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Enhancement of hydrogen storage capacity on co-functionalized GaS monolayer under external electric field

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HIGHLIGHTS

- 2D GaS monolayer system has been investigated for hydrogen storage materials.
- Co-functionalized GaS sheet by Li, Na, K and Ca atoms enhanced the capacity of binding energies of hydrogen molecules.
- External electric field enhanced the H₂ storage capacity of pristine and co-functionalized GaS system.
- Binding energy per H₂ molecule falls in the range of 0.19 eV to 0.38 eV, which is efficient for practical applications.
- Co-functionalized GaS monolayer is a promising candidate for hydrogen storage.

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ABSTRACT

Hydrogen storage properties of co-functionalized 2D GaS monolayer have been systematically investigated by first-principles calculations. The strength of the binding energy of hydrogen (H₂) molecules to the pristine GaS surface shows the physisorption interactions. Co-functionalized GaS sheet by Li, Na, K and Ca atoms enhanced the capacity of binding energies of hydrogen and strength of hydrogen storage considerably. Besides, DFT calculations show that there is no structural deformation during H₂ desorption from co-functionalized GaS surface. The binding energies of per H₂ molecules is found to be 0.077 eV for pristine GaS surface and 0.064 eV–0.37 eV with the co-functionalization of GaS surface. Additionally, in the presence of applied external electric field enhanced the strength of binding energies and it is found to be 0.09 eV/H₂ for pristine GaS case and 0.19 eV/H₂ to 0.38 eV/H₂ for co-functionalized GaS surface. Among the studied GaS monolayer is found to be the superior candidate for hydrogen storage purposes. The theoretical studies suggest that the electronic properties of the 2D GaS monolayer show the electrostatic behavior of hydrogen molecules which confirms by the interactions between adatoms and hydrogen molecules before and after hydrogen adsorption.

Keywords:

Co-functionalized GaS monolayer
Charge transfer mechanism
Binding of hydrogen molecules
Hydrogenation and dehydrogenation process
Hydrogen storages

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Introduction

In the advanced world, one of the greatest worries is the increasing space between energy requirement and production from non-renewal energy sources (NRS) due to quick financial growth. Besides this, environmental pollution and climate change due to emission of CO₂, is another genuine danger which should be handled [1–3]. Consequentially, the dependence on NRS should be moved towards renewable energy sources which are cleaner and more efficient. Among different accessible choices, hydrogen (H₂) is noticeable due to its rich availability, eco-friendly nature, and having a maximum energy density, hence hydrogen (H₂) possessing the all capacities to grow into the excellent energy carrier [4–16].

In spite of such virtues there are some technical complications correlated with usages of H₂ as a renewable source of energy [17]. The main technical challenge is getting a decent procedure for storing it. Although liquified and pressurized storage of hydrogen is utilized, but because of being expensive and due to security concerns its usage is limited [18,19]. Hydrogen storage based on materials is another revolutionary technique that is used in recent time but getting a better candidate for this also a challenge [20]. The boost of 2D materials has bring about a new age of material science by virtue of their peculiar physical and chemical properties [21]. There is remarkable enthusiasm for 2D materials post the fruitful shedding of graphene [22], that is really a carbon atom's single layer having incredibly interesting properties [23,24]. However, graphene has lucrative properties but the lack of bandgap limits its applications in several technical areas [25]. It inspired researchers to investigate 2D materials other than graphene with such an inherent band gap. Due to their fascinating and technologically valuable features 2D materials can be adopted in a number of ways such as solar cell [26–28] material for gas sensing [29–31], photodetectors [32], battery applications [33] and a lot more. More interestingly, several latest studies show that H₂ can be stored in 2D materials. However, conditions and criteria suggested by Department of Energy of U.S.A., like storage capability, adsorption and desorption of hydrogen at atmospheric circumstances is really a challenging job [34–39]. Material based on Boron such as boranes [40,41], borophene [42,43], boron nitrides [44] have been observed effectively efficient H₂ storage mediums because of their large surface area and morphologies. Although the materials not containing boron such as gallium nitride [45], silicene [46], germanene [47], molybdenum disulphide [48], phosphorene [49], graphene [50–52] and single walled carbon nanotube [53,54] and other monolayered materials [55–59] are also found as a promising material for hydrogen storage. In recent years, some novel features found in gallium sulphide (GaS) monolayer such as high thermal conductivity [60] a promising material for hydrogen evolution

catalyst [61] and the optical properties of monolayer of GaS are obtained in the ultraviolet range, it can be used as a highly promising material in ultraviolet optical nanodevices, nano-electronics, optoelectronics [62].

Inspired by these fascinating properties of 2D GaS system, we have systematically investigated the co-functionalization of Li, Na, K and Ca atoms on GaS surface. In this study, we have been explored the ability of alkali metals and Ca adatom on GaS monolayer as H₂ storage material. This study also contains structural properties, electronic properties, charge distribution, energy assessment, and mechanism of hydrogenation of metal and Ca furnished GaS Monolayer.

Computational methods

All computational work performed within density functional theory (DFT) framework using generalized gradient approximation with the functional of Perdew, Burke and Ernzerhof (PBE) method [63,64] as implemented in the Vienna ab initio simulation package (VASP). The cut-off energy was set to 500 eV. The Brillouin zone sampling was executed with Monkhorst – Pack [65] special K-point meshes. We have chosen K-point grid (3 × 3 × 1) for (3 × 3 × 1) supercell for structural optimizations and (6 × 6 × 1) K-points for electronic structure calculations and the distance between two neighbouring monolayers is 20 Å therefore the interaction between the monolayers could be abolished. The convergence criteria set for ionic relaxation is 10⁻⁶ eV for energy and 10⁻³ eV/Å for force, respectively. The binding energy of alkali metals (AM) and calcium (Ca) with GaS monolayer were calculated by the following reaction,

$$E_b = \frac{E_{(GaS+AM/Ca)} - E_{GaS} - E_{(AM/Ca)}}{n}, \quad (1)$$

where E_(GaS+AM/Ca) is the total energy of functionalized GaS monolayer with AM (Li, N, K) or Ca, E_(GaS) bared monolayer of GaS and E_(AM/Ca) energy of alkali metal or energy of calcium atom and "n" is number of alkali metal or calcium atoms. According to this definition, the negative value of binding energy signifies that the adsorption process is energetically favorable and the gas molecular is tightly bound to the substrate monolayer, while a positive value indicates that they tend to cluster together. Also, the adsorption energies (E_{ads}) per H₂ molecule were calculated as follows:

$$E_{ads} = \frac{E_{(GaS+AM/Ca+nH_2)} - E_{(GaS+AM/Ca)} - nE_{H_2}}{n}, \quad (2)$$

In equation (2), first term responds to energy of hydrogen adsorbed AM/Ca decorated GaS monolayer second term responds to energy of GaS monolayer with AM/Ca, last term refers to energy of hydrogen molecules and n is the number of

hydrogen molecule adsorbed. Additionally, for the transfer analysis between the GaS monolayer and hydrogen molecules, the Bader charge approach is employed [66].

Results and discussion

Structural stability and electronic properties

We first studied the structural properties of the pristine GaS monolayer in order to determine the precision of the computing methodology used in this work. The optimized structure with top and side view of GaS monolayer is presented in Fig. 1. The bond lengths between Ga–Ga, Ga–S and S–S are found to be 2.474 Å, 2.352 Å and 4.712 Å and optimized lattice parameters $a = b = 3.585$ Å (see Table 1) which is good consistent with previous reported work by experimentally as well as theoretically [67,68].

Further to check the stability of GaS monolayer, we have computed the phonon dispersion spectra as presented in Fig. 2 (a). The phonon dispersions spectra of the GaS monolayer calculated along the high symmetry points $\Gamma \rightarrow M \rightarrow K \rightarrow \Gamma$ and the Acoustic vibrational modes converge to zero near to Γ point. The vibrational optical modes shifted higher frequency side. Also, the vibrational phonon density of states (VDOS) for GaS monolayer is presented in Fig. 2(b). This VDOS has highest peak around 1.75 states/THz and lowest peak of 0.02 states/THz at vibrational phonon frequencies of 3 THZ and 11.5 THZ but the majority of the monolayer states dominate high frequency sites which indicate that the system is dynamically stable. Also, the vibrational states is zero (frequency gap) around 7.5 THz frequency which occurs due to the mass difference in atoms Ga and S.

Now, we have discuss the electronic properties of pristine GaS system. The electronic band structure and projected density of states (PDOS) as shown in Fig. 3. The top of valence band maximum (VBM) lies between Γ to M k-point and while bottom of the conduction band minimum (CBM) lies at Γ k-point that why the electronic band structure shows indirect bandgap (2.47 eV) semiconductor. The calculated band gap is good consistent with previous work [67,68]. Furthermore, to understand the electronic band structure, we have now discuss about the projected density of states which is

Table 1 – The computational parameters, including bond lengths, bond angle and lattice parameters of pristine 2D GaS monolayer.

System	Bond length(Å)	Bond angle (°)	parameter (Å)
Ga–Ga	2.474	\angle GaSGa	99.25
Ga–S	2.352	\angle SGaS	99.25
S–S	4.712	\angle GaGaS	118.39

presented in Fig. 3(b). The valence band is mainly contributed by p-orbitals of Ga and S atoms while the conduction band near the Fermi level is contributed by s-orbital of Ga atom. From PDOS, the VBM and CBM near the bandgap are mainly dominated by s, p-orbitals of Ga and partially by p-orbitals of S located at the edges.

Binding of H₂ molecules on GaS monolayer

For the binding of hydrogen molecules on the GaS monolayer, we have taken the optimized structure with (3 × 3 × 1) supercell of GaS monolayer. The (3 × 3 × 1) supercell of GaS monolayer contains 36 atoms (Ga-18 and S-18) and has cell parameters $a = b = 10.755$ Å.

Initially, we have study the physical interactions of H₂ molecules on the surface of pristine GaS monolayer at different possible binding sites of GaS system such as centre of hexagonal ring, top of the Ga and S atoms, between Ga and S bond. In these possible sites, we have taken lowest binding energy configurations in which the H₂ molecules placed parallel to the pristine GaS monolayer surface and H₂ molecules vertically placed 2.4 Å from GaS surface. From structural optimizations, we found that the H₂ molecules is slightly tilted with an particular angle from its axis to the surface, as depicted in Fig. 4. The binding energy (E_b) of the nH₂ molecules ($n = 1$ to 6) is calculated as 0.07 eV/H₂ (the physisorption interactions of H₂ with GaS surface) as presented in Table 2 and similar results was found to be in the previously reported work on graphene [69,70].

There is no structural distortion of the GaS monolayer with the physical interactions of H₂ molecules as shown in From

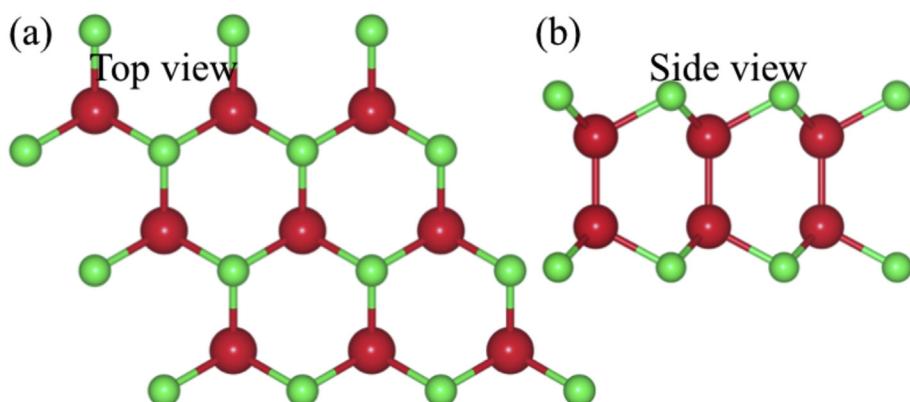


Fig. 1 – Fully optimized structures of (a) top view and (b, c) side views of pristine GaS monolayer.

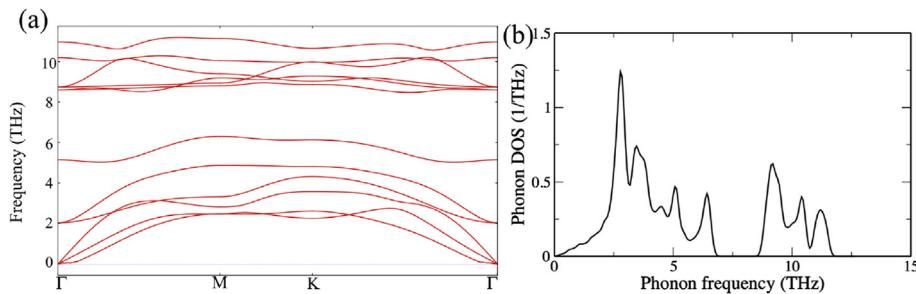


Fig. 2 – (a) Phonon dispersions curve, and (b) vibrational density of states of 2D GaS monolayer.

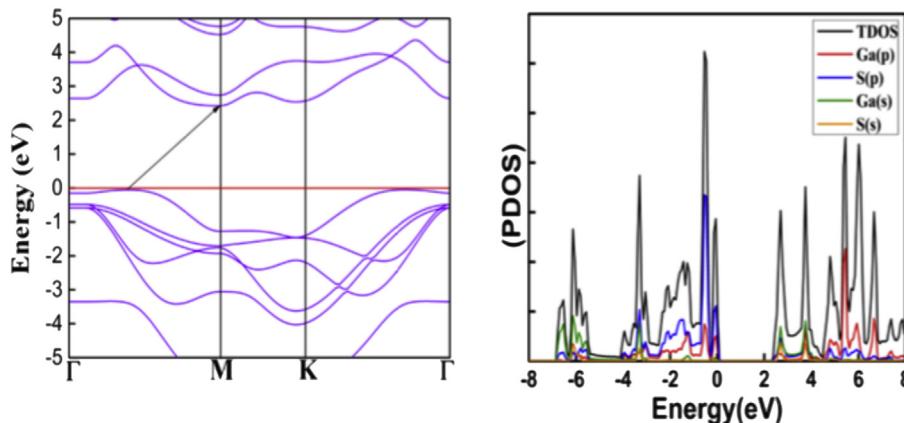


Fig. 3 – The electronic band structure and corresponding projected density of states (PDOS) of GaS system.

Fig. 4. Due to strong physisorption interaction between GaS surface and hydrogen molecules, the $n\text{H}_2$ molecules shifted 2.887 Å to 3.007 Å away from the surface. Also, from the Bader analysis, we found the very less charge transfer from hydrogen molecules to pristine GaS surface which is vary from 0.002 e^- to 0.006 e^- as shown in [Table 2](#).

Furthermore to see the effect of hydrogen molecules on the pristine GaS monolayer, we have computed the electronic density of states. For the comparision, we have projected the total density of states of pristine GaS monolayer and $n\text{H}_2$ molecules on GaS surface as presented in [Fig. 5](#). From [Fig. 5](#),

there is no effect on density of states with $n\text{H}_2$ molecules on GaS surface in valence band and conduction band near to the Fermi level because with the absorption of hydrogen molecules, GaS sheet remains same structural configuration (there is no structural deformation). But due to the presence of $n\text{H}_2$ molecules on GaS surface, the $n\text{H}_2$ molecules shows some electronic states at deep energy level around -2 eV to -5 eV in the valence band and beyond 5 eV in conduction band as presented in [Fig. 5](#). The very small charge transfer from hydrogen molecules to GaS surface shows with Bader analysis which is quantify by density of states.

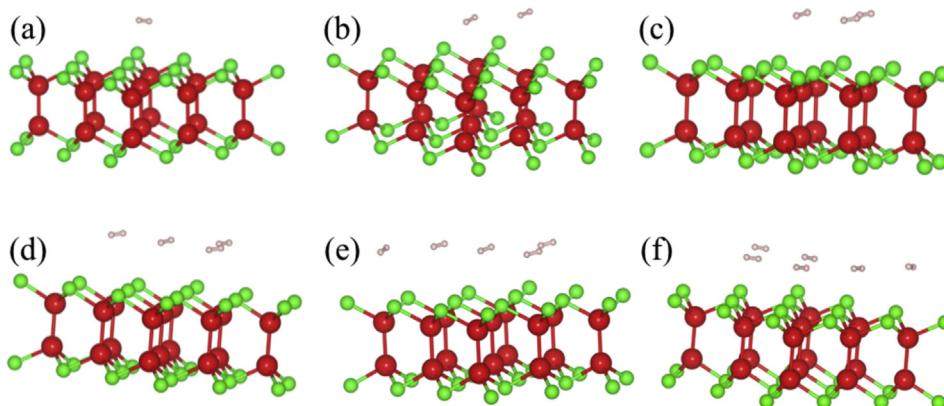


Fig. 4 – The absorption of hydrogen molecules ($n\text{H}_2$, $n = 1, 2, 3, 4, 5, 6$) on the surface of pristine GaS monolayer.

Table 2 – The bond length $d_{(H-H)}$ (d_1), Adatom to S atoms distance $d_{(S-adatom)}$ (d_2) and adatom to H_2 distance $d_{(M-H_2)}$ (d_3), binding energies of H_2 molecules and the Bader charges (ΔQ) on H_2 molecules for all hydrogenated systems are listed with and without functionalized 2D GaS monolayer as efficient for hydrogen storage materials.

System	$d_1(\text{\AA})$	$d_1(\text{\AA})$	$d_3(\text{\AA})$	$E_b(\text{eV}/H_2)$	ΔQ
1 H_2	0.751		3.007	0.07612	0.0061
2 H_2	0.751		2.887	0.07254	0.0024
3 H_2	0.751		2.893	0.07386	0.0040
4 H_2	0.751		2.926	0.07383	0.0037
5 H	0.752		2.911	0.07526	0.0026
6 H_2	0.751		2.924	0.07677	0.0020
GaS+3Li		2.251			0.9900
3Li+3 H_2	0.751		2.260	0.15952	-0.00022
3Li+6H	0.751		2.604	0.23142	-0.0025
GaS+3Na		2.826			0.5030
3Na+3 H_2	0.751		2.707	0.18471	-0.0430
3Na+6H ₂	0.751		2.677	0.14368	-0.0342
GaS+3K		2.996			0.6006
3K+3 H_2	0.751		3.032	0.04903	-0.02398
3K+6H ₂	0.751		3.041	0.06387	-0.0316
GaS+4Ca		2.642			1.2300
4Ca+12H ₂	0.751		2.551	0.37880	-0.00337

Effect of adatom on GaS monolayer

Moreover to enhancing the hydrogen molecule binding strength on GaS monolayer, we decorated the Li, K, Na and Ca adatom on GaS sheet. Next, we study the physical interactions of Li, K, Na and Ca adatom on GaS surface. For the

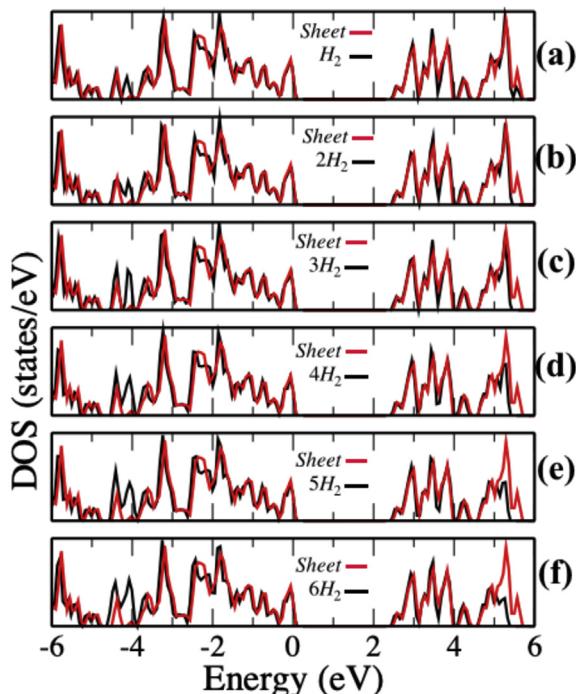


Fig. 5 – The density of states (DOS) of pristine GaS monolayer and hydrogenation (nH_2 , $n = 1$ to 6) on GaS surface.

functionalization of GaS sheet with four different configurations by Li, K, Na and Ca atoms, we have taken different possible adsorption sites for each decorated adatom, including centre of hexagonal ring, over the Ga and S bond and top of the Ga and S atoms. The lowest energy configurations of the GaS system for each adatom is found to be over the centre of hexagonal ring, and the corresponding computed binding energy of 1.77 eV/Li, 1.72 eV/Na, 0.85 eV/K and 2.78 eV/Ca for different configurations. We have taken single side functionalized GaS system by the alkali metals Li, K, Na atoms.

While, we have taken two sides for Ca functionalized on GaS surface. The optimized structures of GaS monolayer functionalized with Li, K, Na and Ca atoms are shown in Fig. 6. For the Li-decorated on GaS monolayer, the calculated distances between the S atoms of GaS monolayer to Li atoms range from 2.25 to 2.44 Å. While, the GaS monolayer is slightly distorted and bond lengths between Ga–Ga, Ga–S are 2.625 Å from 2.474 Å and 2.39 Å from 2.35 Å for Li adatom, respectively. During the Li-decoration, each Li atoms transfer 0.99 e⁻ to the GaS surface by Bader charge analysis. Next K, Na and Ca atoms functionalized on GaS surface, the calculated distances between the S atoms of GaS monolayer to K, Na, and Ca atoms range from 2.826 to 4.011 Å, 2.996 to 3.38 Å and 2.64 to 2.66 Å. But in case of the GaS monolayer is slightly distorted and bond lengths between Ga–Ga are 2.49 Å, 2.44 Å, 2.52 Å from 2.474 Å for K, Na and Ca adatom, respectively. Wheile bond lengths between Ga–S are 2.385 Å, 2.36 Å, 2.38 Å from 2.35 Å, for K, Na and Ca adatom, respectively. In case of K, Na, and Ca atoms decorated on GaS surface, the each adatom transfer 0.66 e⁻, 0.50 e⁻ and 1.23 e⁻ to GaS surface, respectively. Each adatom functionalized on GaS monolayer have favorable binding energies and sufficient charge transfer between GaS monolayer and adatoms which will be efficient for binding of hydrogen molecules. After assessing the feasibility of K, Na, and Ca decoration on GaS monolayer, we then study the adsorption of H_2 molecules on Li, K, Na, and Ca decorated GaS monolayers (see Fig. 7).

Binding of nH_2 molecules on functionalized 2D GaS monolayer

Now, we have calculated the most favorable configurations of functionalized GaS monolayer for hydrogen absorption over the Li, K, Na and Ca atoms. The molecular adsorption around the adatom as the most stable nH_2 configuration.

The computed binding energies of functionalized GaS monolayer for hydrogen molecules are shown in Table 2. The interactions of first 3 H_2 molecules with functionalized with Li atom, we found that the binding energies of 0.16 eV per H_2 molecule. In this case, the bond length between adatom Li atom and hydrogen molecules is not affected and it is found to be 2.26 Å from 2.25 Å. If we put more 6 H_2 molecules on the functionalized GaS monolayer with Li, the binding energy is found to be 0.23 eV per H_2 molecule. Whereas with the interactions of 6 H_2 molecules on the functionalized GaS monolayer with Li will enhanced the bond length between Li atom and hydrogen molecules and found to be 2.60 Å from 2.25 Å. During the interactions of 3 H_2 and 6 H_2 molecules on the functionalized GaS monolayer, the adatoms transfer 0.00022 e⁻ and 0.0025 e⁻ per H_2 molecules, respectively.

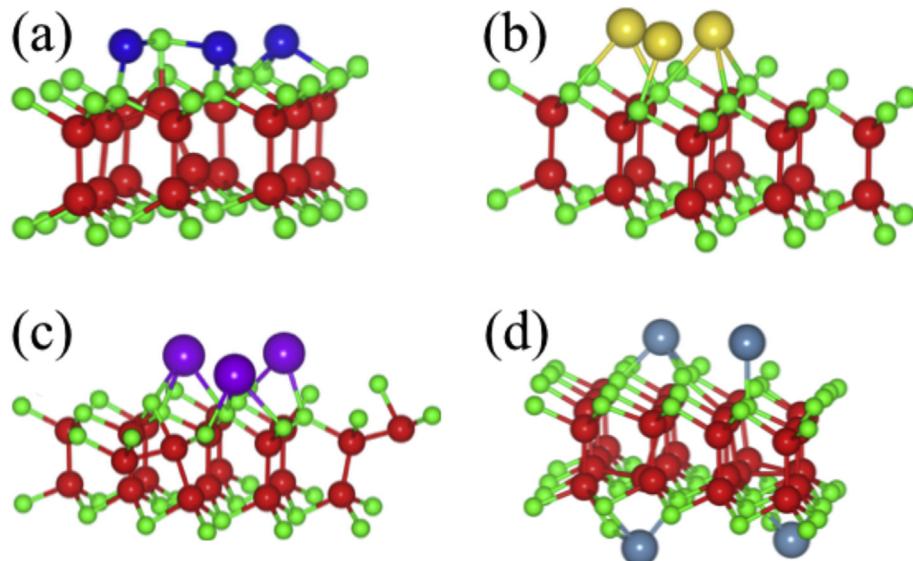


Fig. 6 – The optimized structures of co-functionalization of 2D GaS monolayer with (a) Li, (b) K, (c) Na and (d) Ca atoms.

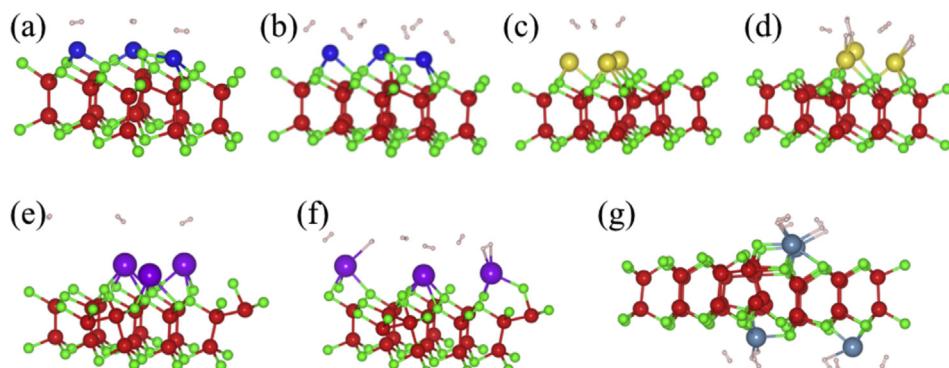


Fig. 7 – The absorption of hydrogen molecules ($n\text{H}_2$) with Li, Na, K, and Ca functionalized on monolayer GaS surface. (a) 3H_2 molecules and (b) 6H_2 molecules with Li adatoms, (c) 3H_2 molecules and (d) 6H_2 molecules with Na adatoms, and (e) 3H_2 molecules and (f) 6H_2 molecules with K adatoms and (g) 12H_2 molecules with Ca adatoms. Blue color-Li atom, yellow color Na atom, purple color K atom and Ca atom having blue-green color. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

In addition, the interactions of 3H_2 and 6H_2 molecules on functionalized GaS monolayer with K, Na atoms, the binding energies are found to be 0.18 eV and 0.05 eV per hydrogen molecules. While in case of 6H_2 molecules, the binding energies is 0.14 eV and 0.06 eV H₂ molecules for functionalized GaS monolayer with K, Na atoms, respectively. It is also gains some electrons 0.043 e^- , 0.034 e^- and 0.024 e^- and 0.032 e^- per H₂ molecule for Na and K functionalized GaS surface in case of 3H_2 and 6H_2 molecules from the adatoms on the functionalized GaS surface, respectively. Moreover, the binding energy of GaS functionalized with Ca atoms gives 0.38 eV per H₂ molecule.

Furthermore, the electronic properties means total density of states strongly influence the GaS monolayer functionalized by Li, K, Na and Ca atoms. The total density of states (TDOS) of GaS monolayer functionalized by Li, K, Na and Ca atoms as shown in Fig. 8. The TDOS of Ca adatom on GaS monolayer shifted conduction band side and shows metallic conducting

nature but with the interactions of H₂ molecule will reduced the electronic states near the Fermi level as presented in Fig. 8(a). Similar results have found in case of Li, K, and Na adatoms on GaS monolayer which make more conductive nature of GaS monolayer as presented in Fig. 8(b–g). Due to the significant changes in electronic properties of GaS monolayer, we have computed the work function of these system. We can see that the hydrogen molecules on pristine GaS monolayer slightly influence as presented in Fig. 9. But in case of functionalized GaS monolayer strongly influence the work function of GaS monolayer system (see in Fig. 9). The changes in work function also support the binding energies per H₂ molecule and charge transfer between GaS system and hydrogen molecules.

Additionally, we have also computed the effect of the applied external electric field perpendicular to the GaS monolayer system. The binding energy as a function of external electric field as presented in Fig. 10. During the

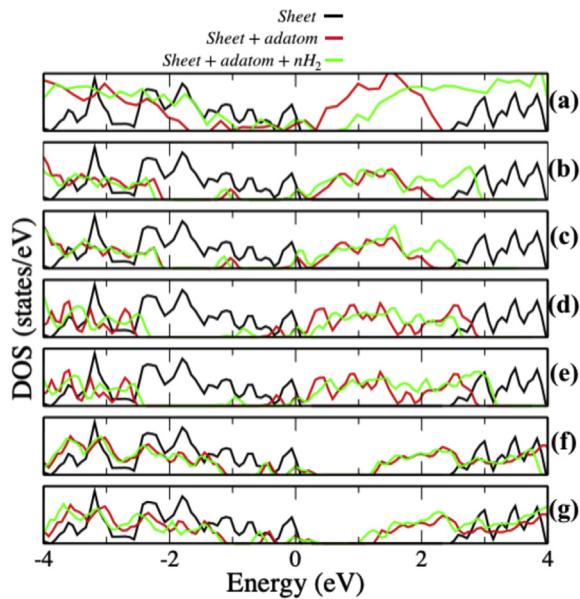


Fig. 8 – The density of states (DOS) of pristine GaS monolayer, adatoms on monolayer GaS surface and hydrogenation ($n\text{H}_2$) on GaS surface. The DOS shows for hydrogenation ($n\text{H}_2$) with (a) 12H₂ molecules with Ca adatoms, (b) 3H₂ molecules and (c) 6H₂ molecules with Li adatoms, (d) 3H₂ molecules and (e) 6H₂ molecules with K adatoms and (f) 3H₂ molecules and (g) 6H₂ molecules with Na adatoms functionalized on the surface of GaS monolayer. The black, red and green color represents the total DOS of pristine GaS monolayer, functionalized GaS monolayer and functionalized GaS monolayer with $n\text{H}_2$ molecules. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

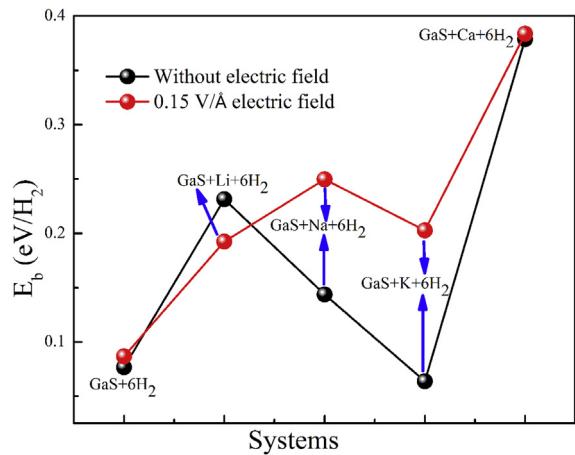


Fig. 10 – The effect of external electric field on binding strength of hydrogen molecules. The black and red line represents the binding energy per hydrogen without and with electric field on the surface of co-functionalized GaS monolayer. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

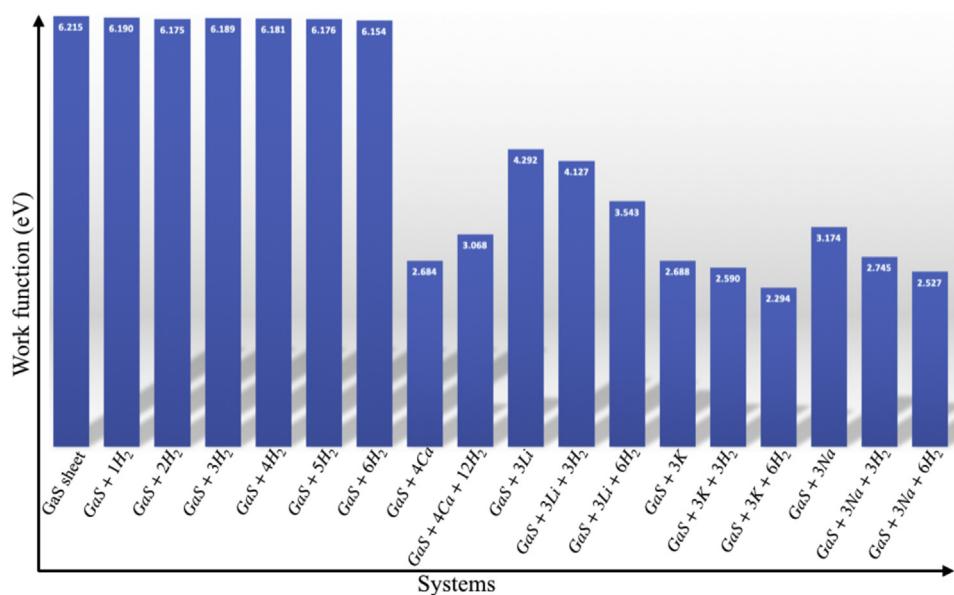


Fig. 9 – Variation of work function without and with various functionalizations on 2D GaS monolayer.

external electric field, the strength of binding energies in the range of 0.087 eV/H₂ to 0.384 eV/H₂, which enhance the hydrogen binding strength for hydrogen storage. Fig. 11, shows the hydrogenation and dehydrogenation cycle on the surface of GaS monolayer without and with functionalized system. After removing the hydrogen molecules on the surface of pristine and functionalized GaS monolayer, the GaS system revise back to original configuration as presented in Fig. 11.

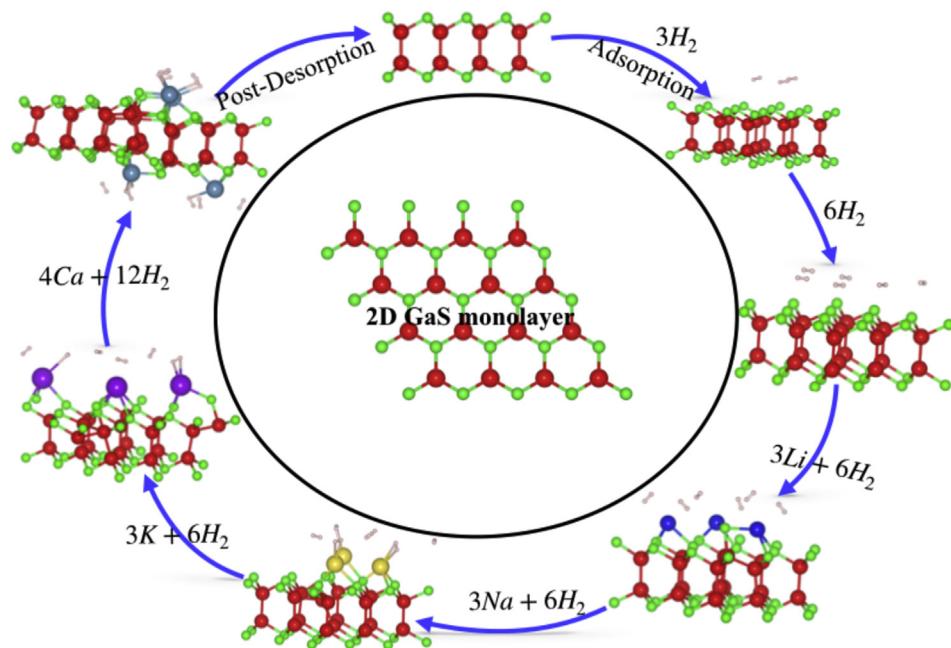


Fig. 11 – The hydrogenation and dehydrogenation process for co-functionalized GaS monolayer system with Li, K, Na and Ca atoms. Optimized structures by three and four adatom over 2D GaS monolayer and without adatom are also given. The atomic colors represented by, Red-Ga, green-S, H-brown, Li-blue, Na-yellow, purple-K, and Ca-blue-green. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Conclusion

In summary, the energy storage performances of hydrogen molecules on 2D GaS monolayer are theoretically studied using first-principles calculations. The strength of binding energy of nH_2 molecules to the pristine GaS surface proceeds through physisorption interactions. The binding energies of hydrogen molecules is found to be approximately $0.07 \text{ eV}/H_2$ on the pristine GaS monolayer. Further, the energetically favorable adsorption sites and the corresponding adsorption energetics for these functionalized GaS surface with Li, Na, K and Ca atoms have been determined. All these functionalized GaS monolayers with Li, Na, K and Ca atoms act as a charge donor and contribute charge to the host monolayer, yet have more influence on the electronic properties of the monolayer. The functionalized GaS monolayer with Li, Na, K and Ca atoms enhanced the capacity of hydrogen storage. The binding energies with functionalized GaS monolayer are found to be $0.064 \text{ eV} - 0.37 \text{ eV}/H_2$. It is found the GaS functionalized with Ca atoms exhibits stronger interaction with host monolayer, followed by Li, K and Na adatom, indicative of GaS monolayer potentially being a more sensitive with Ca adatom for hydrogen storage. More importantly, in the presence of external electric field, the strength of binding energies enhanced and it is found to be $0.09 \text{ eV}/H_2$ for pristine GaS case and $0.19 \text{ eV}/H_2$ to $0.38 \text{ eV}/H_2$ for co-functionalized GaS surface. Due to the efficient binding energy of hydrogen molecules Among the studied GaS monolayer is found to be the most promising candidate for hydrogen storage purposes; with an

efficient hydrogen binding energy. Our theoretical investigations suggest that the functionalized GaS monolayer is a promising candidate for hydrogen storage.

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