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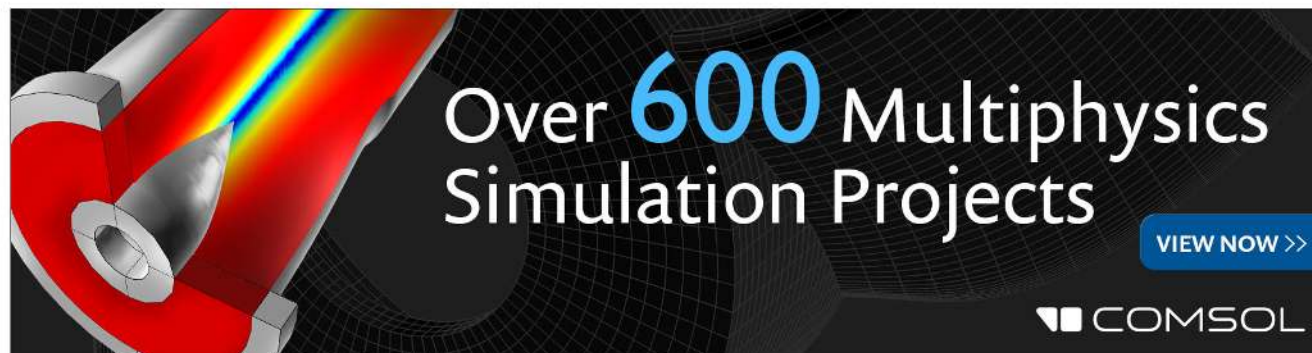
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Lithiated assemblies of metal chalcogenide nanowires

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We study hexagonal assemblies of M_6X_6 ($M=Mo$ and W and $X=S, Se,$ and Te) nanowires from first-principles calculations to understand their structural stability, electronic properties, and the effects of Li intercalation. It is shown that due to van der Waals interactions between the nanowires, the intercalation is achieved without a significant change in their atomic structure. With an increase in Li concentration, we predict a new phase for $Li_3Mo_6S_6$ compound, in which the hexagonal assembly transforms to a monoclinic structure by a change in the orientation of nanowires. The $Li_xMo_6S_6$ assemblies are electrically conductive and can be potentially used as cathode materials in Li-ion batteries for nanoscale applications. The voltage of such a battery, calculated to be 1.7 V, can be manipulated such as by iodine doping without a significant change in the atomic structure.

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Quasi-one-dimensional materials are attractive for Li-ion battery applications^{1,2} and carbon nanotube bundles have been studied as potential candidates for Li storage³ because graphite is used as anode material in commercial batteries. However, carbon nanotubes do not have unique structural and electronic properties¹ and, in as prepared samples, the amount of Li stored is similar to that obtained in graphite (LiC_6). Nanowires of metal chalcogenides such as MoS_x are interesting alternative^{4,5} to carbon nanotubes and are currently of much interest. Their assemblies have been produced^{4,6,7} with unique structure such as in the family of Mo_2S_3 with iodine doping. These nanowires are almost defect free and this leads to their unique physical and chemical properties. Recently Mo_6S_6 type nanowires have also been predicted to have higher stability^{8,9} compared to those with Mo_2S_3 composition. Here we study assemblies of these nanowires and report results of our first-principles studies on their intercalation with Li as well as the effects of iodine doping.

Mo_6S_6 nanowires (diameter ~ 0.8 nm) can be described in terms of condensed octahedral Mo_6 clusters^{8,10} with chalcogen atoms decorating this metallic core. Chalcogen atoms decorate this metallic core of the Mo_6S_6 nanowire. The nanowires are metallic^{5,8,11} because of the partially occupied $4d$ band of Mo and can be assembled into a hexagonal array (space group $P63/m$) which is interestingly stabilized by weak van der Waals (vdW) interactions between the nanowires. Therefore, Mo_6S_6 type nanowire assemblies have similarity to carbon nanotube bundles from the point of view of bonding between the nanowires but the former could have advantage as MoS_x nanowire assemblies could be prepared with ease in a controlled fashion and the nanowires are very thin.^{4,7} The void space in between the nanowires can be used for Li intercalation,^{2,6} very similar to the case of carbon nanotubes. It could lead to interesting electron and ion conduction properties of such assemblies due to their one-dimensional nature. We find that Li intercalation of nanowire assemblies can be achieved without much change in the nanowire structure and with a voltage close to 1.7 V that is

used in commercial batteries. This also makes Mo_6S_6 nanowire based systems good candidates for cathode material because in commercial Li ion batteries the cathode oxide material has a major problem of structural damage during charging-discharging cycles.¹² Furthermore, doping of iodine could be used to refine their electronic properties without much structural changes^{5,8} and it could lead to the design of suitable materials for batteries.

We use plane wave ultrasoft pseudopotential method¹³ within the density functional theory (DFT). The exchange-correlation energy is treated within generalized gradient approximation (GGA).¹⁴ The cutoff energy for the plane wave expansion is taken to be 500 eV. The Brillouin zone of the nanowire assemblies is sampled by $4 \times 4 \times 8$ k points. The ionic positions as well as the lattice parameters of assemblies are allowed to relax without any symmetry constraint. The ionic relaxation process is repeated until the force on each ion is converged to a few meV/Å.

We study M_6X_6 assemblies with $M=Mo$ and W and $X=S, Se,$ and Te , and their intercalation with Li in order to explore the possibilities for Li battery applications. The results are given in Table I. The accuracy of the calculations is verified in the case of $K_2Mo_6S_6$ for which experimental structural data is available.¹⁵ Further calculations have been done for bulk Li to obtain battery voltage. We find that in this family, Mo based nanowires with $X=S$ and Se give the high-

TABLE I. Optimized lattice constants and OCV of hexagonal assemblies of nanowires of metal chalcogenides compounds.

Compounds	a (Å)	c (Å)	OCV (V)
Mo_6S_6	~ 9.00	4.35	
$Li_2Mo_6S_6$	8.24	4.41	1.69
Mo_6Se_6	8.96	4.44	
$Li_2Mo_6Se_6$	8.52	4.50	1.58
Mo_6Te_6	9.45	4.58	
$Li_2Mo_6Te_6$	9.11	4.60	1.26
W_6S_6	9.04	4.35	
$Li_2W_6S_6$	8.25	4.42	1.41
W_6Se_6	9.12	4.44	
$Li_2W_6Se_6$	8.56	4.49	1.33
W_6Te_6	9.42	4.56	
$Li_2W_6Te_6$	9.19	4.57	1.12

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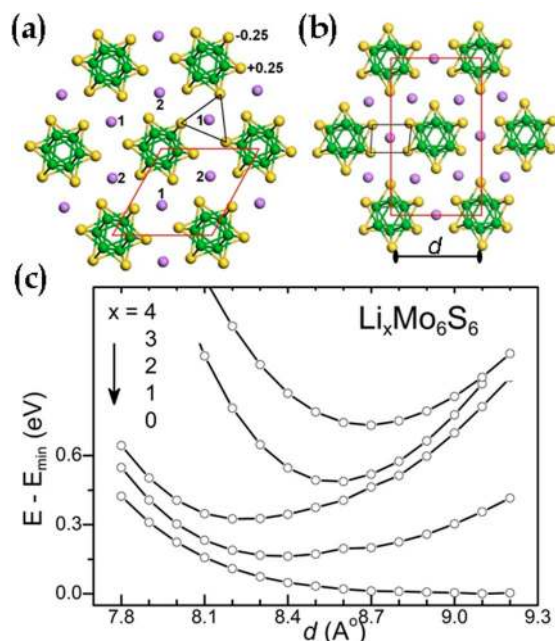


FIG. 1. (Color online) (a) Projection of the crystal structure of $\text{Li}_2\text{Mo}_6\text{S}_6$ compound along the nanowire axis. Green, yellow, and violet balls represent Mo, S, and Li atoms, respectively. The unit cell in the plane perpendicular to the nanowire axis is marked by a rhombus. The positions of the S atoms along the z axis are indicated in terms of the lattice constant c . (b) The monoclinic atomic structure of $\text{Li}_3\text{Mo}_6\text{S}_6$ (space group $C2/m$) projected along the z axis. Li atoms now lie at the center of S rectangle (see small rectangle) between two neighboring nanotubes. The unit cell in the plane perpendicular to the z axis is marked by large rectangle. (c) The variation of energy with the separation, d , between two nanowires. E_{\min} is the value of the energy at the equilibrium position.

est voltage. In the following, we focus our attention on Mo_6S_6 nanowire assemblies and study the effects of different amounts of doping of Li and I on the structural stability and electronic properties.

The optimized Mo_6S_6 nanowire assembly has a hexagonal lattice as shown in Fig. 1(a) (without Li). The lattice constants are given in Table I along with the values for the Li-intercalated case. There are strong covalent interactions in the condensed octahedral units in a nanowire but the weak vdW interactions between the nanowires make it difficult to obtain the lattice constant along the x or y axis (a) properly for the nonintercalated case within GGA. However, with Li intercalation, the bonding between the nanowires changes [see Fig. 1(c)] and it induces some changes in the lattice constants. Along the nanowire axis, the lattice parameter c for the $\text{Li}_2\text{Mo}_6\text{S}_6$ case is slightly ($\sim 1.4\%$) enhanced, as shown in earlier work.¹⁶ However, perpendicular to the nanowire axis, there is a contraction in the lattice parameter of the Li intercalated Mo_6S_6 nanowire assembly. Note that for the assembly without Li intercalation, we expect GGA (Ref. 14) to significantly overestimate the lattice parameter (a), while for Li intercalated cases our accuracy should be much better as our test calculation has shown. Therefore our results suggest that in this system the changes in the lattice parameters should be small (within a few percent) when Li is intercalated and it should not be a problem as the nonintercalated system is easily compressible (note the nearly flat energy surface near the equilibrium value of a). These changes in the lattice constants for the Li intercalated nanowire assembly are much smaller as compared to the lattice expansion in

the currently used oxide systems for Li ion batteries such as LiNiO_2 , where the change in the lattice constants a and c are $\sim 4\%$ and $\sim 9\%$, respectively, when compared to NiO_2 .¹² Therefore, Li intercalation of the Mo_6S_6 nanowire assemblies can be achieved without destruction of the lattice.

For Li intercalated system, LiMo_6S_6 , Li atoms occupy positions 1 (or equivalently 2) in the trigonal voids between the S atoms [see projection along the nanowire axis in Fig. 1(a)] formed by three neighboring nanowires in a threefold symmetric manner. For $\text{Li}_2\text{Mo}_6\text{S}_6$, all the six such triangular positions, 1 and 2 are occupied as shown in Fig. 1(a). However, Li atoms in positions 1 and 2 are not in the same plane and are separated by $c/2$ along the nanowire axis. This structure is similar to $\text{Li}_2\text{Mo}_6\text{Se}_6$ known before.^{15,17} When one more Li atom is added in the unit cell to obtain $\text{Li}_3\text{Mo}_6\text{S}_6$, interestingly we find that the orientation of the nanowires in the optimized structure changes by about 18° so that Li atoms now lie at the centers of rectangles formed by S atoms of two neighboring nanowires. It also leads to a change in the symmetry of this structure from hexagonal to monoclinic, as shown in Fig. 1(b). Beyond 3 Li atoms, the distribution of Li atoms becomes asymmetric, but the atomic structure of Mo_6S_6 nanowires is preserved. However, the atomic structure of Mo_6S_6 nanowires is preserved.

For practical applications of such nanoassemblies in Li batteries, we calculated the intercalation voltage [open circuit voltage (OCV)] from¹²

$$V = \frac{\mu_{\text{Li}}^{\text{cathode}} - \mu_{\text{Li}}^{\text{anode}}}{qF}, \quad (1)$$

where q is the charge (in electrons) transported by Li in the electrolyte, F is the Faraday's constant, and μ , is the chemical potential of Li. By neglecting the entropic and $P\Delta V$ (P =pressure and ΔV =change in volume) contributions, the difference between the chemical potentials of cathode and anode can be directly related to the total energies, E of $\text{Li}_{x_2}\text{Mo}_6\text{S}_6$, $\text{Li}_{x_1}\text{Mo}_6\text{S}_6$, and Li metal as $V = [E(\text{Li}_{x_2}\text{Mo}_6\text{S}_6) - E(\text{Li}_{x_1}\text{Mo}_6\text{S}_6) - (x_2 - x_1)E(\text{Li})] / (x_2 - x_1)q$. The calculated value of the potential (OCV) is 1.69 V for the case of $\text{Li}_2\text{Mo}_6\text{S}_6$. This value is interesting as most of the commercial batteries use 1.5 V and it is possible to achieve it without large changes in the structure as well as the unit-cell volume during the charge-discharge cycles. Similar calculations for MoSe and MoTe systems show (Table I) that the OCV value for the case of MoS nanowire assembly is relatively higher as compared to other compounds in this family. Our calculated OCV for $\text{Li}_2\text{Mo}_6\text{Se}_6$ compound is 1.6 V, which is quite comparable to the experimental value of ~ 1.5 V.¹⁷ Hence, it can be expected that MoS nanowire assemblies could be good candidates for cathode material in Li battery.

As shown in Fig. 1(c), the vdW interaction between the nanowires is significantly affected by increasing x . The lattice constant (a) at equilibrium initially shows a contraction due to the change in the bonding nature and then it increases with x . The increase in the value of a for the case of $x=3$ is also due to a change in the orientation of the nanowires. For the nonintercalated Mo_6S_6 assembly, this orientation is energetically less favorable⁵ and the internanowire separation is larger than for the equilibrium phase. The OCV is found [Fig. 2(d)] to significantly depend on the value of x and it decreases with an increase in x . The small decrease in the

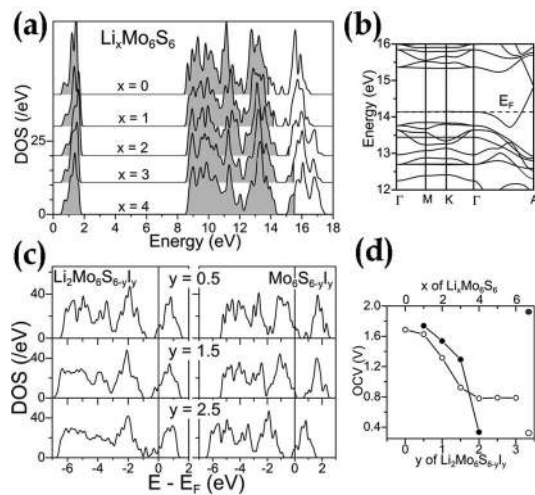


FIG. 2. (a) Total DOS of $\text{Li}_x\text{Mo}_6\text{S}_6$ ($x=0-4$) nanowire assemblies. Gray shaded region shows the occupied states. (b) The band structure along high symmetry directions of the hexagonal assembly for $x=1$. (c) Total DOS for $\text{Mo}_6\text{S}_{6-y}\text{I}_y$ systems (both Li intercalated and nonintercalated). With increasing I doping, the E_F moves up in a nearly rigid-band-like manner. (d) Calculated OCV for $\text{Li}_2\text{Mo}_6\text{S}_{6-y}\text{I}_y$ and $\text{Li}_x\text{Mo}_6\text{S}_6$ systems.

value of OCV for x up to 3 suggests that the gain in energy due to Li intercalation continues to be similar to that obtained for lower intercalation concentration. Beyond $x=3$, the decrease is more rapid because of the relatively lower stability of the intercalated assemblies.

To further understand the effects of iodine doping on Li intercalation we studied $\text{Mo}_6\text{S}_{6-y}\text{I}_y$ (up to $y=3$) nanowire assemblies because an extensive study has been recently carried out on iodine doped Mo_6S_6 nanowires. Iodine doping was shown¹⁶ to be electronically equivalent to Li as both act as electron donor to nanowires. Also, nanowires with $y=2$ have high stability among the different I compositions. For assemblies, we find that iodine doping leads to a significant distortion in the hexagonal lattice constants, as ionic radius of iodine is significantly larger than that of the sulfur. However, no local structural changes in Mo–S nanowires are observed. The Li intercalation properties of I doped assemblies are similar to those of $\text{Li}_x\text{Mo}_6\text{S}_6$ nanowires. The variation in the value of OCV in Fig. 2(d) shows that for low concentration of I, the behavior is similar to that of Li. But, $y>2$, there is a nearly flat behavior. Therefore it may become possible to manipulate the variation in OCV with Li concentration by codoping nanowires with a suitable element.

Li intercalated and I doped nanowire assemblies are metallic as it can be seen from the total density of states (DOS) in Fig. 2. For $\text{Li}_x\text{Mo}_6\text{S}_6$, there is a rigid-band-like behavior as x is increased. The band width of the occupied states for each x remains quite similar as there is no significant change in the structure of Mo_6S_6 nanowires. Also even for $x=3$, the monoclinic structure does not significantly affect the DOS due to predominantly the one-dimensional nature of these systems which does not change by a small rotation of the nanowires. It is noted in Fig. 2(a) there is a pseudogap close to 15 eV. The band structure of $\text{Li}_1\text{Mo}_6\text{S}_6$ has a predominantly one-dimensional character as significant dispersion is along the nanowire axis. A free electron-like band [Fig. 2(b)] crosses the Fermi energy (E_F) and it leads to low DOS in this energy region. This band gets fully occupied for $x=2$ and there is a higher stability at this composition. The monoclinic

phase ($x=3$) is also metallic as shown in Fig. 2(a).

E_F moves up as increasing the iodine doping concentration (y) in Mo_6S_6 nanoassemblies [see Fig. 2(c)]. For $x=0$ and $y=2$, the free electron-like band is also fully occupied as electronically this is equivalent to the case of $x=2$ and $y=0$. For $x=2$ and $y>2$, the OCV shows a nearly flat behavior [Fig. 2(d)]. For the electronically equivalent cases of $x=4$, $y=0$ and $x=2$, $y=2$, the decrease in the value of OCV is slower for I doped nanowires. Therefore, it should be possible to manipulate the properties of such assemblies without affecting the structure much. The one-dimensional nature of the nanowire assemblies is expected to also lead to faster diffusion of Li ions and improved electronic and ionic transport properties. Finally, such systems are also interesting for the nanoscale applications which are currently attracting much attention as well as for flexible Li ion batteries similar to those recently achieved by using multiwall carbon nanotubes.¹⁸ We hope that our work will stimulate further experiments and lead to realization of these interesting battery materials as Mo_6S_6 type nanowire assemblies studied here have higher OCV as well as higher stability compared with those of $\text{Mo}_6\text{S}_{9-y}\text{I}_y$ nanowires that have been prepared in laboratory.⁶

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