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External Electric Field Induced Hydrogen Storage/Release on Calcium-Decorated Single-layer and Bilayer Silicene

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Abstract

Hydrogen storage and release are two essential parameters that define the efficiency of a hydrogen storage medium. Herein, we investigate the effects of the external electric field F on the adsorption/desorption of H_2 on Ca-decorated silicene system (Ca/silicene) based on density functional theory calculations. Our study demonstrates that nine H_2 per Ca atom can be adsorbed and 6.4 wt% H_2 can be adsorbed on Ca/silicene with average binding energy 0.19 eV/ H_2 , while the appropriate F can be used to effectively enhance the hydrogen storage/release on Ca/silicene system. The high synergetic effect may be attributed to that F induces an enhancement of the charge transfer between H_2 molecules and Ca/silicene system. Thus, the Ca/silicene system together with the synergy of F can efficiently facilitate H_2 adsorption/desorption, completing the whole hydrogen storage/release cycle.

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1. Introduction

Ever-increasing energy demand can lead to energy crisis in near future if energy resources are mainly based on depleting fossil fuels. In addition, fossil fuels produce greenhouse gases that induce serious climate changes. Therefore, environmental-friendly energy sources are urgently required. Hydrogen is generally considered to be one of the cleanest renewable energies because it does not produce pollutants or greenhouse gases.¹⁻³ However, finding materials to store hydrogen safely and economically is crucial for the realization of so-called hydrogen fuel economy.⁴⁻⁷

An effective hydrogen storage material requires moderate binding energy of $\sim 0.2\text{--}0.6$ eV for hydrogen because of stable storage and easy release.⁸⁻¹³ Recently, it has been revealed that carbon nano-materials such as fullerene,¹⁴⁻¹⁸ nanotube,¹⁹⁻²⁴ and graphene²⁵⁻²⁸ decorated with alkali metals or transition metals satisfy this requirement. These nano-materials can exhibit the storage capacity higher than 5.5 wt % that is the gravimetric goal set by the U.S. Department of Energy by 2017.²⁹ In this case, transition metal decorated nanostructured materials can yield higher binding energy³⁰⁻³³ due to the Kubas interaction³⁴ which stems from the hybridization of H_2 σ or σ^* orbitals with transition metal d orbitals.^{35, 36} On the other hand, the electric field produced by a positively charged metal ion can polarize the H_2 molecule, which can bind to the metal cation in quasi-molecular form.³⁷ However, metal atoms, particularly transition metal atoms, tend to be readily clusterized because of high cohesive energy (~ 4 eV).^{17, 38} In addition, clusterized metal atoms may dissociate H_2 molecules, resulting in a dramatic decrease of hydrogen storage capacity.¹⁰ Hence, to increase the hydrogen storage capacity, clustering of

metal atoms should be prevented and instead of the metal adatoms should be isolated.

Stimulated by the miraculous properties of graphene, other two dimensional monolayer material, such as silicene, *h*-BN, and boron sheet have been studied.³⁹⁻⁴⁴ To date, although isolated silicene has not been reported experimentally yet, silicene is considered to be a good two-dimensional (2D) material.³⁹ For example, phonon dispersion calculations and first-principles calculations based on density functional theory (DFT) have clearly confirmed that freestanding silicene is stable and energetically degenerating.^{41, 42} In addition, many studies of silicene for Li and Na-Ion storage,^{45, 46} sensors,⁴⁷ and catalysts⁴⁸ have been reported. Silicene could also act as efficient hydrogen storage material because of unique electronic and structural properties.⁴⁹⁻⁵² Chemisorption of hydrogen in the form of Si-H is not so good for hydrogen storage due to the high binding energy of ~ 3.16 eV.^{53, 54} On the contrary, physisorption of hydrogen molecules on silicene is not effective for hydrogen storage, either, because the binding energy is too small (~ 0.06 eV/H₂).⁴⁹ To overcome these, we here propose Ca-decorated silicene as a hydrogen storage medium. In addition, it has been reported that clustering of Ca atom can be suppressed on silicene because of high binding energy (~ 2.19 eV) of Ca decorated silicene.^{55, 56}

Meanwhile, it has been reported that an electric field can effectively modify the electronic properties of low dimensional systems, e.g., 1D quantum wires,^{57, 58} carbon nanotubes,^{22, 59} and 2D sheets⁶⁰⁻⁶⁴ For example, Zhou *et al.* found that H₂ adsorption can be externally enhanced on nano-scale BN sheet via superimposition of an external electric field.⁶⁰ Furthermore, Sun *et al.* found that CO₂ capture/release on BN sheet controlled by switching on/off an electric field.⁶¹ Inspired by this, we present a novel strategy of hydrogen storage on Ca-decorated silicene under

electric field.

In this contribution, both single-layer (SL) and bilayer (BL) silicene will be chosen as prototypes in our calculations. The efficient storage/release of hydrogen on Ca/silicene can be controlled: increase of the bonding during the hydrogen adsorption process and decrease of the bonding during the hydrogen desorption process by changing the direction of electric field. We observed that SL silicene as well as BL silicene can exhibit good hydrogen storage properties under the electric field.

2. Computational Framework

All calculations in this study were performed using the spin-polarized first-principle method as implemented in the DMol³ code.⁶⁵ The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was used,⁶⁶ in combination with the double numerical plus polarization (DNP). The empirically-corrected density functional theory (DFT +D) method within the Grimme scheme was employed in all the calculations to consider the van der Waals forces.⁶⁷ All-electron relativistic (AER) procedure, which includes all core electrons and introduces some relativistic effects into the core, was used for the core treatments.

A uniform (2×2) silicene supercell was established with a lattice parameter of 3.86 Å. The modulus supercell vector in the *z* direction was set to 20 Å, which led to negligible interactions between the system and their mirror images. For geometric optimization, the Brillouin zone integration was performed with 24×24×1 k-point sampling, which brings out the convergence tolerance of energy in 1.0×10^{-5} hartree, and that of maximum force in 0.002 hartree. Charge

transfer was calculated with the Mulliken charge analysis method. Electric fields with different field intensity were applied perpendicular to the silicon atom sheets in the upward (defined as "+") or downward (defined as "-") directions. $E_b(F)$ values are indicative of the binding energy obtained under an electric field with a magnitude of F , and this value is given by:

$$E_b(F) = [E_F(\text{Ca} + \text{Si}_m) + nE_F(\text{H}_2) - E_F(n\text{H}_2 + \text{Ca} + \text{Si}_m)] / n, \quad (1)$$

where n and m indicate the numbers of hydrogen molecules and Si atoms, respectively. The physical storage mechanism is primarily physisorption with van der Waals forces in nature, thus hydrogen maintains its molecular identity. To further study the intensity-dependent behavior, a series of fields ranging from -0.004 to $+0.004$ au were imposed on 9 H_2 molecules adsorbed on Ca-decorated SL and BL silicene.

3. Results and Discussion

SL silicene is composed of mixed sp^2 - sp^3 bonded silicon atoms that are densely packed in a honeycomb crystal lattice (Fig. 1a). The distance between two nearest Si atoms projected on the axis perpendicular to the plane is 0.44 \AA . The optimized atomic configuration is in agreement with previous theoretical work.⁶⁸ At first, we calculated the binding energy of single H_2 molecule on SL silicene at three different adsorption sites (top, bridge and hollow sites). The calculation results show that hollow site is more stable than other sites, where hydrogen is nearly parallel to silicene sheets (Fig. 1b). The calculated value of E_b for the hollow site is 0.11 eV . Second, our calculation on the Ca decorated sites indicates that the most stable position of Ca atom is above the center of a hexagonal silicon ring (Fig. 1c). The bond length between Ca atom and the

nearest Si atom is calculated to be 2.82 Å, which corresponds well with a theoretical result (2.78 Å).⁵⁵ Moreover, calculation based on the Mulliken charge analysis shows that about 1.103 e charge (Q) is transferred from Ca atom to silicene sheet. If H₂ molecule is adsorbed on Ca-decorated SL silicene (Ca/SL silicene), the binding energy and the bond length are modified: E_b of single H₂ molecule is enhanced to 0.27 eV, the bond length of H₂ molecule is slightly elongated from 0.75 to 0.77 Å (Fig. 1d). Increase of E_b of H₂ from 0.11 to 0.27 eV indicates that the adsorption ability of silicene is significantly enhanced via Ca decoration.

Similar calculations were performed for BL silicene. In this calculation, BL silicene with AA stacked configuration and without puckering was considered (Fig. 1e).⁴⁶ The lattice constant and the layer distance of the BL silicene are 4.13 Å and 2.41 Å, respectively. Similarly to the SL silicene, the most preferable site for single H₂ molecule is hollow site and that for Ca atom is above the center of a hexagonal silicon ring. The calculated value of E_b of single H₂ molecule on BL silicene is 0.14 eV, which is slightly higher than those of SL silicene (Fig. 1f). In contrast, when Ca atom is adsorbed on BL silicene, Ca transfers a portion of its charge to BL silicene and thus carries 0.969 e (Fig. 1g). Meanwhile, E_b of single H₂ on Ca/BL silicene is increased to 0.26 eV, while the bond length of a H₂ molecule is elongated to 0.76 Å (Fig. 1h).

Before we consider the adsorption behaviors of multiple H₂ molecules on Ca/silicene system, the stability of the Ca/silicene with or without the substrate due to possible aggregation problem of Ca was studied. In the previous research works,^{55,56} E_b of Ca on freestanding silicene is about 2.19 eV, which is larger than the cohesive energy (1.84 eV) of bulk calcium. Thus, the clustering problem of Ca on freestanding silicene is absent and Ca/silicene system is the energetically

stable structure. For the case of silicene with supporting substrate, Vogt *et al.* provided experimental evidence for monolayer large area silicene sheets on Ag (111) surface.⁴⁴ Based on STM and low energy electron diffraction (LEED) results together with DFT calculations the authors demonstrated that a (4×4) 2D Si adlayer on Ag (111) is a real 2D silicene sheet. On the basis of the above evidence, we calculated the E_b of Ca on the (3×3) silicene with (4×4) Ag (111) substrate (Fig. 2). In our calculations, the Ag (111) substrate is modeled by a 4-atomic-layer slab, which is separated from its periodic images by 20 Å vacuum regions (Fig. 2a). From the calculated result, the E_b of Ca on silicene/Ag (111) is about 2.03 eV (Fig. 2b), being relative smaller than that of freestanding silicene with $E_b = 2.19$ eV. It may be attributed to the interactions between silicene and Ag (111) substrate. Meanwhile, the clustering of Ca also can be suppressed due to the low cohesive energy (1.84 eV) of bulk calcium. Therefore, we can deduce that the substrate has a relative small effect on E_b of Ca/silicene system.

As shown in Fig. 3, the behavior of hydrogen adsorption can be achieved when two or more hydrogen molecules are introduced on Ca/SL and Ca/BL silicene systems. All relaxed H–H bonds tilt on silicene sheet and located symmetrically around the Ca atom As shown in table 1, the average E_b value H_2 molecules of Ca/SL silicene decrease from 0.27 to 0.19 eV/ H_2 as n increases to 9. Up to nine H_2 molecules can be attached to a Ca/SL silicene system (9 H_2 on Ca/SL silicene) with a binding energy of ~ 0.19 eV/ H_2 . Meanwhile, there is about 0.146 e charge transfer from 9 H_2 molecules to Ca/SL silicene system. In addition, the average bond length of the H_2 is slightly elongated to 0.76 Å (Fig. 3h). Similarly, the average E_b value of nH_2 –Ca/BL silicene systems gradually decreases from 0.26 to 0.19 eV/ H_2 as n increases to 9 H_2 Ca/BL

silicene system (Fig. 4). Up to 9 H₂ molecules in succession can be bound to the Ca atom, which also brings out the elongation of H–H bond. In addition, there is 0.268 *e* charge transfer from 9 H₂ molecules to Ca/BL silicene system. The relaxed hydrogen geometries on the SL silicene (Fig. 3) and BL silicene (Fig. 4) are very close to each other. In fact, regardless of the initial molecular configurations, the same final structures are achieved. Since all hydrogen molecules are tilted after full relaxation, one of the two H atoms of each adsorbed hydrogen molecule becomes relatively closer to the Ca atom. From the results of calculation, we can conclude that both Ca/SL and Ca/BL silicene increase the binding energy of H₂ molecules, and thus, the hydrogen storage ability of the silicene is enhanced.

To further understand the hydrogen adsorption behaviors, the density of states (DOS) plots were analyzed for 9H₂ on Ca/SL and Ca/BL silicene systems (Fig. 5). In the case of Ca/SL silicene, it is readily seen that many peaks of Ca overlap with Si peaks at the energy range from –4.11 to 4.31 eV, which is responsible for the orbital hybridization of Ca-3d and Si-2p orbitals (Fig. 5a). For the case of 9 H₂ on Ca/SL silicene, all of the peaks of H and Ca highly overlap with each other in the energies of –3.83 to 4.05 eV, which confirms that Ca-3d orbital strongly hybridizes with H₂ σ* orbital (Fig. 5b). Similar hybridization behavior was analyzed for Ca/BL silicene. In the case of Ca/BL silicene, the Ca-3d orbital hybridize with Si-2p orbital at –4.51~3.07 eV (Fig. 5c). For the case of 9 H₂ on Ca/BL silicene, the peaks of H located at –2.23~3.01 eV overlap with Ca peaks, indicating that the hybridization orbitals of Ca-3d and H₂ σ* orbital (Fig. 5d). Note that the analysis of DOS of Ca/SL and Ca/BL system, we confirm that

the adsorption of H₂ molecules on both Ca-SL and Ca-BL silicene is attributed to the electronic hybridization between Ca and H₂ orbitals.

Since a perpendicular electric field F will lead to a polarization of charge density, it affects the binding strength of H₂ molecules on Ca decorated silicene. Herein, we investigated the effect of F on the hydrogen storage/release behavior on Ca/SL and Ca/BL silicene system (Fig. 6). The intensity-dependent results for the E_b value for the 9 H₂ on Ca/SL system, from which the binding strength is gradually enhanced when a positive F increases from 0 to +0.004 au. The E_b value for the 9 H₂ on Ca/SL system increases dramatically to 0.36 eV/H₂ under $F = +0.004$ au, which is almost double that of $E_b = 0.19$ eV/H₂ under $F = 0$ au (Fig. 6a-b). In order to understand E_b variations induced by the positive F , the Mulliken charge analysis was carried out for 9 H₂ on Ca/SL silicene system (Table 2). There is about 0.185 e charge transfer from 9 H₂ molecules to Ca/SL silicene system under $F = +0.004$ au, which is more than that of $Q = 0.146 e$ under $F = 0$ au. Meanwhile, the charges nearest Si atoms (hexagonal silicon ring) carried decrease from -1.005 to $-1.098 e$, and the charge of Ca (Q_{Ca}) carried increases significantly from 0.914 to 0.929 e on Ca/SL silicene system. These results are attributed to the downward charge transfer in the presence of a positive field. Since Ca is more positive and silicene is more negative, $F = +0.004$ au renders an extra dipole moment and thus enhances the hydrogen adsorption. The E_b value confirms that a positive field can evidently enhance the interactions between H₂ molecules and the Ca/SL silicene system. Comparing with several previous works, we found that the magnitude of E_b and Q_{Ca} of Ca/silicene (0.36 eV/H₂, 0.929 e) are larger than (or equivalent to) those of recently used storage media such as Ca/graphene (0.29 eV/H₂, 0.96

e),⁶⁹ Ca/zigzag edge of graphene (~ 0.2 eV/H₂),¹⁰ Ca/BC₂N sheet (~ 0.3 eV/H₂)⁷⁰, Ca/graphyne ($0.2\sim 0.34$ eV/H₂)⁷¹⁻⁷³ and Ca/B-doped graphene (~ 0.4 eV/H₂, $0.51 e$).²⁸ Note that the E_b of Ca on graphene is relatively small at about ~ 0.9 eV,⁶⁹ which is less than the cohesive energy (1.84 eV) of bulk calcium. The clustering problem of Ca still remains, which considerably reduces the binding energy of H₂ molecules and hence the number of adsorbed H molecules. However, the clustering of Ca can be suppressed on silicene due to the high binding energy (2.19 eV).^{55, 56} In contrast, opposite binding trends are observed when changing the orientation of F . The E_b value decreases from 0.19 to 0.02 eV/H₂ when F changes from 0 to -0.004 au (Fig. 6c). Meanwhile, there is only $0.068 e$ charge transfer from 9 H₂ molecules to Ca/SL silicene system, which efficiently induces the decrease of the binding strength between 9 H₂ molecules and Ca/SL silicene system. In addition, the charge Ca carried decreases significantly from 0.914 to 0.902 e . The corresponding charges carried by nearest Si atoms are approximately increased, ranging from -1.005 to $-0.905 e$. This charge redistribution is evidently attributed to the upward charge transfer induced by a negative field. Since the ionizations of both Ca and Si have changed considerably, the hydrogen binding will be weakened and this is presumably the reason why a negative field facilitates the release of hydrogen.

Similarly, the E_b value for the 9H₂ on Ca/BL silicene system increases dramatically to 0.37 eV/H₂ under $F = +0.004$ au, which is larger than that of $E_b = 0.19$ eV/H₂ under $F = 0$ au (Fig. 6d-e). Meanwhile, there is $0.329 e$ charge transfer from 9 H₂ to Ca/BL silicene system, which is more than that of $Q = 0.268 e$ under $F = 0$ au (Table 2). For the case of BL silicene system, the electrons obtained from Ca are not accumulated in this hexagonal ring, but will flow to the

remaining Si atoms in the same ring of the lower Si sheet (Fig. 6e). It is confirmed by the considerable charge variations in the second layer, where the charges of silicon ring decrease from -1.255 to $-1.292 e$. The charge carried by Ca atom increases considerably from 0.977 to $0.983 e$ under $F = +0.004$ au. For the case when negative F changes from 0 to -0.004 au, the E_b value oppositely decreases from 0.19 to 0.02 eV/H₂ for 9 H₂ on Ca/BL silicene system (Fig. 6f). There is only $0.207 e$ charge transfer from 9 H₂ to Ca/BL silicene system, which is smaller than that of $Q = 0.268 e$ under $F = 0$ au. Meanwhile, the charges nearest Si atoms (hexagonal silicon ring) carried increase to $-1.213 e$, and the charge of Ca carried decreases significantly to $0.961 e$ on Ca/BL silicene system. Thus, the negative field may significantly weaken the hydrogen adsorption.

From the above discussion, we can conclude that the external electric field can be utilized as a switch to control the entire adsorption and desorption in the hydrogen storage systems, completing the hydrogen storage/release cycle.

4. Conclusions

In conclusion, DFT calculations with F are employed to study the interactions between the H₂ molecules and the Ca/SL and Ca/BL silicene systems. When $F = +0.004$ au, the doubled binding enhancement is achieved for H₂ on Ca/SL silicene system, where the E_b increases considerably from 0.19 to 0.36 eV/H₂. When $F = -0.004$ au, on the contrary, binding weakness can be observed for 9 H₂ on Ca/SL and Ca/BL silicene systems, where the E_b decreases considerably to 0.02 eV/H₂. The Mulliken charge analysis indicates that the enhanced hydrogen storage/release is attributed to the charge redistribution between H₂ molecules and Ca/silicene

systems induced by a positive/negative F . Our calculated results show that the Ca/silicene system together with the synergy of F is a good candidate for hydrogen storage/release.

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Table 1. Calculated average E_b (eV/H₂) for the Ca/SL and Ca/BL silicene, with different hydrogen numbers.

Hydrogen number (n)	Single layer	Bilayer
1	0.27	0.26
2	0.27	0.26
3	0.28	0.26
4	0.28	0.26
5	0.27	0.24
6	0.20	0.23
7	0.19	0.21
8	0.19	0.20
9	0.19	0.19

Table 2. Calculated average E_b (eV/H₂) and charges of H atoms for the 9 H₂ on Ca/SL and Ca/BL silicene under different F .

9 H ₂ on Ca/SL system									
F (au)	-0.004	-0.003	-0.002	-0.001	0	0.001	0.002	0.003	0.004
Charges of H atoms	0.068	0.77	0.091	0.106	0.146	0.148	0.157	0.174	0.185
E_b (eV/H ₂)	0.02	0.08	0.11	0.13	0.19	0.21	0.27	0.32	0.36
9 H ₂ on Ca/BL system									
F (au)	-0.004	-0.003	-0.002	-0.001	0	0.001	0.002	0.003	0.004
Charges of H atoms	0.207	0.222	0.234	0.251	0.268	0.285	0.299	0.314	0.329
E_b (eV/H ₂)	0.02	0.08	0.10	0.13	0.19	0.22	0.28	0.33	0.37

Captions:

Figure 1. Top (upper) and side (lower) views of the geometric structures of (a) single layer silicene (SL), (b) H₂ adsorbed on SL silicene, (c) H₂ adsorbed on Ca/SL silicene, (d) bilayer silicene (BL) silicene, (e) H₂ adsorbed on BL silicene and (f) H₂ adsorbed on Ca/BL silicene. The yellow, white, and green spheres represent Si, H, and Ca atoms, respectively.

Figure 2. Top (upper) and side (lower) views of the geometric structures of (a) (3 × 3) silicene on (4 × 4) Ag (111), (b) Ca adsorbed on (3 × 3) silicene/(4 × 4) Ag (111). The yellow, light blue, and green spheres represent Si, Ag, and Ca atoms, respectively.

Figure 3. The relaxed hydrogen storage systems based on the Ca/SL silicene. The plots a-h show the relaxed models when hydrogen number increases from 2 to 9. The yellow, white, and green spheres represent Si, H, and Ca atoms, respectively.

Figure 4. The relaxed hydrogen storage systems based on the Ca/BL silicene. The plots a-h show the relaxed models when hydrogen number increases from 2 to 9. The yellow, white, and green spheres represent Si, H, and Ca atoms, respectively.

Figure 5. The DOS plots for 9H₂ on Ca-decorated silicene with different layers: (a) Ca/SL silicene, (b) 9 H₂ on Ca/SL silicene, (c) Ca/BL silicene, and (d) 9 H₂ on Ca/BL silicene. The Fermi level is set to zero and indicated by a dotted line.

Figure 6. Mulliken charge analysis for 9 H₂ on Ca/SL and Ca/BL silicene under different intensity and direction of electric field F . The black (red) numbers indicate the charge carried by the upper (lower) atoms.

Figure 1

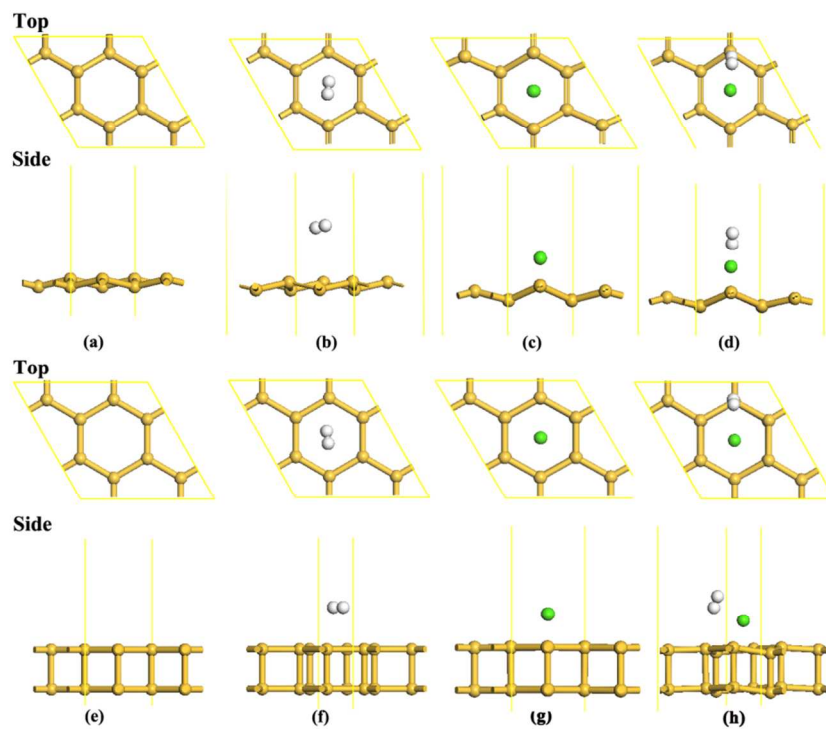


Figure 2

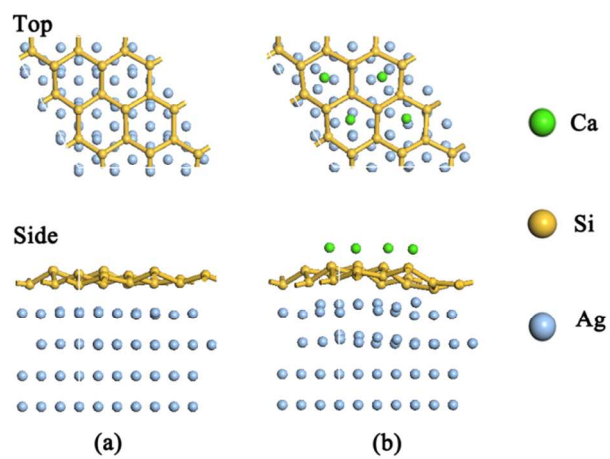


Figure 3

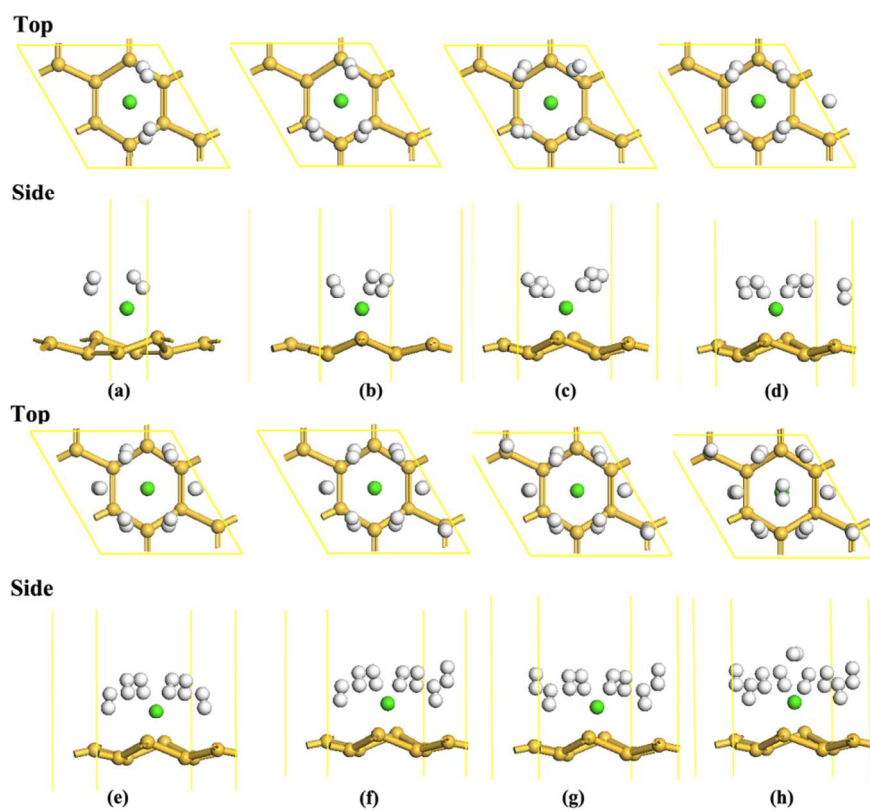


Figure 4

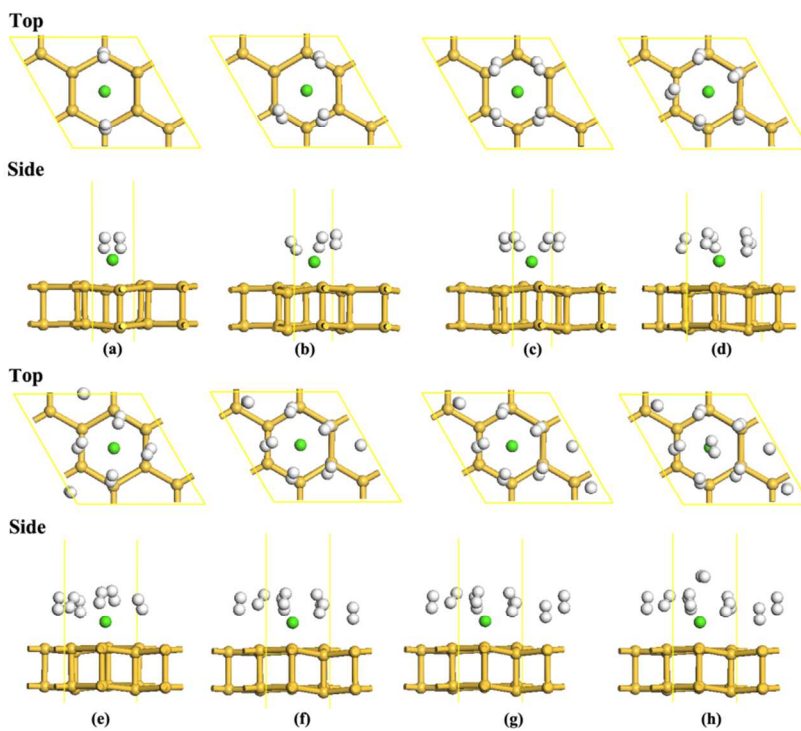


Figure 5

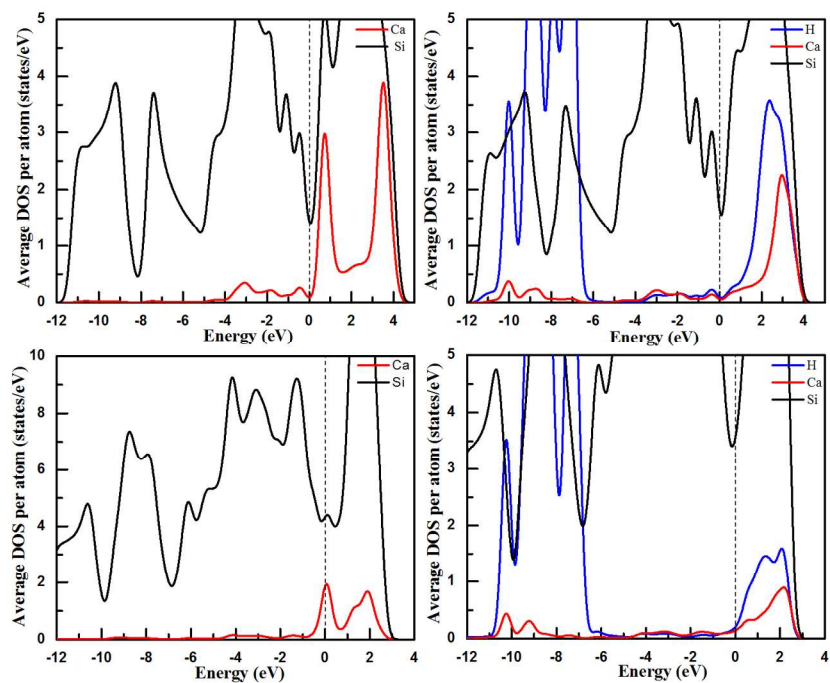
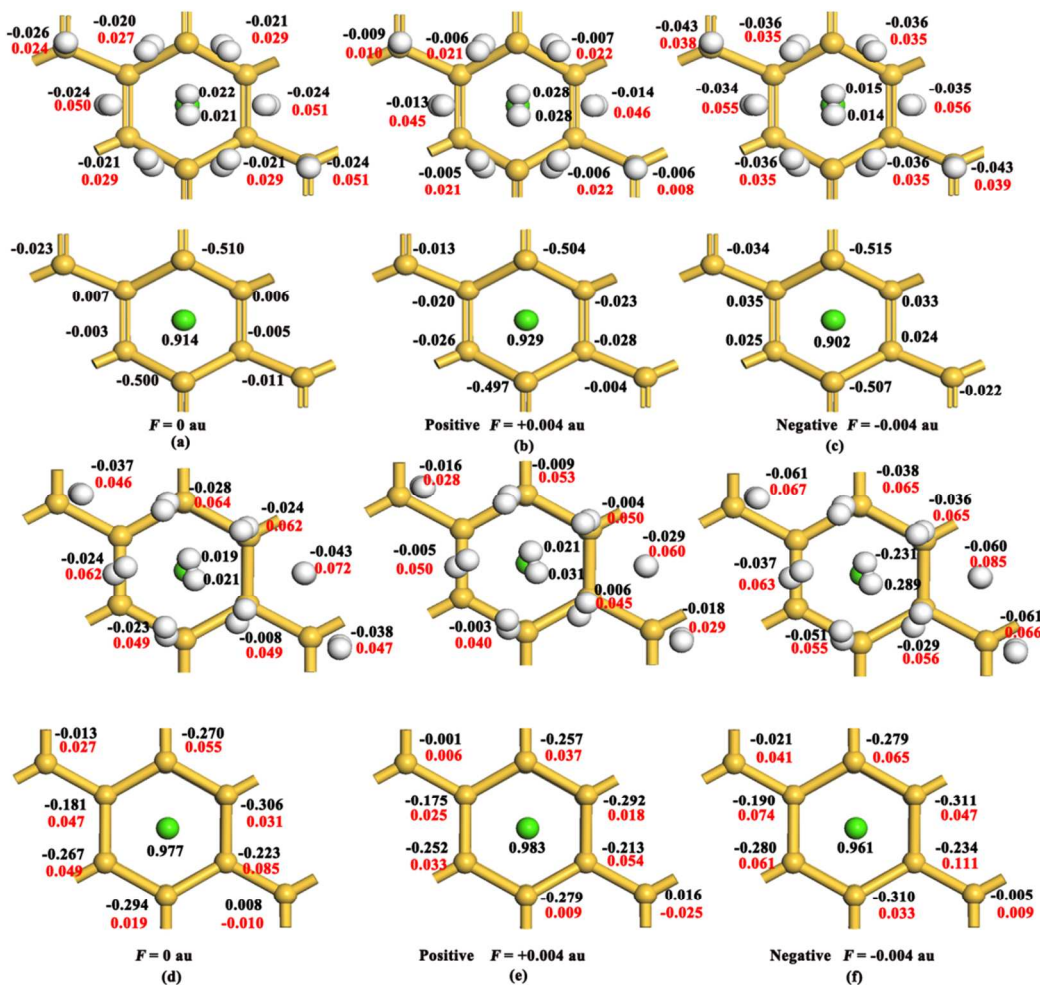
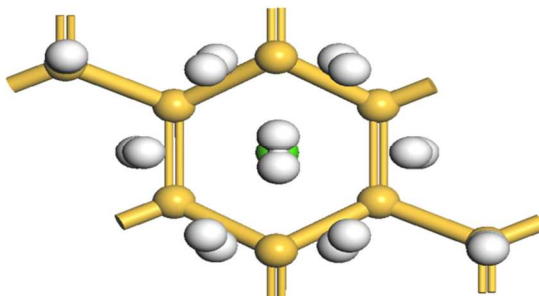


Figure 6



Colour graphic:



Text: The appropriate F can be used to effectively enhance the hydrogen storage/release on Ca/silene system