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First Principles Modeling of Mo$_6$S$_9$ Nanowire via Condensation of
Mo$_4$S$_6$ Clusters and Effect of Iodine Doping on Structural and
Electronic Properties

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By employing first principles DFT calculations, we propose new stable model for Mo$_6$S$_9$ nanowire (NW) obtained by condensing tetrahedral Mo$_4$S$_6$ clusters rather than octahedral Mo$_5$S$_8$ clusters, which are known as magic clusters in Mo-S polyhedral cluster family. The pristine NW is found to be metallic and its local structure and physical properties can be tuned by doping of iodine atoms. This doping increases the number of Mo-Mo bonds in the NW, thus, Mo$_6$ tetrahedra are initially fused to Mo$_5$ octahedron, and then, to Mo$_9$ dodecahedron. Further, a close correlation among the Mo-Mo bonding in the local structure, mechanical and electronic properties is observed from our study. Finally, the stability of the pristine and iodine doped Mo$_{6-8}$S$_{9-12}$ NW structures obtained from condensation of Mo$_4$ tetrahedra, are found to be quite comparable with that of already reported Mo$_5$S$_8$NWs with Mo$_6$ octahedra as building blocks.

Introduction

In recent years, Mo-S based nanostructured compounds have been studied due to their interesting properties such as tunable electronic and magnetic behaviour, high tensile strength, and unique optical response. These properties pave the way for obtaining nanostructures with various dimensions that find potential applications in fabricating compact and efficient nano-electronic, optoelectronic, photovoltaic, and energy storage devices. Among them, single layer of 2H-MoS$_2$ nanosheet besides being semiconducting in nature, with a direct band gap of 1.8 eV exhibits valley polarization. While the 1-D Mo-S compounds, such as sub-nano meter sized Mo$_5$S$_8$ and Mo$_6$S$_9$ nanowires (NWs), have tunable electronic, magnetic, and mechanical properties that can be achieved by either addition of Li or doping of iodine atoms. Also, they were proposed to be useful in developing new molecular sensors, interconnects, and switches, and low dimensional superconductors and energy storage devices. Interestingly, 0-D MoS$_{2+x}$ planar clusters that have good catalytic properties towards hydrogen evolution reaction and hydro desulfurization, were formed in different geometries on various substrates like Au, graphite, TiO$_2$ and graphene.

Additionally, it was also reported that Mo$_5$S$_8$ and Mo$_6$S$_9$ clusters are found to be stable among small sized Mo$_x$S$_y$ polyhedral clusters. Particularly, the Mo$_5$S$_8$ and Mo$_6$S$_9$ clusters are found to have ultrahigh stability as they possess high structural symmetry and large highest occupied molecular orbital – lowest unoccupied molecular orbital (HOMO-LUMO) gap. Structurally, Mo$_5$S$_8$ cluster consists of a Mo$_5$ octahedral core with eight S atoms capped on its faces. Its highly symmetric structure and the nature of orbitals provide it a tendency to condense into one dimensional structures such as Mo$_5$S$_y$NWs. The proposed structure from the atomic pair distribution function (PDF) analysis of powder X-ray diffraction data show that the skeleton of the former NW is Mo$_9$ octahedra which is decorated with six S/I atoms on its faces and three S/I atoms on the bridging sites in between the octahedral. Another report, the pristine form of this NW has been condensed by alternate stacking of Mo$_5$S$_8$ octahedron and two Mo$_5$S$_8$ triangles that are interconnected by addition of three S atoms. However, this NW was reproducibly synthesized only for a certain range of doping of I atom (i.e., y = 4.5 to 6.0). It was also observed by first principles calculations that shortage of I atoms leads to deformation of the Mo$_9$ octahedra into Mo$_5$ triangles or prism, due to insufficient electrons to form Mo-Mo network.

On the other hand, Mo$_5$S$_8$ cluster consists of a Mo$_4$ tetrahedron with six S atoms capped on its edges and a larger HOMO-LUMO gap of $\approx$1.57 eV as compared to that of Mo$_5$S$_8$ cluster ($\approx$ 0.91 eV). The studies using density functional theory (DFT) and Auger spectroscopy on this cluster deposited on metallic surfaces have been carried out to understand their thermal and chemical properties. Till date, there is no report on condensation of Mo$_5$S$_8$ cluster. Indeed, it is one of the ways to derive new nanostructures. In the present study, we show, by employing first principle density functional calculations that two Mo$_5$S$_8$ clusters prefer to...
condense linearly as similar to fusion of octahedrals clusters. Then, the condensation is extended for understanding the structural stability and electronic properties of (MoS\textsubscript{x}S\textsubscript{12})\textsubscript{n} nano-rods with \( n = 1 \) to 8 as well as NWs. Interestingly, our calculations reveal that pristine MoS\textsubscript{12} NW, obtained from condensation of MoS\textsubscript{12} clusters, is energetically more stable as compared to the existing model of MoS\textsubscript{8} NW which was reported\textsuperscript{32}. Although, MoS\textsubscript{12}S\textsubscript{6} NWs with \( x = 2 - 8 \) are found to be less stable, both the NWs with \( x = 10 \) have almost equal structural stability. Further, the structural, mechanical, and electronic properties of the MoS\textsubscript{12} NW are tuned by varying the local structure of Mo clusters via \( \Gamma \) atom doping.

**Computational Methods**

The atomic structure of Mo-S clusters and NWs are self-consistently optimized using first principles DFT calculations as implemented by Vienna \textit{Ab initio} Simulation Package (VASP)\textsuperscript{41}. The wave functions are expanded using plane wave basis set within projector augmented wave pseudo-potential formalism\textsuperscript{42} and electron-electron correlation effects are corrected by generalized gradient approximations\textsuperscript{43}, invoking GGA (Perdew-Wang 91) functional. The electronic optimizations are carried out with convergence factor of 10\textsuperscript{-6} eV and then, the ions are relaxed iteratively until the absolute values of forces between the ions become less than 0.01 eV/Å. The Mo-S cluster is kept in a periodic unit-cell with a vacuum space of 15 Å in all directions, which is necessary to avoid the interactions between the cluster and its periodic images. Similarly, MoS\textsubscript{12}I\textsubscript{4} NWs are oriented along z-axis of the unit-cell, in which, both x and y directions are considered to have a vacuum space of 15 Å. Then, the lattice constant of the NW is manually optimized by varying steps of 0.01 Å. To deduce the DOS and band structure, the non-self-consistent calculations are performed, in which makes use of the charge density and wave functions that are previously obtained from self-consistent calculations. For self-consistent and non-self-consistent calculations, the Brillouin zone of the simulation cell is sampled by \( 1 \times 1 \times 6 \) and \( 1 \times 1 \times 200 \) k-meshes, respectively. To find the magnetic properties of the NWs, the spin-polarized calculations were carried out. Our study confirmed that all the NWs were observed to be non-magnetic, because Mo atoms are firmly bonded as well as I atoms are symmetrically distributed in NWs\textsuperscript{2,39}. For comparing the stability of MoS\textsubscript{12}I\textsubscript{4} NWs, similar calculations were repeated for MoS\textsubscript{8}I\textsubscript{4} NWs whose atomic structures were reported\textsuperscript{41}.

**Results and discussion**

Initially MoS\textsubscript{12} cluster is modeled by edge-capping S atoms on a Mo\textsubscript{4} tetrahedron (refer Figure 1) and this cluster is optimized by first principles calculations. It has HOMO-LUMO gap of 1.57 eV which is in agreement with earlier works\textsuperscript{28,29}. Note that the average Mo-Mo and Mo-S bond lengths in the cluster are 2.56 and 2.32 Å, respectively. It is also observed that the HOMO of the cluster is localized on S atoms while the LUMO lies mainly on Mo atoms (refer Figure 1). This indicates that the Mo atoms of one tetrahedron can interact with the S atoms present in another tetrahedron for making Mo-S bonds through sharing of electrons, when two MoS\textsubscript{6} clusters are fused to form a dodecahedron cluster. In addition to that, the symmetry of HOMO and LUMO enables the clusters to condense together.

To begin with, two units of the MoS\textsubscript{6} cluster can fuse into two possible ways: viz. A-A and B-B configurations (shown in Figure 1). In A-A configuration, two tetrahedra interact by forming two Mo-S bonds with their apexes pointing each other, while in the B-B, their triangular bases lie face to face, thereby forming six Mo-S bonds. Our calculations show that the B-B configuration is 2.22 eV more stable than the A-A counterpart due to having more Mo-S bonds. Therefore, we proceed with further condensation of MoS\textsubscript{6} cluster onto B-B configuration, to obtain (MoS\textsubscript{6})\textsubscript{n} NW, in which, both A-A and B-B linkages are present because a third unit can be added only via A-A bridge. In similar fashion, (MoS\textsubscript{6})\textsubscript{n} nano-rods with \( n = 2 - 8 \) are obtained and the optimized structures are shown in Figure S1 (Supplementary Information). To understand the stability of (MoS\textsubscript{6})\textsubscript{n} nano-rods, the condensation energy per MoS\textsubscript{6} formula unit (f.u.) is deduced from \( E_{\text{cond}} = \frac{n \times (\text{MoS}_{6})_{\text{n}} - (\text{MoS}_{6})_{n}}{n} \). The calculated \( E_{\text{cond}} \) value and the HOMO-LUMO gap of nanorods are reported in Figure S2 (Supplementary Information). It shows that the \( E_{\text{cond}} \) value increases gradually with \( n \), whereas, the HOMO-LUMO gap decreases due to the creation of new electronic energy levels that originate from Mo-S bonds formed during condensation. Further, trend of this plot indicates that the MoS\textsubscript{6} units are plausibly condensed to form the infinite MoS\textsubscript{12} NW, whose unit-cell contains two units connected alternatively through B-B and A-A linkages. We also performed the first principles calculations on 2-D assembly which is possible to construct only through A-A configuration, because of the geometrical
constraint in making Mo-S bond along x and y direction due to the presence of B-B linkage. The optimized structure and its energetics are reported in Figure S3 and S4 (Supplementary Information).

The atomic structure of Mo$_8$S$_{12}$ NW is provided in Figure 1 and its lattice constant is calculated to be 9.91 Å. In this structure, average Mo-Mo and Mo-S bond lengths in the constituent Mo$_4$ tetrahedra are 2.75 Å and 2.32 Å, respectively. Note that the Mo-Mo bond length in isolated Mo$_8$S$_{12}$ cluster is 2.56 Å which is quite shorter than that in the NW, owing to the formation of more number of Mo-S bonds during the condensation of clusters. It is also observed that the Mo-S bond in A-A bridging site is larger by 0.2 Å as compared to that bond in B-B site. Further, we noticed that there is possibility to form Mo$_8$ octahedron in region where triangular bases of two Mo$_4$ units are interconnected with a Mo-Mo separation of 3.12 Å. In this region, the atomic structure of this NW is quite similar to Mo$_8$S$_8$ NW. Also we noticed that the Mo-Mo bond (= 2.60 Å) in the triangular base is quite shorter as compared to Mo-Mo bond along NW axis (2.75 Å). This suggests that the Mo$_{12}$ triangles will not break easily when the system undergoes structural changes due to the external causes such as, chemical doping or mechanical stress.

Next, we carried out the doping of I atoms into Mo$_8$S$_{12}$ NW to understand its effect on the local atomic structure and electronic properties. For this, three different sulfur sites are identified in the NW, viz. $S_{oct}(3c)$, $S_{tet}(3c)$, and $S(2c)$ which are present at bridging, octahedral, and tetrahedral sites, respectively (shown in Figure 1) and 3c and 2c stand for three and two coordination of sulfur atom, respectively. Substitution of I atom in the aforesaid sites shows that it prefers to replace $S_{tet}(3c)$ atom, rather than $S_{oct}(3c)$ or S(2c) atom. As compared to former site, doping of I atom on other two sites increases the ground state energy by 35.48 and 10.78 meV/f.u., respectively. Considering this, two $S_{oct}(3c)$ atoms are replaced with I atoms to get the Mo$_8$S$_{10}$I$_2$ NW. Our calculations on this NW show that the strength of Mo-Mo interaction at octahedral site is significantly increased as this distance is decreased to 3.02 Å from 3.12 Å (of pristine NW). On the contrary, same bond distances at tetrahedra as well as bridging sites are slightly increased, which is the symptom of formation of Mo$_8$ octahedron in Mo$_8$S$_{12-4I}$ NW with $x = 2$ (refer Figure 2). In the subsequent step of doping of two more I atoms ($x = 4$), the average Mo-Mo bond distances at octahedral ($d_o$) and bridging ($d_b$) sites are further decreased to 2.85 and 2.96 Å respectively, whereas, those at tetrahedral site ($d_t$) are increased from 2.81 Å (for $x = 2$ NW) to 2.96 Å. Hence, we conclude that the deformation of Mo$_8$ tetrahedra significantly starts from $x = 4$ onwards. With further doping of I atoms ($x = 6$), the Mo-Mo bond at d$_t$ site almost reaches bulk Mo-Mo distance (=2.72 Å), which indicates that the NW has enough electrons to form a Mo$_8$ octahedron (Mo-Mo = 2.78 Å). Also the Mo-Mo bonds at d$_b$ site get strengthened enough to maintain the A-A bridging bonds (Mo-Mo@d$_b$ = 2.91 Å). Hence, obviously the bonds at d$_b$ become too weak to keep the Mo$_4$ tetrahedra intact anymore, as seen in Figures 1 and 2. From these discussions, we have clearly demonstrated that the octahedral geometry is stable in iodine doped NWs while the tetrahedral geometry is preferred in pristine NWs.

Interestingly, we further discerned that the weakly interacting apex Mo atoms in Mo$_8$S$_8$I$_6$ NW are pulled back towards the Mo$_8$ octahedron when two more I atoms ($x = 8$) are substituted at $S{2c}$ sites ($d_b$) which was shown to be the next feasible site for doping of this atom. It is a trait of formation of Mo$_8$ dodecahedral unit which reduces the Mo-Mo bond lengths at d$_o$ site (refer Figure 2). Thus, for the Mo$_8$S$_{12-4I}$ NW with $x = 8$, the Mo-Mo bond lengths at d$_o$ decrease significantly, while those at d$_b$ site increase to the same extent. The same trend is continued in the structure of NW when $x$ is increased to 10. Finally, when all the S atoms are replaced with I atoms, the resulting atomic structure of Mo$_8$I$_{12}$ NW is found to be broken into weakly interacting dodecahedral clusters with Mo-Mo bond distance of 4.69 Å at d$_o$ site and the I-I distance of 4 Å (refer Figure S5, Supplementary Information). The larger radius of I atom as compared to S atom completely shields the Mo atom and prevents interaction between them. Note that Mo-Mo bond length in Mo$_8$ cluster is 2.56 Å, which is equal to corresponding distance in Mo$_8$S$_8$ isolated cluster. The above discussions show that the core Mo$_4$ tetrahedral structure of the pure NW first deforms into Mo$_8$ octahedron and later all the Mo atoms fuse into a Mo$_8$ dodecahedral cluster due to availability of sufficient number of electrons. Thus, we demonstrated that the local backbone geometry of Mo$_8$ clusters in the NW network flexibly changes its structure from tetrahedra to octahedral one and then, finally to dodecahedral structure during the doping of I atoms.

To understand the stability of the NWs, the cohesive energy per atom (CE) and the formation energy per atom (FE) are calculated from the following formulae:

\[ CE = \frac{1}{N} \sum_{i=1}^{N} E_i - \frac{1}{2} E_{\text{bulk}} \]

\[ FE = CE - \frac{1}{2} E_{\text{bulk}} - E_{\text{atoms}} \]

Here, $E_i$ is the total energy of the NW with $i$ atoms, $E_{\text{bulk}}$ is the total energy of the isolated bulk material, and $E_{\text{atoms}}$ is the total energy of the isolated atoms.
Similar formulae are adopted for calculating the CE and FE of Mo, S, I atoms and total energy of Mo$_{8}$S$_{12-x}$I$_{x}$ NW, respectively. It is worth to mention that all atomic energies are approximated by energy difference of 38.19 meV/atom (refer Figure S6, Supplementary Information). It is because of the fact that the building blocks of Mo$_{8}$S$_{12}$ NW (Mo$_{3}$ triangular clusters) have been found to be less stable than the magic tetrahedral and octahedral clusters. Moreover, the I atom doped Mo$_{8}$S$_{12}$ NWs show the greater stability, because the atomic structure of Mo$_{8}$S$_{12-x}$I$_{x}$ NW has one or two weakly bonded Mo$_{6}$ cluster units. However, for $x = 10$, the CE values are almost equal for both the NWs due to formation of Mo$_{8}$ dodecahedron with more Mo-Mo bonds. Similarly, the FE is also decreased with increased concentration of I atoms. Initially, for the NWs with $x = 2$ and 4, the FE comes down gradually because of breaking of tetrahedral clusters but decreases very slowly after $x = 6$ due to formation of octahedral clusters in the structure. Finally the FE falls down to a minimum value for weakly interacting dodecahedral clusters. The FE plot is linearly approximated (shown by dashed line in Figure 5) by connecting the FE of $x = 0$ and $x = 10$ case, to deduce the synthesizable composition of NWs. Note that the NW with $x = 12$ is not considered due to weakly interacting dodecahedral units. From this plot, we conclude that the substitution of S by I is more feasible in $x = 2 - 4$ region and the NW in this region is expected to be observed by experiment. We also understand the growth direction of Mo$_{8}$S$_{x}$ clusters by comparing CE and FE of 1-D and 2-D assemblies (refer Figure S4, Supplementary Information). Our calculations show that for pristine case, the 2-D assembly is energetically more favored than 1-D NW, however, all iodine doped 2-D systems become less stable as compared to respective 1-D NWs, due to its geometrical constraint in increasing the number of Mo-Mo bonds. Overall, it is concluded that this cluster is preferred to grow linearly without the help of any substrate.

For Mo$_{8}$S$_{12-x}$I$_{x}$ NW,  

$$CE = \frac{1}{20} [8E(Mo) + (12-x)E(S) + xE(I) - E(Mo_{8}S_{12-x}I_{x})]$$

$$FE = \frac{1}{20} [8\mu(Mo) + (12-x)\mu(S) + x\mu(I) - E(Mo_{8}S_{12-x}I_{x})]$$

where, $E(Mo)$, $E(S)$, $E(I)$ and $E(Mo_{8}S_{12-x}I_{x})$ are the atomic energies of Mo, S, I atoms and total energy of Mo$_{8}$S$_{12-x}$I$_{x}$ NW, respectively. It is worth to mention that all atomic energies are obtained by performing the spin-polarization calculations. While, $\mu(Mo)$, $\mu(S)$, and $\mu(I)$ are the chemical potentials of respective elements in their rich condition, thus they are obtained from bulk Mo, S and I$_{2}$ clusters, respectively.

Similar formulae are adopted for calculating the CE and FE of Mo$_{8}$S$_{x}$I$_{y}$ NWs whose atomic structures were reported elsewhere. Though the unit cells of Mo$_{8}$S$_{9}$I$_{4}$ and Mo$_{8}$S$_{12-x}$I$_{x}$ NWs contain different number of total atoms, the cohesive energy per atom is calculated for both the NWs independently and then its difference ($\Delta_{CE}$) is calculated between the nanowires for which $y = 3x/4$ that allows direct energy comparisons. For both types of NW, the CE value decreases gradually with increasing concentration of I atoms as a result of increasing ionic nature of NW (refer Figure 3). This figure reveals that the pristine Mo$_{8}$S$_{12}$ NW with tetrahedra as building blocks is found to be more stable than Mo$_{8}$S$_{9}$ NW,

<table>
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<th>$\gamma$ (GPa)</th>
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Table 1. Band gap, Lattice Parameter ($c$), Young’s modulus ($\gamma$) and Cohesive Energy (CE) of 1-D and 2-D Mo$_{8}$S$_{12-x}$I$_{x}$ assemblies ($x = 0 – 12$).
Since the local structures of Mo$_8$S$_{12-x}$I$_x$ NWs are changing with respect to I atom concentration, it is also expected to reflect on its mechanical properties.

The Young’s modulus ($Y$), is calculated from,

$$ Y = \frac{Ac}{A} $$

where ‘$A$’ is the cross sectional area of the NW, obtained from $\pi \times d^2 / 4$, in which ‘$d$’ is the sum of center-to-center distance between farthest atoms on the cross sectional plane of the wire and the covalent radii of the corresponding atoms, ‘$k$’ is the force constant that is deduced from second derivative of plot of total energy ($E$) vs lattice constant and ‘$c$’ is equilibrium lattice constant of the NW. The calculated $Y$ values of the NWs are given in Table 1. The pristine NW has the highest $Y$ value of 133 GPa owing to the covalent nature of Mo-S bonds. For the NW with $x = 2$, covalency is decreased, in addition of distortion of the core tetrahedral structure, which together decrease the $Y$ value to 98.9 GPa. Similarly, more distortion in the structure of tetrahedral network, the $Y$ value of NW with $x = 4$ reduces further to 87.4 GPa. Surprisingly for Mo$_8$S$_8$ NW, the $Y$ value increases to 98 GPa. This reversal in the trend is due to the significant change in the backbone structure of the NW to Mo$_6$ octahedron, where the strength of Mo-Mo bonds overshadow the effect of ionic Mo-I bonds. However, for $x > 6$, the $Y$ value decreases slowly with increasing $x$. Finally, for $x = 12$, there is a huge fall in the value of $Y$ which is observed to be 41.3 GPa, due to weakly interacting Mo$_4$ dodecahedral clusters. It is worthy to discuss that Mo$_8$S$_{12-x}$I$_x$ NWs are always higher $Y$ values as compared to respective Mo$_8$S$_{12}$I$_x$ NWs as former type of NW has almost uniform dimension along its axis.

Next, the deduced density of states (DOS) of all Mo$_8$S$_{12-x}$I$_x$ NWs are shown in Figure 4. It is clear from the DOS of pure Mo$_8$S$_{12}$ NW that it is metallic in nature with strong hybridization between Mo and S states lying between -1.5 to -0.5 eV. Moreover, electronic states are well spread across the Fermi level ($E_F$), which imparts good electronic conductivity to this NW. In contrast, the Mo$_8$S$_8$ NW is semiconducting nature with well localized electronic states around $E_F$. Similar to pristine NW, metallic character is observed in Mo$_8$S$_{10}$I$_2$ NW. Upon further doping, NWs with $x = 4$ and 6 become semiconducting in nature with band gaps ($E_g$) of 0.15 and 0.08 eV, respectively.

As the result of locally increasing Mo-Mo interaction in these NWs, semiconducting nature is observed from our work. In order to get more details about the feature of valence band (VB) and conduction band (CB) of Mo$_8$S$_{12-x}$I$_x$ NWs, the band structures are plotted and reported in Figure 5. It is observed from this figure that the pristine NW has comparatively well dispersed VB than the other NWs and two states are crossing the $E_F$. While for Mo$_8$S$_{10}$I$_2$ NW, the VB is less dispersed that infers the lowering of electron mobility in this NW. Notably, the NWs with $x = 4, 6, 8$ and $10$ are semiconductors with $E_g$ values of 0.15, 0.08, 0.29, and 0.40 eV, respectively. Overall, the $E_g$ of NWs increases with $x$. Thus, we conclude that the electronic properties of the Mo$_8$S$_{12-x}$I$_x$ NWs are tunable via I atom doping.

Conclusions

From our study, we propose a new atomic structure for Mo$_8$S$_x$ NW obtained by condensing Mo$_4$S$_6$ clusters rather than Mo$_8$S$_4$ clusters as attempted earlier. The proposed structure of Mo$_8$S$_{12}$I$_x$ NW is found to be more stable in pristine form. However, iodine doping reduces its stability significantly as compared to NW having Mo$_6$ octahedra as building block. Interestingly, the local structure of proposed NW is strongly influenced by I atom doping which in turn affects its mechanical and electronic properties, mainly due to the variations in Mo-Mo bonding. Further, we deduced electronic properties of the pristine NW and found them to be metallic in nature with well dispersed VB; whereas, the iodine doped NWs have semiconducting nature with narrowly dispersed VB and the $E_g$ value increases with the dopant concentration.

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Notes and references