

# DFT Study of Ca-adsorbed MoS<sub>2</sub> Monolayer for Hydrogen Storage Application

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## Abstract

Surface metal adsorption on 2D structures is demonstrated to be an effective tool for improving hydrogen storage capacity. In the current work, the behavior of Ca atom adsorption on monolayer MoS<sub>2</sub> is studied and subsequently its hydrogen storage capacity is investigated computationally using van der Waals (vdW) revised Density Functional Theory. It is found that the Ca binds strongly with the MoS<sub>2</sub> monolayer without being clustered, leading to high hydrogen storage capacity. It is further shown that five hydrogen molecules to each Ca atom can be adsorbed with the average adsorption energy of 0.23eV per hydrogen molecule, indicating it to be a good choice for reversible adsorption/desorption of H<sub>2</sub> molecules at ambient conditions. It is revealed that hybridizations between s orbitals of H<sub>2</sub> and p orbitals of S are also responsible for adsorption mechanism, along with coulomb interactions. It is demonstrated that a steady and uniform high Ca coverage can be achieved without clustering and with enhanced binding energy which can be used as high hydrogen capacity storage system. Copyright © 2018 VBRI Press.

**Keywords:** Hydrogen storage, MoS<sub>2</sub>, monolayer, adsorption, DFT, Ca.

## Introduction

Due to the adverse effects of fossil fuels on the environment and their limited availability, sustainable energy sources are urgently required. Hydrogen is regarded as one of the best alternatives to such existing sources, because of its abundance, efficiency and environment friendly nature [1-5]. It possesses higher energy density than the conventional energy sources such as methane, gasoline, etc but the volumetric density of hydrogen is quite low (0.09 kg/m<sup>3</sup>) [2, 3]. This means it requires ample amount of space for storage. Hence, the development of a stored hydrogen transporter, for e.g., fuel cell for powering vehicles has now become a global challenge. Conventional hydrogen storage systems such as liquid storage and compressed gas are inefficient and unsafe with respect from transport applications [1-4]. Hydrogen molecules adsorbed on the surface of 2D nanomaterials are gaining immense interest as an alternative energy storage system from the perspective of safety, high efficiency and fast adsorption/desorption rate. For storing hydrogen, materials should be light weight and the adsorption energies of hydrogen molecules should reside between physisorption and chemisorption energy range (0.2 eV to 0.6 eV per H<sub>2</sub> [2, 5]) i.e., neither too strong nor too weak so that reversible adsorption/desorption should take place in the ambient conditions. In the recent times, materials such as carbon nanostructures, 2D Transition Metal Dichalcogenides (TMDC), BN sheets, SiC, etc are acquiring immense interest for

hydrogen storage application because of their large surface area [6, 7]. However, many theoretical studies [8, 9] have reported that they are either unable to hold the hydrogen molecules because of their chemical inertness or exhibit very low capacity hydrogen storage system by very weakly interacting with the system. Incorporation of metals on such structures makes them active for hydrogen adsorption. Alkali and alkali-earth metals are preferred over transition metals because of their lower weight and lower cohesive energies in order to avoid clustering and hence could help in achieving higher storage capacities of hydrogen [10, 11]. Further, many recent studies have shown that by decorating surface host with alkaline earth metal, particularly, Ca has larger effect on the adsorption energies than alkali metals such as Li, Na [12-17]. Moreover, Ca occurs abundantly in nature and hence it is relatively cheaper than other metals. Many carbon-based nanostructures decorated with Ca atoms are reported as hydrogen storage system but adsorption energy of H<sub>2</sub> molecules is not sufficient enough in such systems [18-20]. Although, by creating defects and by doping carbon structures with boron do facilitate hydrogen adsorption but to form such defects require large energies and concentration of impurity is also limited. Hence, lot of emphasis is now being devoted in the development of novel hydrogen storage materials. Recently, hydrogen adsorption on Li-decorated MoS<sub>2</sub> was investigated using first principles study [21]. They found adsorption energy above 0.20 eV/H<sub>2</sub> upto three H<sub>2</sub> molecules and for fourth and fifth molecules, energies reduced. Also, Ca adsorbed

MoS<sub>2</sub> has been reported as promising hydrogen storage medium [22].

In the present work, large supercell of MoS<sub>2</sub> is modeled for the adatom-MoS<sub>2</sub> system. For Ca/MoS<sub>2</sub> system, the various trends in the geometric parameters, adsorption energies in terms of different sites, and electronic structures in terms of PDOS and charge transfer are studied based on first-principles calculations. Subsequently, hydrogen adsorption on Ca/MoS<sub>2</sub> system is investigated where Ca adatom acts as a primary hydrogen source and the MoS<sub>2</sub> monolayer as secondary. It is shown that each Ca atom can adsorb up to five hydrogen molecules, and the adsorption energy of the sixth H<sub>2</sub> molecule is relatively low. Our results are little different from previous reports [22] that each Ca atom can adsorb up to six H<sub>2</sub> molecules for single-sided Ca-decorated MoS<sub>2</sub> system where the height of the H<sub>2</sub> molecule from Ca atom and adsorption energy of the individual molecule are not considered. It is further shown that a stable and uniform coverage of Ca ions on MoS<sub>2</sub> monolayer is possible without clustering. Thus, more adsorption sites are available for the hydrogen adsorption that can lead to high hydrogen storage capacity.

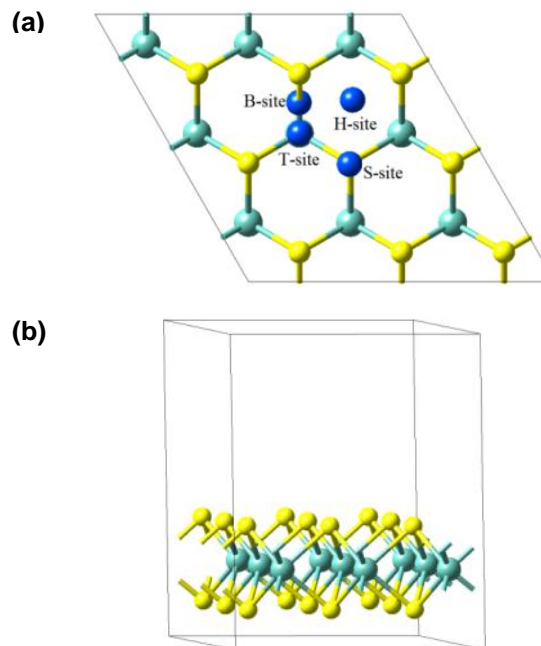
## Methodology

All the calculations are carried out using Density Functional Theory, using the Vienna ab initio simulation package (VASP) [23] as implemented in medea ver 2.8.10. The generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE) is used to approximate exchange and correlation potential. In order to better account for the interlayer interactions, van der Waals interactions are added by means of a DFT-D2 forcefield, which adds a semi-empirical correction potential energy term to the conventional Kohn-Sham energy in the form of  $\frac{C_6^{A,B}}{r_{AB}^6}$ , where  $C_6^{A,B}$  and  $r_{AB}^6$  are the dispersion coefficient and distance for atoms A and B respectively [24]. Such van der waals (vdW) interactions are the origin of physisorption of gas molecules onto the surface of solid as it has been revealed in previous studies [25, 26] related to adsorption that such corrections enhances adsorption energies and our calculations have also shown the similar enhancement. A system of 3×3 supercell (including 9 Mo and 18 S atoms) is modeled, with a gamma-centered 3×3×1 k-point mesh. Periodic images of the monolayer are separated by a distance of more than 12 Å in the z-direction to avoid the interactions between them. A cutoff energy of 280 eV is employed for the plane wave expansion of wavefunctions throughout all calculations, and the system is relaxed until the forces on each atom are smaller than 0.01 eV/Å, with the convergence threshold energy of 10<sup>-4</sup>eV.

## Results and discussion

First, the bulk structure of MoS<sub>2</sub> is relaxed and the lattice constant is obtained to be 3.18Å which is quite close to the experimental one [27]. A 3×3 hexagonal supercell of

a MoS<sub>2</sub> monolayer is formed by applying periodic boundary conditions in x and y directions and the periodic images in the z direction are well separated by a distance of more than 12 Å to avoid interlayer interactions [Fig. 1]. Other structural parameters such as S-Mo bond length, Mo-Mo distance, and vertical S-S distance are calculated to be 2.415Å, 3.189Å and 3.127Å respectively.



**Fig. 1.** Schematic of 3×3 supercell MoS<sub>2</sub> (a) Top view (indicating the various adsorption sites for Ca in blue balls), (b) side view. Yellow and turquoise balls represent S and Mo atoms respectively.

### Ca/MoS<sub>2</sub> system

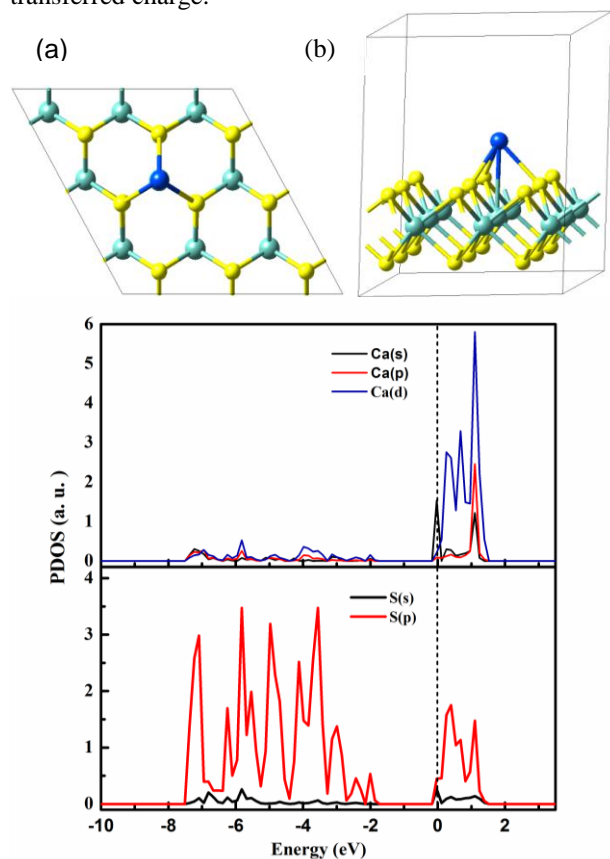
The possible adsorption sites for a single Ca atom on MoS<sub>2</sub> monolayer are investigated. They are: (a) at the top site of Mo (T-site), (b) at the top site of S (S-site), (c) at the hollow center of the hexagonal ring (H-site), and (d) at the top of Mo-S bond length (B-site), as shown in **Fig. 1(a)**. The adsorption energy of Ca atom on the pristine MoS<sub>2</sub> monolayer is defined as:

$$E_{\text{ad}} = - \left[ \frac{E_{\text{total}} - nE(\text{Ca}) - E(\text{MoS}_2)}{n} \right]$$

where,  $E_{\text{total}}$  denotes the total energy of the MoS<sub>2</sub> + Ca system,  $E(\text{Ca})$  denotes the total energy of free Ca atom,  $E(\text{MoS}_2)$  denotes total energy of the pristine MoS<sub>2</sub> and  $n$  denotes the number of Ca atoms adsorbed. After having the Ca atom relaxed at the B-site, it migrated to the T-site, making this site to be practically unfavorable for the adsorption. The most stable adsorption site of Ca atom is the toposite of Mo as shown in **Fig. 2(a)**, which is in accordance with the previous report [11, 22], with a binding energy of 1.65eV per atom. The adsorption energies calculated with various functionals using LDA, PBE without DFT-D2 and PBE with DFT-D2 for the T-site are summarized in Table S1<sup>†</sup>. It can be seen that the values of adsorption energy are overestimated by LDA and underestimated by GGA-PBE exchange-correlation

functional whereas PBE-vdW gives the reasonable values. All the values of  $E_{ad}$  are large enough indicating that the interaction between Ca and MoS<sub>2</sub> is strong and hence exhibit chemisorption nature. H-site and S-site share nearly identical adsorption energy. This shows that the diffusion barrier between them and Mo-site is quite low. The calculated adsorption energy of Ca is greater than the theoretical cohesive energy of bulk Ca atom (1.64 eV/atom [28]) which ensures that there is no Ca clustering. Besides, vertical distance of Ca atom from the basal plane of sulfur atoms,  $d$  (Å), and charge transfer,  $\Delta q$  of Ca atom adsorbed on different sites are also presented. The smaller vertical height and larger charge transfer result in the greater adsorption energy of Ca at T-site as compared to the other sites.

As illustrated in the PDOS of the Ca/MoS<sub>2</sub> system [Fig. 2(b)]. It is seen that there exists a weak hybridization between Ca 3d states and S 3p state which causes an emergence of a few Ca 3d states in the PDOS. This shows that a small amount of charge is donated back to Ca from the MoS<sub>2</sub> layer. By Bader charge analysis [29], we find that the Ca atom transfers 1.25e charges to MoS<sub>2</sub> and becomes a positively charged ion. This further confirms its ionic bonding with MoS<sub>2</sub>. Such charge transfer polarizes the system which establishes an electric field between Ca atom and MoS<sub>2</sub>. It will be shown that the hydrogen adsorption is induced by charged Ca ion and the strength of binding depends on the amount of the transferred charge.



**Fig. 2.** (a) Relaxed Structure model of Ca adsorbed MoS<sub>2</sub> (a) Top view, (b) side view. Blue ball represents Ca atom, (c) PDOS of Ca/MoS<sub>2</sub> system. The Fermi level is scaled to zero.

### Hydrogen storage on the Ca-MoS<sub>2</sub> system

For studying the adsorption behavior of H<sub>2</sub> on the Ca-MoS<sub>2</sub> system, H<sub>2</sub> molecule is placed on different positions which are 2.0 Å far from the Ca atom. Similar to the expression for the adsorption energy of a Ca-adsorbed MoS<sub>2</sub> layer, the average adsorption energy of H<sub>2</sub> molecule is given by

$$E_{ad} = - \left[ \frac{E(nH_2 + Ca + MoS_2) - nE(Ca + MoS_2) - nE(H_2)}{n} \right]$$

And the adsorption energy of the  $n$ th H<sub>2</sub> molecule in the Ca/MoS<sub>2</sub> system is given by

$$E_n = - [E(nH_2 + Ca + MoS_2) - E(Ca + MoS_2 + (n-1)H_2) - E(H_2)]$$

In the case of single H<sub>2</sub> molecule uptake on MoS<sub>2</sub> with Ca atoms adsorbed on the surface indicates that the H<sub>2</sub> molecule seated above the hexagon in a slight tilted fashion is the most stable configuration as shown in **Fig. 3(a)**. This tilt is due to the coulomb interaction between H<sub>2</sub> molecule and positively charged Ca ion. The distance separating the nearest H atom with the S atom is 2.94 Å which is different from the H-S bond length of 1.33 Å [30] in the H<sub>2</sub>S compound.

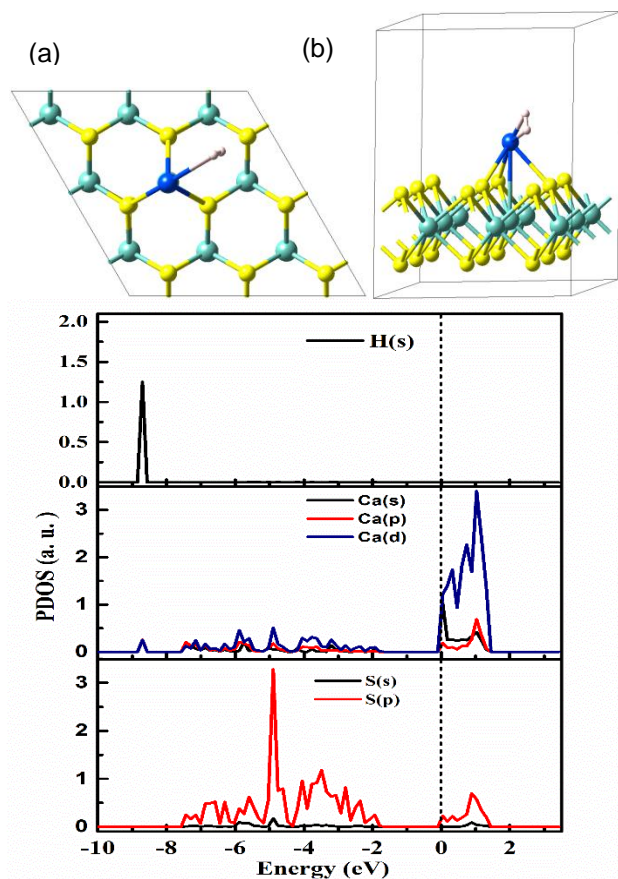
**Table 1.** Energetics of H<sub>2</sub> molecules adsorbed over Ca-MoS<sub>2</sub>: Average adsorption energy per H<sub>2</sub> molecule ( $E_{ad}$ ), adsorption energy of the last adsorbed H<sub>2</sub> molecule ( $E_{nth}$ ). Along with, distance between Ca and the last added H<sub>2</sub> molecule ( $d_{Ca-nH_2}$ ), average H-H bond lengths ( $d_{H-H}$ ), charge transferred by Ca to MoS<sub>2</sub> during H<sub>2</sub> adsorption ( $\Delta q_1$ ), and total charge transferred by Ca-MoS<sub>2</sub> to H<sub>2</sub> molecules ( $\Delta q_2$ ).

No. of H <sub>2</sub> molecules (n)	$E_{ad}$ (eV)	$E_{nth}$ (eV)	$d_{Ca-nH_2}$ (Å)	$d_{H-H}$ (Å)	$\Delta q_1$	$\Delta q_2$
1	0.23		2.59	0.765	1.33e	0.04e
2	0.23	0.23	2.62	0.764	1.36e	0.06e
3	0.23	0.24	2.63	0.762	1.38e	0.07e
4	0.24	0.26	2.64	0.764	1.38e	0.15e
5	0.23	0.18	2.63	0.761	1.41e	0.13e
6	0.21	0.11	4.95	0.757	1.41e	0.15e

As shown in **Table 1**, the Ca-MoS<sub>2</sub> system transfers the total charge of 0.04e to the H<sub>2</sub> molecule during the process and average adsorption strength of the system is 0.23 eV/H<sub>2</sub>, which is in good agreement with the optimal energy required for H<sub>2</sub> sorption/desorption at ambient conditions. On further increasing the number of H<sub>2</sub> molecules, we find that such system can uptake the maximum of five H<sub>2</sub> molecules on it with average adsorption energy of 0.23 eV/H<sub>2</sub> as shown in **Fig. 4(a)**. On addition of the fourth molecule leads to the enhancement in the average adsorption energy (0.24 eV) of the system and large charge transfer takes place. The adsorption strength of the fourth H<sub>2</sub> molecule (0.26 eV) is largest amongst the set of systems investigated, showing that such system is the most favorable adsorption configuration. Relaxed configurations of 2H<sub>2</sub> to 4H<sub>2</sub> adsorbed systems are shown in Fig. S1<sup>†</sup>. Adsorption energy of the last added H<sub>2</sub> molecule decreases after the

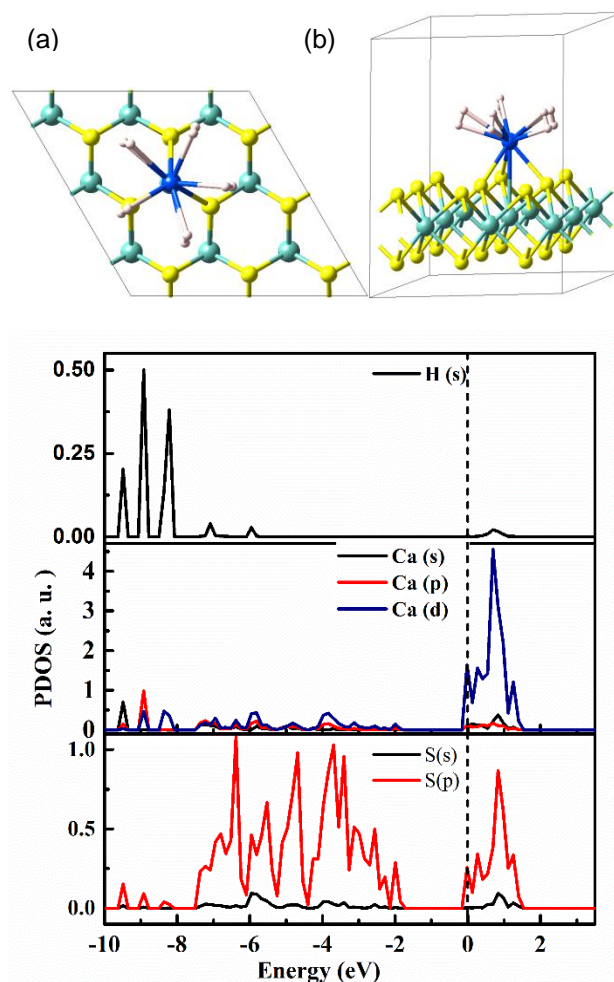
addition of fourth  $H_2$  molecule. This decrease is attributed to the crowded surface because of the small distance between neighboring  $H_2$  molecules. But these interactions are dominated by the coulomb interaction between  $H_2$  molecule and Ca ion on account of charge transfer of  $0.03e$  between them at the expense of lowering of adsorption energy. The H-H bond lengths ( $0.761\text{\AA}$ - $0.765\text{\AA}$ ) are slightly stretched upon adsorption as compared to the isolated  $H_2$  molecule ( $0.750\text{\AA}$ ) but the molecular feature is still retained. With increasing number of  $H_2$  molecules adsorption, Ca atom becomes more positively charged. This leads to the coulomb interactions between Ca and  $H_2$  molecules.

To further clarify the interaction mechanism between  $H_2$  molecule and the Ca/MoS<sub>2</sub>, we study PDOS of  $1H_2$ /Ca/MoS<sub>2</sub> and  $5H_2$ /Ca/MoS<sub>2</sub> systems. In the former, there is weak coupling between  $H_2$  molecules and Ca atom at  $-8.71\text{ eV}$  [Fig. 3(b)]. Due to the transfer of small charge  $0.04e$  from Ca ion to  $H_2$  molecule makes the neutral system of  $H_2$  molecule polarized with a separation of charge between  $H_2$  molecules as confirmed by Bader charge analysis i.e., one of the  $H_2$  molecule gains  $0.11e$  charge and becomes negatively charged while another one loses  $0.07e$  and becomes positively charged. Since the charge transferred by the Ca ion is small, it is indeed a physisorption process. Hence,  $H_2$  molecules interact with Ca via coulomb interactions.



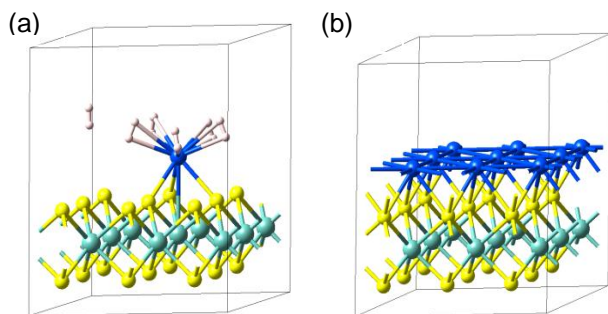
**Fig. 3.** (a) Relaxed configuration of single  $H_2$  adsorbed on Ca-MoS<sub>2</sub> system (Top view and Side view). White ball represents hydrogen atom, (b) PDOS of the  $H_2$  adsorbed on Ca/MoS<sub>2</sub> system. The Fermi level is scaled to zero.

In the PDOS analysis of  $5H_2$ /Ca/MoS<sub>2</sub> system, splitting of peaks is observed in hydrogen PDOS, indicating interaction between them. Also, an orbital hybridization is observed between  $H_2$  molecules and S atom at  $-9.47\text{ eV}$ ,  $-8.91\text{ eV}$  and  $-5.96\text{ eV}$  as depicted in Fig. 4(b). Therefore, along with coulomb interactions, hybridizations between s orbitals of  $H_2$  molecule and p orbitals of S atom are also responsible for the adsorption mechanism.



**Fig. 4(a)** Relaxed structure of  $5H_2$ /Ca/MoS<sub>2</sub> system (Top view and Side view), (b) PDOS of the  $5H_2$  adsorbed on Ca/MoS<sub>2</sub> system. The Fermi level is scaled to zero.

On placing the sixth  $H_2$  molecule on the Ca/MoS<sub>2</sub> system, it moves far away from the Ca ion as illustrated in Fig. 5(a). It becomes more weakly bound to the system than the other  $H_2$  molecules with adsorption energy of  $0.11\text{ eV}$ , attributed to the repulsion from the other hydrogen molecules which are strongly bound to the system already and also the charge transferred from Ca ion to sixth  $H_2$  molecule being almost negligible i.e., about  $0.0012e$ . In addition, it lies perpendicular with no tilt towards Ca ion. This further confirms its extremely weak interaction nature with Ca ion. Also, since its molecular nature is retained (H-H bond length =  $0.753\text{\AA}$ ), we can infer that it stays as an isolated molecule away from the system.



**Fig. 5**(a)Relaxed configuration of six H<sub>2</sub> adsorbed on Ca-MoS<sub>2</sub> system, (b)Relaxed configuration of full Ca coverage on MoS<sub>2</sub> monolayer

### Ca High Coverage

For increasing the hydrogen storage capacity, the binding energies of high Ca coverage on the monolayer MoS<sub>2</sub> are calculated so that there can be more adsorption sites for H<sub>2</sub> molecule. Coverage can be defined as

$$\frac{\text{Total number of Ca atoms}}{\text{Total number of } T_M \text{ adsorption sites}}$$

**Table 2** depicts that the binding energy has significantly increased on increasing the coverage and is greater than the Ca bulk cohesive energy in each case. Even at full coverage [Fig. 5(b)], the average binding energy of Ca atom (1.80 eV) is remarkably better than the 0.1 coverage (1.65 eV) though it is lesser than the 0.6 coverage (1.89 eV). There is an increase in the Ca adatom height in case of full coverage which is due to the increased repulsive interactions among positively charged Ca ions. Additionally, the Ca-Ca interaction is indeed negligible attributing to the large distance of 3.19 Å. Hence hydrogen uptake capacity can be checked at such incremented available sites for adsorption with no cluster formation and can possibly serve as a potential high capacity hydrogen storage system.

**Table 2** Average adsorption energy per Ca atom ( $E_{ad}$ ), and average Ca-Mo distances ( $d_{Ca-Mo}$ ) for high coverages.

Ca coverage	$E_{ad}$ (eV/atom)	$d_{Ca-Mo}$ (Å)
0.6	1.89	3.72
1	1.80	3.78

### Conclusion

To summarize, we report a study of Ca adsorbed MoS<sub>2</sub> monolayer as hydrogen storage system in terms of adsorption energy, density of states and charge transfer using Bader charge analysis. Based on density functional theory we find Ca binds strongly with pristine MoS<sub>2</sub> and further serves as a binding center for five H<sub>2</sub> molecules with a good average adsorption energy lying between the required physisorption and chemisorption energy range. Further we find that the sixth H<sub>2</sub> molecule is very weakly adsorbed by the system and hence lowers the average adsorption energy of the system with negligible charge transfer. We also find on increasing the Ca coverage, the

binding energies have significantly increased and hence can serve as a high capacity hydrogen storage system.

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### Author's contributions

Conceived the plan: AS, ANU, MH, ASR, MSK; Performed the calculations: AS; Data analysis: AS, MSK; Wrote the paper: AS. Authors have no competing financial interests.

### Supporting information

†Supporting informations are available from VBRI Press.

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