

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.

Keywords: Vanadium disulfide, Stability, Formation energy, Nanostructures.

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1. INTRODUCTION

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-3d with S-3p 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

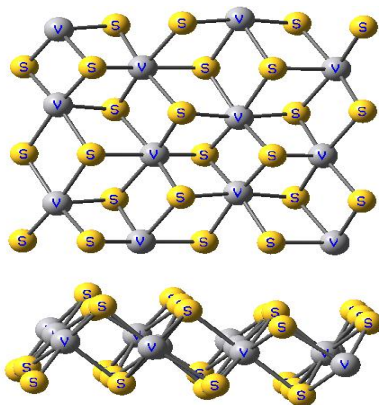
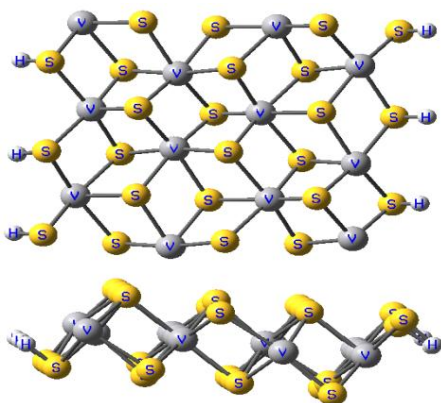
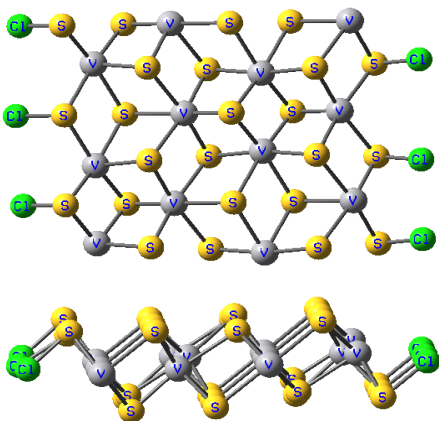
The present work is carried out using Gaussian 09 package for optimization of pristine, hydrogenated and chlorinated VS₂ nanostructures [9]. In this work both the structural stability and electronic properties are explored using Becke's three-parameter hybrid functional in combination with Lee-Yang-Parr 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 10⁻⁵eV 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 VS_2 nanostructureFig. 2 – Hydrogenated VS_2 nanostructureFig. 3 – Chlorinated VS_2 nanostructure

3.1 Structural Stability and Electronic Properties of VS_2 Nanostructures

The structural stability of isolated VS_2 , chlorine and hydrogen substituted VS_2 are perceived from their formation energy given by:

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

where $E(VS_2 \text{ nanostructure})$ 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 VS_2 and functionalized VS_2 nanostructures are shown in Table 1. The formation energies of pristine VS_2 , hydrogenated and chlorinated VS_2 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 VS_2 nanostructures

Nanostructures	Formation Energy (eV)	DM (Debye)	PG
pristine VS_2	-4.0	12.5	C_1
Hydrogenated VS_2	-3.76	8.66	C_1
Chlorinated VS_2	-3.4	6.45	C_1

It is observed that the structural stability of hydrogenated and chlorinated VS_2 decreases compared with pristine VS_2 . Even though the structural stability of hydrogenated and chlorinated VS_2 decreases it is found to be stable. In addition, the electronic properties can be tailored with hydrogenation and chlorination of VS_2 nanostructures. The dipole moment (DM) provides the information regarding the distribution of charges along VS_2 nanostructures. The dipole moment of pristine VS_2 , hydrogenated and chlorinated VS_2 nanostructures is found to be 12.5, 8.66 and 6.45 Debye respectively. From the results of DM , for pristine VS_2 nanostructures the distribution of charge is found to be uneven compared with the functionalized VS_2 nanostructures. Furthermore, for all VS_2 nanostructures, C_1 point group is observed, which have only identity operation with no symmetry. The electronic properties of pristine, hydrogenated and chlorinated VS_2 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 VS_2 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 VS_2 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 VS_2 is functionalized with Cl and H. Thus the band gap can be tailored with proper functionalization along VS_2 borders, which can be used for development of new molecular device. The localization of charges along VS_2 nanostructures in different energy intervals is visualized using density of states (DOS) spectrum. The DOS energy spectrum for all VS_2 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 VS_2 base material and adsorbent. These peak maxima in VS_2 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 VS_2 nanostructures in the development of molecular device.

The electronic properties of VS_2 nanostructures can also be studied using electron affinity (EA) and ionization potential (IP) [17-19]. Fig 5 depicts the IP and EA for VS_2 nanostructures. As known, IP refers to the

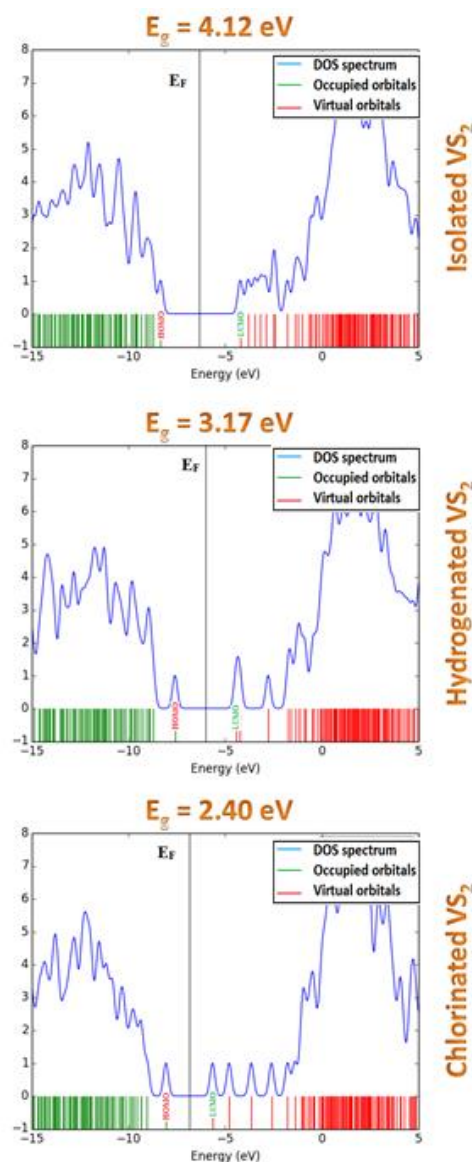


Fig. 4 – Visualization of HOMO-LUMO and DOS spectrum of isolated, hydrogenated and chlorinated VS_2 nanostructure

amount of energy required to remove the electrons from VS_2 nanostructures. EA represents the change in energy due to addition of electrons in VS_2 nanostructures. Moreover, the IP values of isolated and functionalized VS_2 nanostructures are found to be almost same. It infers that removal of electrons from VS_2 nanostructure required more energy. However, EA of VS_2 nanostructures found to vary drastically upon chlorination of VS_2 nanostructure. Since the EA value for chlorinated VS_2 nanostructures is found to be maximum compared with isolated counterpart, it infers that chlorinated VS_2 nanostructures can be used as a base material in chemical sensors.

Fig. 6 illustrates the electron density of isolated and functionalized VS_2 nanostructures. The electron density diagram shows the presence of electron density over a particular VS_2 nanostructure. Moreover, the electron bonds with hydrogen will give rise to the increase in the energy density along hydrogenated VS_2 nanostructures. Furthermore, the density of electrons is found to

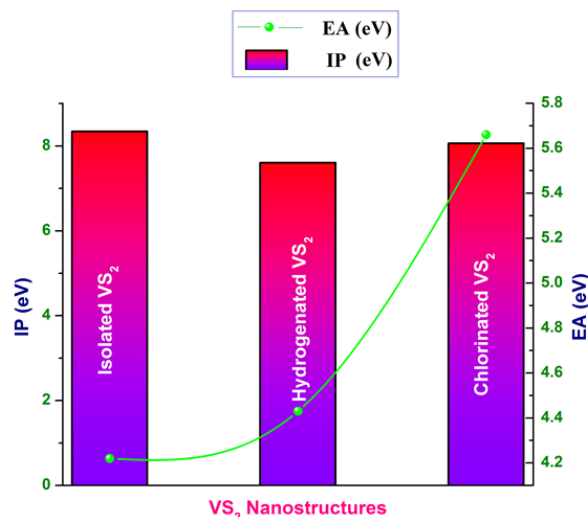


Fig. 5 – IP and EA of VS_2 nanostructure

be more in the sulfur sites than in vanadium sites. Since group-VI elements such as sulfur has high electron affinity such that it attracts more electrons towards it along VS_2 nanostructures. Besides, the termination of the electron density is found to be more for hydrogenated VS_2 nanostructure rather than pristine and chlorinated VS_2 nanostructure.

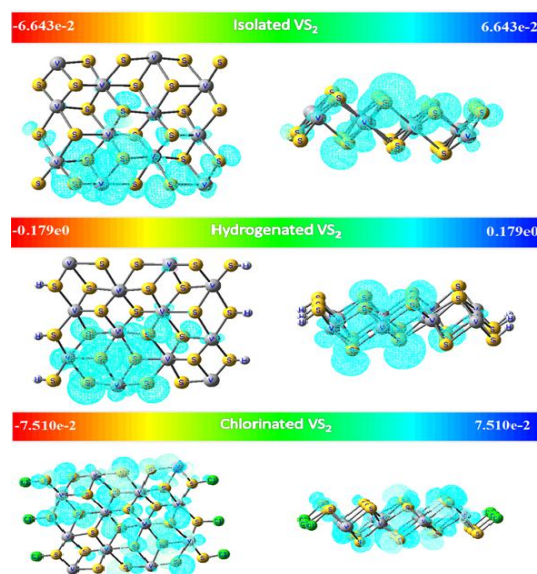


Fig. 6 – Electron density of isolated VS_2 , hydrogenated VS_2 and chlorinated VS_2 nanostructure

The chemical properties of VS_2 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 VS_2 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

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 VS_2 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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