Exploring the Structural Stability and Electronic Properties of VS₂ Nanostructures – a DFT Study

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The structural stability and electronic properties of pristine, hydrogenated and chlorinated VS₂ nanostructures were investigated using density functional theory. The optimization of VS₂ nanostructures were carried out successfully with the help of B3LYP/ LanL2DZ basis set. Initially the structural stability was confirmed using formation energy. The electronic properties were discussed in terms of HOMO-LUMO gap, density of state (*DOS*) spectrum, electron affinity (*EA*), and ionization potential (*IP*). The chemical hardness (*CH*) and chemical potential (CP) of VS₂ nanostructures are also reported. The results will give the insights on structural stability and electronic properties of hydrogenated and chlorinated *VS₂* nanostructures.

1. INDRODUCTION

The advancement of research in two dimensional nanomaterials leads to the development of new generation nanoelectronic devices. The electronic properties can be tailored by functionalization and impurity substitution in vanadium disulfide (*VS₂*) nanomaterials. The most exclusively studied 2D nanomaterials is graphene, which has tunable mechanical, thermal and electronic properties leading graphene for wide range of applications. Although graphene has attracted the research community, its limitations hinders the design and development of electronic devices using graphene. Moreover, the synthesis of large-area graphene thin films with high conductivity is quite expensive, bandgap opening, limits the application in electronic devices [1]. In recent years, transition metal dichalcogenides compound attracts a greater importance due to its tunable magnetic, optical, electrical, physical, chemical and mechanical properties. Thus these materials gives rise to wider applications like energy storage devices [2], catalysis [3], Li-ion batteries [4] and touch sensing devices [5] and information storing devices [6]. Based on these facts, literature survey was made and to our knowledge there is only limited reports on studying the electronic properties of functionalized and impurity substituted VS₂ nanostructures. Moreover, vanadium disulphide crystal is one of the member of transition metal dichalcogenide (*TMD's*) family and its configuration resembles one vanadium metal layer sandwiched between two layers of sulphide with weak vander Waals force holding up the structure [7]. VS₂ materials can exist both in trigonal prismatic 2H and 1T phases with different magnetic and electronic property [8]. Strong hybridization of *V*-3*d* with *S*-3*p* orbitals is responsible for the strong inplane covalent bonding of *VS₂*. The present work investigates the structural stability and electronic properties of pristine, hydrogenated and chlorinated *VS₂* nanostructures using density functional theory (*DFT*) method and the results are reported.

2. COMPUTATIONAL DETAILS

The present work is carried out using Gaussian 09 package for optimization of pristine, hydrogenated and chlorinated *VS₂* nanostructures [9]. In this work both the structural stability and electronic properties are explored using Becke's three-parameter hybrid functional in combination with Lee-Yang-Parr correlation functional (*B3LYP*), B3LYP/LanL2DZ basis set . The atomic number of vanadium and sulfur is twenty three and sixteen respectively in which B3LYP/LanL2DZ can be used as a possible basis set [10, 11]. Furthermore, selection of possible basis set is important factor for successful optimization of *VS₂* nanostructures. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), HOMO-LUMO gap and density of states (DOS) of VS₂ nanostructures are executed using Gauss Sum 3.0 package [12]. The convergence energy in the range of 10^{-5} eV is obtained while optimizing *VS₂* nanostructures.

3. RESULTS AND DISCUSSION

In order to ascertain the structural stability of pristine and functionalized *VS₂* nanostructure, the formation energy of *VS₂* nanostructure is studied. In addition, the electronic properties of *VS₂* nanostructures are discussed in terms of electron affinity (EA) , ionization potential (*IA*), HOMO – LUMO gap , Density of states (DOS) spectrum. Also chemical potential (CP), chemical hardness(*CH*), dipole moment (*DP*) of VS₂ nanostructures are reported. Fig. 1 – 3 illustrated the schematic representation of pristine, hydrogenated and chlorinated *VS₂* nanostructures, which contains 12 vanadium atoms, 24 sulfur atoms in pristine *VS₂*, whereas hydrogen and chlorine functionalized *VS₂* has additional 6 hydrogen atoms and chlorine atoms respectively.

The pristine MgSe nanostructure contains thirteen Mg atoms and thirteen Se atoms. Cr incorporated MgSe nanostructure consists of twelve Mg atoms, thirteen Se atoms and one Mg atom is replaced with one Cr atom.

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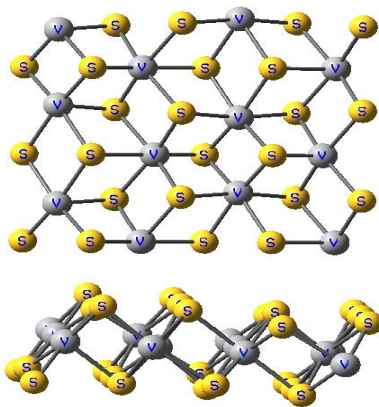
Fig. 1 – Pristine *VS₂* nanostructure
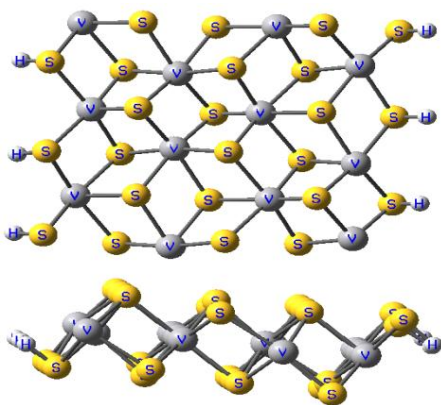
Fig. 2 – Hydrogented *VS₂* nanostructure
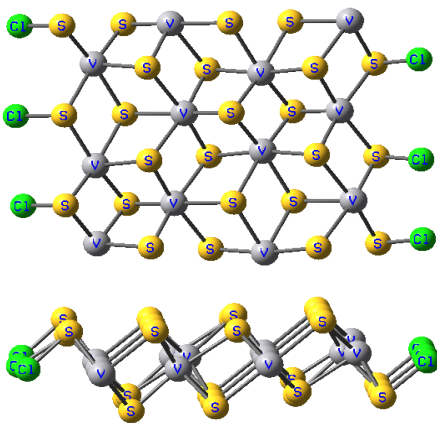
Fig. 3 – Chlorinated *VS₂* nanostructure

3.1 Structural Stability and Electronic Properties of *VS₂* Nanostructures

The structural stability of isolated *VS₂*, chlorine and hydrogen substituted *VS₂* are perceived from their formation energy given by:

$$E_{form} = 1/n[E(VS_2 nanostructure) - pE(V) - qE(S) - rE(F)]$$

where $E(VS_2)$ nanostructure) refers the total energy of VS_2 nanostructure, $E(V)$, $E(S)$ and $E(F)$ denotes the corresponding energy of isolated *V, S* and functionalized elements namely *H* and *Cl. x, y, z* represents the total number of *V, S* and dopant atoms respectively.

The formation energy, dipole moment and point symmetry for pristine *VS₂* and functionalized VS₂ nanostructures are shown in Table 1. The formation energies of pristine *VS₂*, hydrogenated and chlorinated VS₂ nanostructures are found to be -4.0 eV, -3.76 eV and -3.4 eV respectively.

Table 1 – Formation energy, dipole moment and point symmetry of *VS₂* nanostructures

Nanostructures	Formation Energy (eV)	DM (Debye)	PG
pristine *VS₂*	-4.0	12.5	C_1
Hydrogenated *VS₂*	-3.76	8.66	C_1
Chlorinated *VS₂*	-3.4	6.45	C_1

It is observed that the structural stability of hydrogenated and chlorinated *VS₂* decreases compared with pristine *VS₂*. Even though the structural stability of hydrogenated and chlorinated *VS₂* decreases it is found to be stable. In addition, the electronic properties can be tailored with hydrogenation and chlorination of *VS₂* nanostructures. The dipole moment (*DM*) provides the information regarding the distribution of charges along VS₂ nanostructures. The dipole moment of pristine *VS₂*, hydrogenated and chlorinated *VS₂* nanostructures is found to be 12.5, 8.66 and 6.45 Debye respectively. From the results of *DM*, for pristine *VS₂* nanostructures the distribution of charge is found to be uneven compared with the functionalized *VS₂* nanostructures. Furthermore, for all *VS₂* nanostructures, *Cl* point group is observed, which have only identity operation with no symmetry. The electronic properties of pristine, hydrogenated and chlorinated *VS₂* nanostructures are explored with the help of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital(LUMO) [13-16]. The HOMO-LUMO gap of pristine, hydrogenated and chlorinated *VS₂* nanostructures is found to be 4.12 eV, 3.17 eV, 2.40 eV respectively. From the results it is figured out that HOMO-LUMO gap decrease, upon functionalization of *VS₂* with H and *Cl*. The variation in HOMO LUMO gap is observed due to the orbital overlapping of hydrogen and chlorine atoms with *V* and *S* atoms. Hence less energy is required to move the electrons from HOMO to LUMO level when *VS₂* is functionalized with *Cl* and *H*. Thus the band gap can be tailored with proper functionalization along *VS₂* borders, which can used for development of new molecular device. The localization of charges along *VS₂* nanostructures in different energy intervals is visualized using density of states (*DOS*) spectrum. The *DOS* energy spectrum for all *VS₂* nanostructures are shown in Fig. 4, from the observed peaks in the virtual orbitals it is inferred that the transfer of charge take place easily between *VS₂* base material and adsorbent. These peak maxima in *VS₂* nanostructures arise due to orbital overlapping of *V* and *S* atoms with *Cl* and *H* atoms. The tunable electronic property facilitates the possible application of *VS₂* nanostructures in the development of molecular device.

The electronic properties of *VS₂* nanostructures can also be studied using electron affinity (*EA*) and ionization potential (*IP*) [17-19]. Fig 5 depicts the *IP* and *EA* for *VS₂* nanostructures. As known, *IP* refers to the
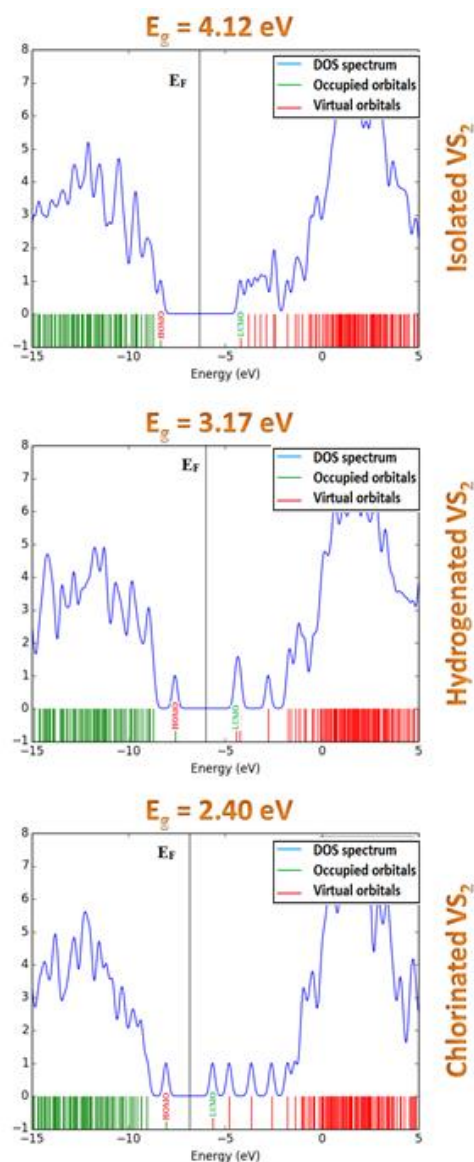
Fig. 4 – Visualization of HOMO-LUMO and *DOS* spectrum of isolated, hydrogenated and chlorinated *VS₂* nanostructure

Fig. 5 – *IP* and *EA* of *VS₂* nanostructure

be more in the sulfur sites than in vanadium sites. Since group-VI elements such sulfur has high electron affinity such that it attracts more electrons towards it along *VS₂* nanostructures. Besides, the termination of the electron density is found to be more for hydrogenated *VS₂* nanostructure rather than pristine and chlorinated *VS₂* nanostructure.

Fig. 6 – Electron density of isolated *VS₂,* hydrogenated *VS₂* and chlorinated *VS₂* nanostructure

amount of energy required to remove the electrons from *VS₂* nanostructures. *EA* represents the change in energy due to addition of electrons in *VS₂* nanostructures. Moreover, the *IP* values of isolated and functionalized *VS₂* nanostructures are found to be almost same. It infers that removal of electrons from *VS₂* nanostructure required more energy. However, *EA* of *VS₂* nanostructures found to vary drastically upon chlorination of *VS₂* nanostructure. Since the *EA* value for chlorinated *VS₂* nanostructures is found to be maximum compared with isolated counterpart, it infers that chlorinated *VS₂* nanostructures can be used as a base material in chemical sensors.

Fig. 6 illustrates the electron density of isolated and functionalized *VS₂* nanostructures. The electron density diagram shows the presence of electron density over a particular *VS₂* nanostructure. Moreover, the electron bonds with hydrogen will give rise to the increase in the energy density along hydrogenated *VS₂* nanostructures. Furthermore, the density of electrons is found to
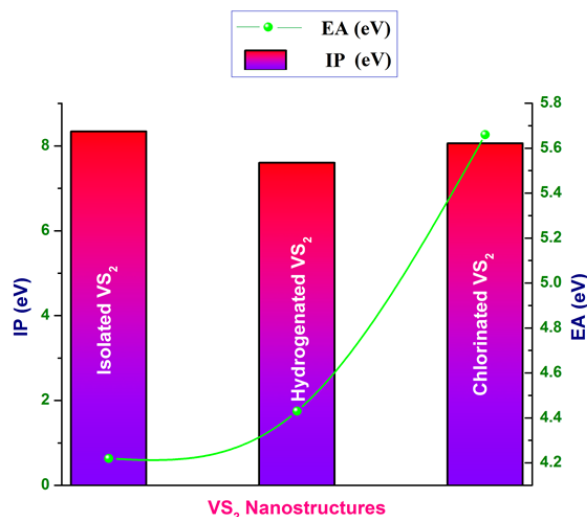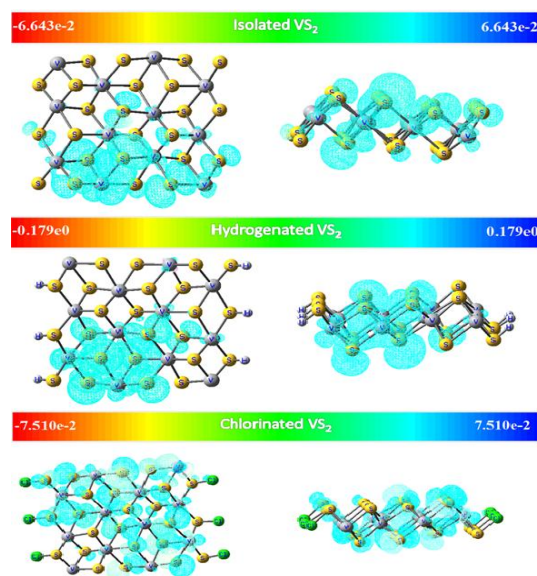
The chemical properties of *VS₂* nanostructures can be described in terms of *CH* and *CP* [20 – 24]. Chemical potential (*CP*) and chemical hardness (*CH*) can be studied using the equation $\mu = -(IP + EA)/2$ and $\eta = (IP - EA)/2$ respectively, which is tabulated in Table 2. The effect of *CP* and *CH* can also be studied with the help of effective fragment potential for *VS₂* nanostructures. In most of the time, chemical hardness is illustrated as electronegativity, which is one of the important factors in semiconductor physics. Various trends are recorded on both *CP* and *CH*. Furthermore, depending upon the charge states, both chemical potential and chemical hardness gets modified. In addition, the chlorinated

Table 2 – Chemical potential and chemical hardness of VS_2 nanostructures

Nanostructures	Chemical potential (eV)	Chemical hardness (eV)
pristine VS_2	− 6.28	2.06
Hydrogenated VS_2	− 6.015	1.585
Chlorinated VS_2	− 6.86	1.2

VS_2 nanostructures are observed to have high negative value of *CP* but low positive value is found in *CH*. The same trends have been recorded in all the cases. Thus, the structural stability of VS_2 nanostructure mainly related to functionalization of hydrogen and chlorination in VS_2 nanostructure.

4. CONCLUSIONS

In conclusion, the DFT method is utilized to study the electronic properties of isolated VS_2, hydrogenated

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and chlorinated VS_2 nanostructures using B3LYP/LanL2DZ basis set. The structural stability of isolated VS_2 functionalized VS_2 nanostructures are studied in terms of formation energy. Among all the VS_2 nanostructures, pristine VS_2 nanostructure is found to be more stable rather than functionalized VS_2 nanostructure. The electronic properties are studied in terms of HOMO LUMO gap, *DOS* spectrum, electron affinity, ionization potential and electron density. The observations from the study confirm that the electronic properties can be tailored with functionalized VS2 nanostructure along its borders. The chemical properties of VS_2 nanostructures are also described in terms of chemical potential and chemical hardness. Moreover, the structural stability and electronic properties of VS_2 nanostructure can be improved with functionalization of hydrogen and chlorination on VS_2 nanostructure and this can be utilized as a gas sensor in mixed environment.

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