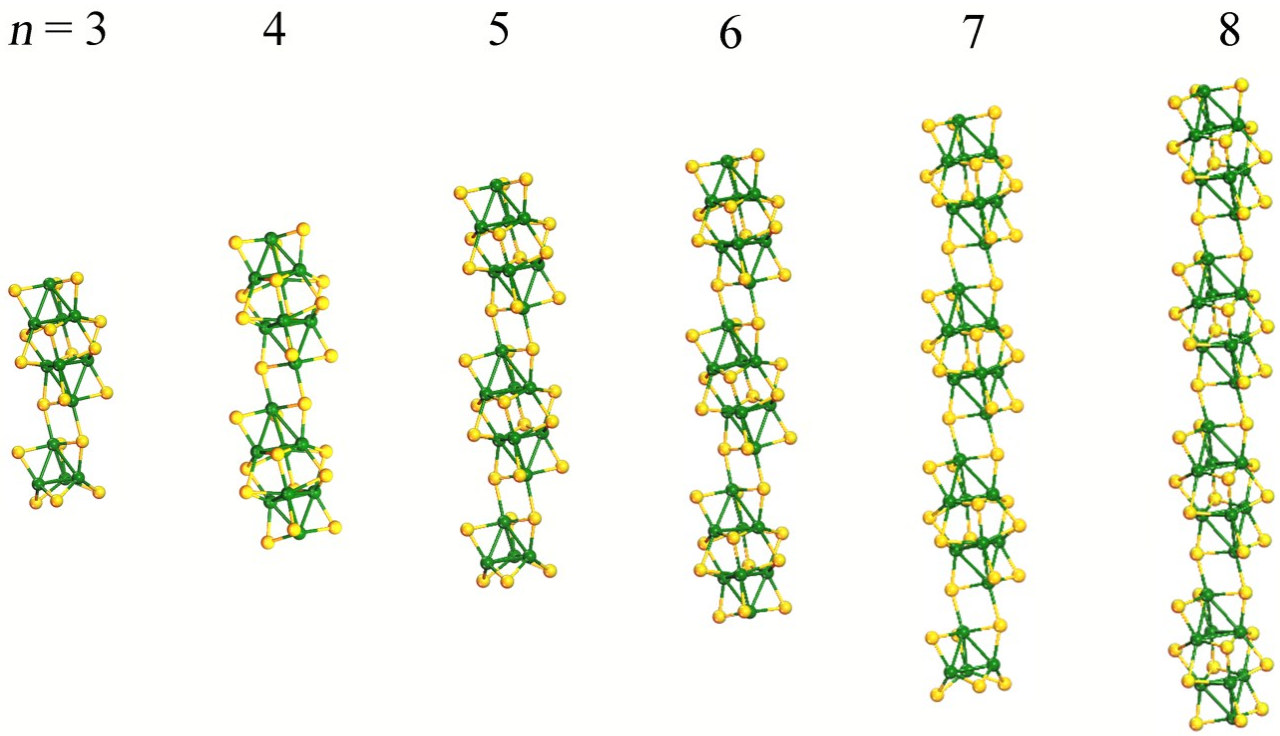

Figure S1. Optimized structures of $(Mo_4S_6)_n$ finite nanorods.

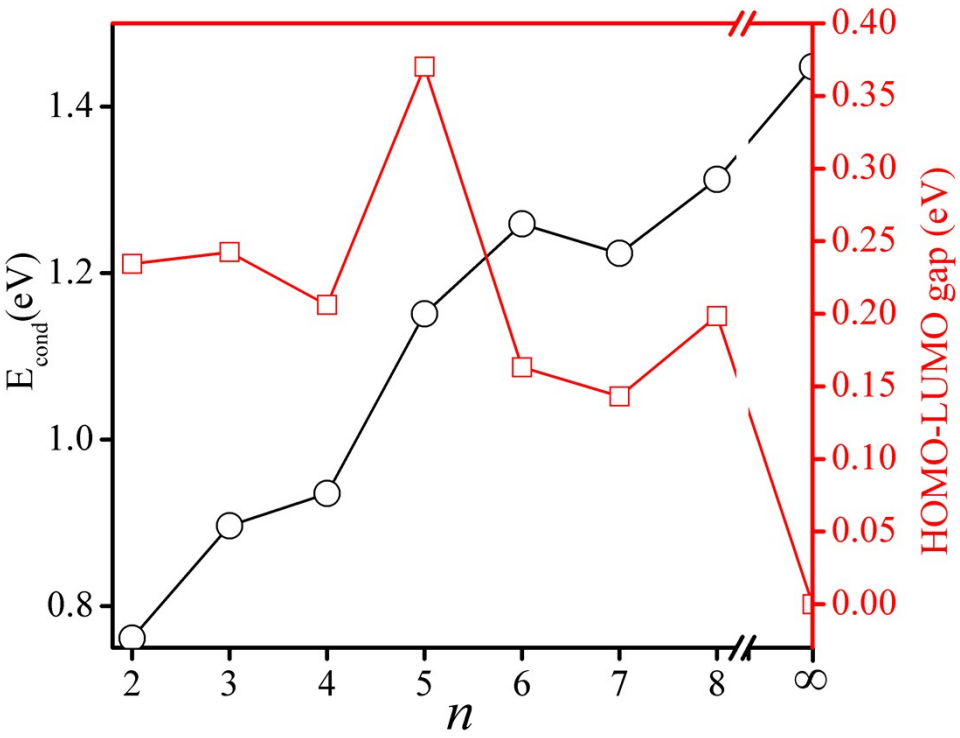

Figure S2. E_{cond} and HOMO-LUMO gap of $(Mo_4S_6)_n$ nanorods and those values are compared with infinite NW.

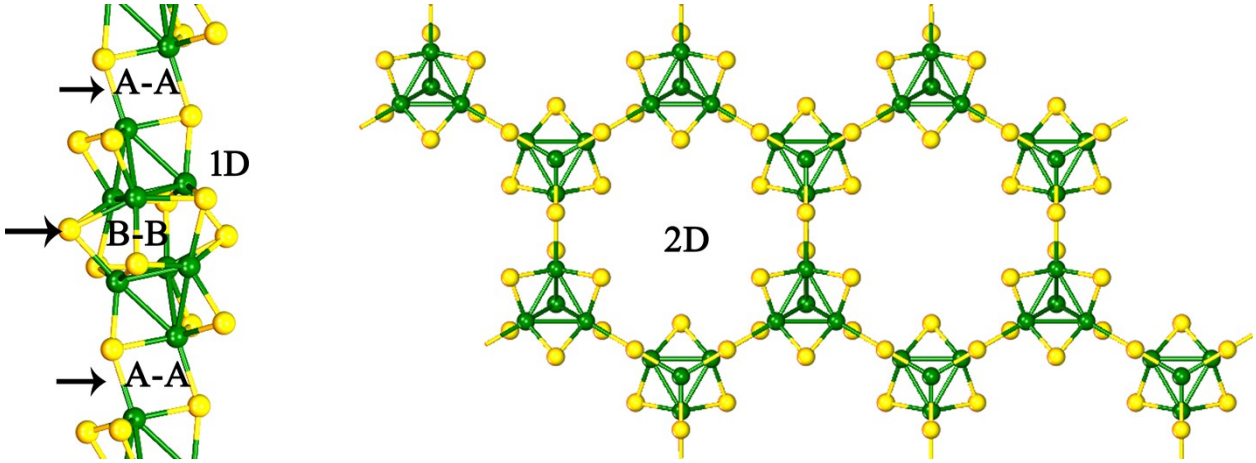

Figure S3. Optimized structures of pristine 1D NW and 2D hexagonal assembly.

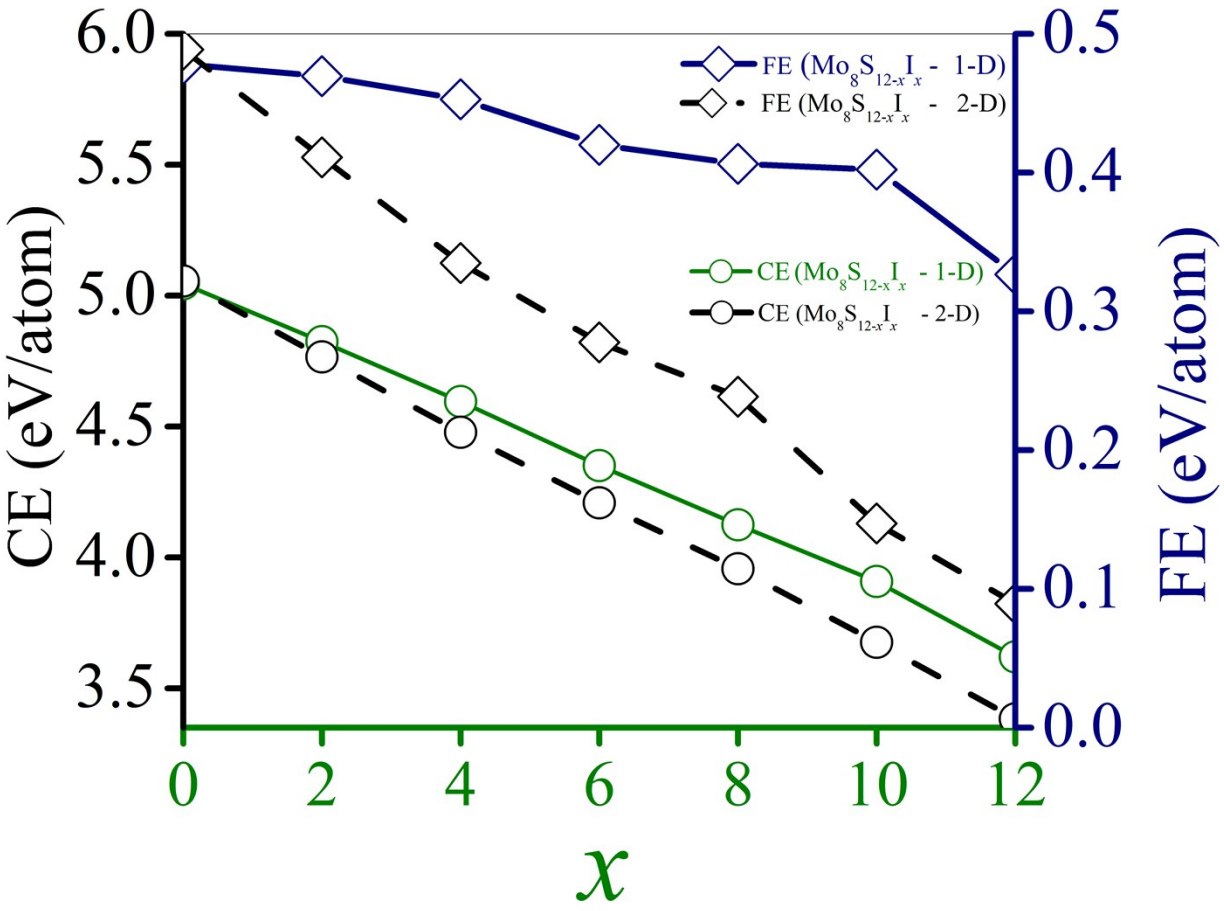

Figure S4. FE and CE of $Mo_8S_{12-x}I_x$ 1-D and 2-D assemblies.

The hexagonal 2-D assembly is constructed by condensing Mo4S6 clusters via A-A bridge. Note that the pristine form of this assembly is more stable, by 19 meV/atom, as compared to 1-D assembly. However, iodine doping increases the relative stability of 1-D assembly, comparing the 2D assembly, due to increasing more number of Mo-Mo bonding. On the other hand, if two Mo_4S_6 clusters are condensed by forming bonds via B-B bridge, by considering the maximum Mo-S bond formation, the best way to connect

next unit is through the corner Mo atoms, which obviously leads to 1D NW. This clearly shows that lesser possibility to form 2D sheets.

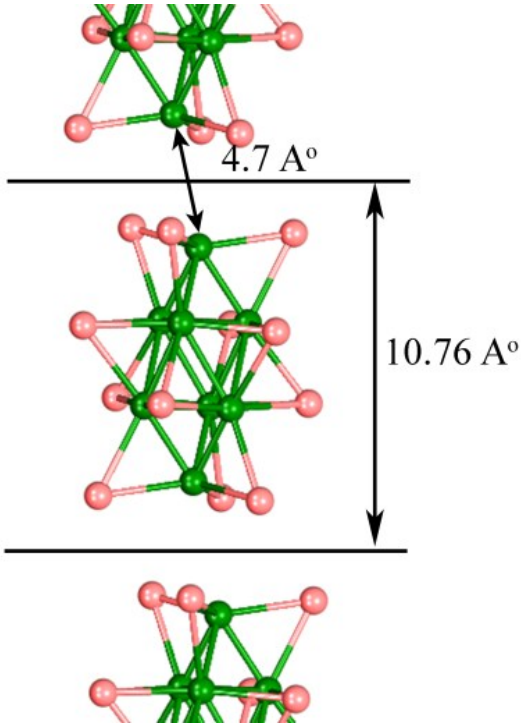

Figure S5. Optimized structure of Mo_8I_{12} NW. It is noticed that dodecahedron clusters are weakly connected.

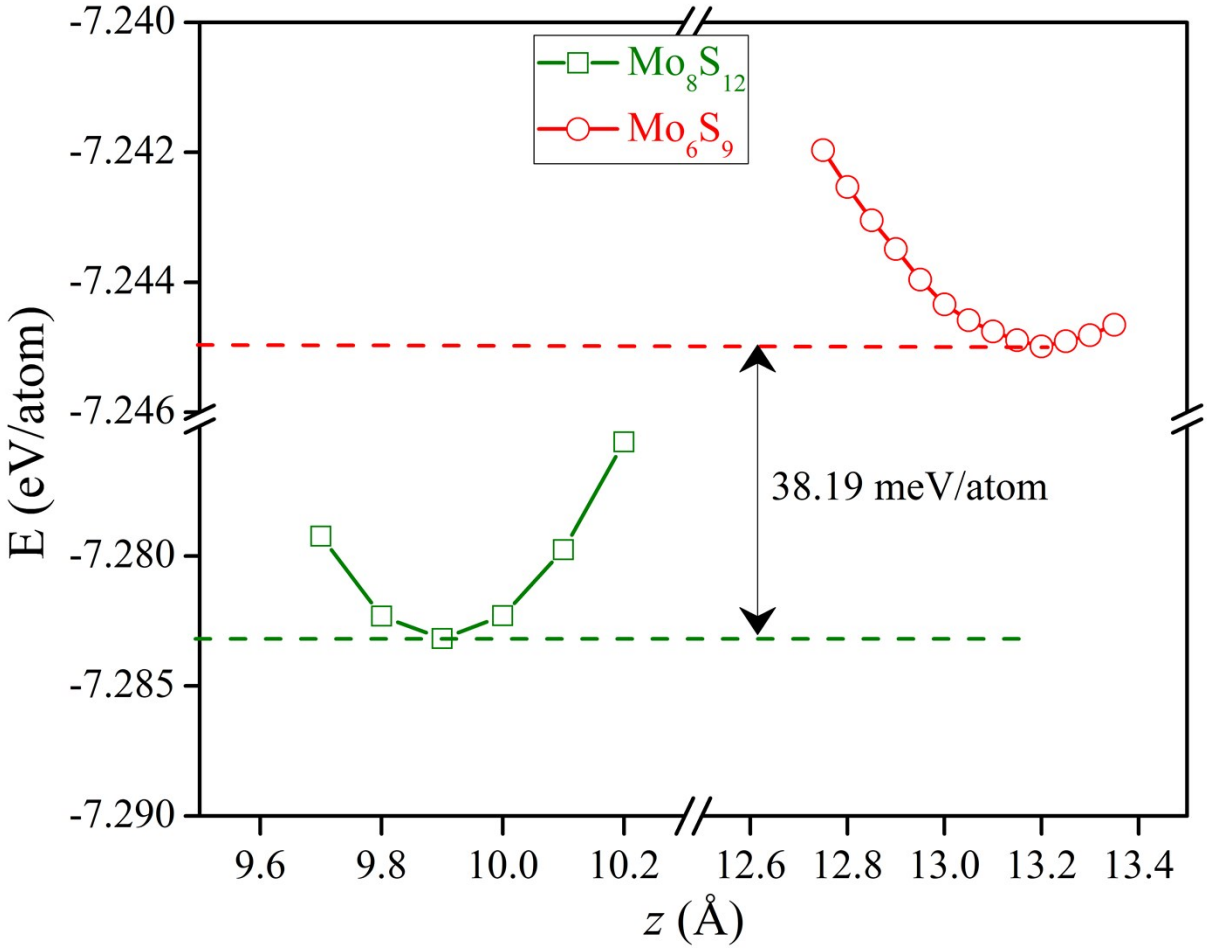

Figure S6. Plot of total energy per atom (E) *vs.* lattice parameter (*z*) for Mo_8S_{12} and Mo_6S_9 NWs