

First-principles study on the adsorption of hydrogen molecules on alkali-decorated germanene for energy storage

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Abstract:

We have performed density functional theory-based calculations to study the geometrical structures and stability of pristine germanene, alkali atoms-adsorbed germanene and also the adsorption properties of H₂ molecules, ranging from one to seven molecules, on alkali atoms-decorated germanene. Using the information of adsorption energy of alkali atoms at different adsorption sites of a germanene supercell, it has been observed that the position at the center of one of the hexagons of the honeycomb structure is the preferred site for the adsorption of the alkali atoms. On comparing adsorption energy per H₂ molecule on pristine and alkali atoms-adsorbed germanene, we find that the presence of alkali atoms enhances the binding strength of H₂ molecules. The adsorption energy of the H₂ molecules to the alkali atoms is in the range of physisorption. The K-decorated germanene has the largest storage capacity, being able to bind up to seven H₂ molecules. These results may lead to materials with more hydrogen storage capacity for use in alternative energy sources.

Keywords:

2D materials, Density Functional Theory, Germanene, Hydrogen storage, Renewable energy storage

1. Introduction

Hydrogen is one of the most promising candidates for the replacement of current carbon-based energy sources because it is a source of clean energy that is abundant and has three times the energy per unit mass than that of hydrocarbons [1]. Although hydrogen is an ideal fuel there are many problems associated with its use, such as the cost of the production mechanism, which is at least

three times the cost of natural gas production [2,3], and storage efficiency [1,4]. The significance of storage efficiency can be seen when hydrogen fuel is used for mobile applications such as transportation where the high gravimetric density and the easy to store feature is needed. Among storage methods that exist today are compression, physisorption, metal hydrides via chemical reactions and liquefaction. Within these methods, physisorption is a good choice for applications due to its lightweight and easy-to-store features. Physisorption stores the hydrogen by means of low energy van der Waals attraction to a surface [5]. Research on several materials have shown that hydrogen can bind on surfaces either molecularly or through dissociative adsorption [6–10]. The challenge in physisorption-based storage is to find the most efficient and safe material for adsorption that would yield high gravimetric and volumetric density.

Most of the materials investigated involve carbon nanostructures due to their high surface area and reduced weight, particularly graphene [11–14]. Graphene, a two-dimensional honeycomb network of carbon atoms, is currently a material of much interest because of its unique electronic properties [15,16]. Unfortunately, graphene, with its high surface area, cannot hold that much hydrogen [5]. As a solution, some studies have used decorating atoms on graphene [17,18]. However, this decoration resulted in clustering that can significantly reduce the hydrogen storage capacity [19,20]. As an alternative, two-dimensional hexagonal lattices of Si and Ge, so called silicene and germanene [21,22], respectively, have been theoretically studied [23–25].

Pure germanium is a semiconductor with a smaller band gap than diamond and silicon and is regarded well in the transistor industry. Compared with graphene, germanene has a larger hexagonal lattice parameter. Germanene has been synthesized recently by several research groups [26–30]. A single-layer of fully hydrogenated germanene was also fabricated successfully [31]. Recently, atom adsorption on germanene is also studied [32,33]. Similar to silicene, atoms bind much stronger to germanene than graphene, which is mainly caused by the sp^2 – sp^3 hybridization of Ge atom.

Little attention has been focused on hydrogen-molecule adsorption on germanene. Pang et al. [34] carried out a detailed investigation of the structural, energetic, and electronic properties of Li, Na and K atoms adsorbed on germanene for a wide range of coverages using first-principle methods, finding that these metals bind strongly to germanene. These results may be important to hydrogen storage on 2D materials because other theoretical investigations [35,36] have found that Li functionalization yields high H storage capacity without clustering. The use of alkali metals would be advantageous because these are the lightest elements on the periodic table, which theoretically would mean a high gravimetric capacity. A recent investigation by Rojas et al. [24] showed that K- and Ca-decorated germanene may adsorb up to 9 and 8 hydrogen molecules, respectively. Considering this, in this work we study the adsorption of several hydrogen molecules on Li-, Na- and K-decorated germanene.

2. Computational details

The total energy, electronic and geometrical structures of all systems studied in this work were obtained by means of Density Functional Theory (DFT) [37,38]. All calculations involved were performed using the SIESTA code [39]. The generalized gradient approximation (GGA) in the Perdew-Burke-Erzsff (PBE) [40] form was employed to describe the exchange and correlation energy. Optimized double- ζ polarized basis sets [41,42] and norm-conserving Troullier-Martins pseudopotentials [43] in their fully non-local form were used [44]. Since long-range interactions play a crucial role in the geometries and binding energies of the adsorbents, the effect of van der Waals interactions was taken into account by using the semiempirical method of Grimme with the inclusion of a long-range dispersion correction [45]. The real-space grid for numerical integrations was defined by an energy cutoff of 500 Ry. A supercell consisting of 4×4 germanene unit cells is employed for all the calculated structures. There is a vacuum layer of 30 Å along the z-direction to avoid interactions between adjacent periodic images. The 2D Brillouin zone was sampled with a Monkhorst-Pack grid [46] of 24×24 k -points. Geometric relaxations were performed by using a

conjugated gradient method as implemented in the SIESTA code, with no symmetry constraints. Atomic positions were allowed to relax until the force between any pair of atoms was lower than 0.01 eV/Å.

Fig. 1 shows the structure of germanene, we calculated the buckling value (perpendicular distance between the two Ge planes) as 0.74 Å. Upon the formation of the sp^3 -bonded honeycomb lattice, the covalent bond length of Ge-Ge is 2.46 Å, with an angle between two adjacent bonds of 111.81°. The lattice parameter calculated of 4.12 Å is in good agreement with reported results [47,48]. The electron charge transfers between the germanene and the adsorbates were estimated by using Voronoi electronic population analysis [49]. All calculations of adsorption and binding energies are corrected for basis set superposition error with the counterpoise correction, as described by Boys et al [50].

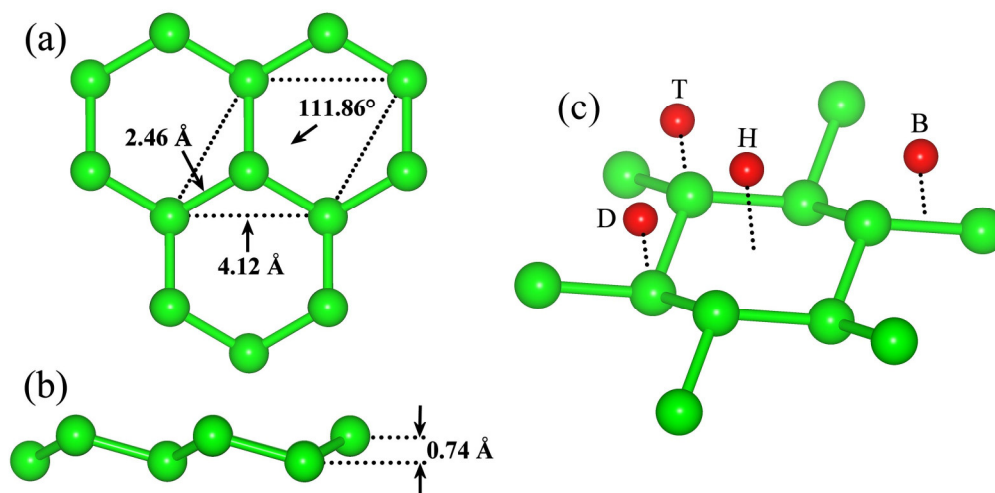


Figure 1. Atomic structure of germanene: (a) top view and (b) side view. (c) Preferred adsorption sites: hollow, top, down and bridge, on the germanene lattice. Green spheres represent germanium atoms. Red spheres represent any possible adsorbed atom.

3. Results and discussion

In order to address the possible use of germanene as hydrogen storage, we calculated the adsorption energies of H_2 molecules on pristine germanene and metal-adsorbed germanene. The adsorption energies (E_A) are calculated for three schemes: adsorption of H_2 molecules on pristine germanene, adsorption of alkali metal atoms on germanene, and adsorption of H_2 molecules on metal-adsorbed germanene.

3.1. Adsorption of a H_2 molecule on pristine germanene

In this section, we discuss the geometry and the stability of adsorption of H_2 on pristine germanene. We have considered a number of different initial geometric configurations to study the interaction between pristine germanene and a hydrogen molecule: the H_2 molecule was located over the monolayer with its bond axis in parallel and perpendicular orientations with respect to the monolayer (hereon referred to as horizontal and vertical orientations, respectively), and also we considered four different initial positions over the honeycomb lattice: the Hollow site (H), at the center of an hexagon; the Bridge site (B), over a Ge—Ge bond; and the Top and Down sites, over adjacent Ge atoms [see Fig. 1(c)].

The adsorption energy of a H_2 molecule on pristine germanene is calculated from the optimized geometry of a hydrogen-adsorbed germanene supercell using the next equation:

$$E_A = E_H + E_{\text{Ger}} - E_{\text{H/Ger}} + \Delta_{\text{BSSE}}, \quad (1)$$

where E_H is the total energy of a hydrogen molecule, E_{Ger} is the total energy of pristine germanene and $E_{\text{H/Ger}}$ is the total energy of the hydrogen-adsorbed germanene. Δ_{BSSE} refers to the basis set superposition error correction. All models are calculated using same-sized supercells of germanene.

Table 1 shows the adsorption energy and the H_2 —germanene equilibrium distance for the four adsorption sites, and the two molecule orientations. The results show that the adsorption energy is the largest and the equilibrium distance is the shortest for a vertically oriented H_2 molecule at the H site of germanene, which means that this configuration is the most energetically stable of all modeled configurations. The calculated values of adsorption energy of H_2 on pristine germanene in the present work go from 0.18 to 0.2 eV. These energy values are bigger than previously reported values on graphene [51]. The small adsorption energy for single hydrogen adsorption is insufficient to be considered a chemical bond, and the molecule may be interacting with germanene through van der Waals forces. There are no chemically active sites on the germanene monolayer because all germanium atoms are bonded tetrahedrally. The repulsion between the electronic charge density of the molecule and the monolayer may be too strong to high the molecule to be more strongly adsorbed on the monolayer.

Table 1. Adsorption of a hydrogen molecule on pristine germanene. The adsorption sites are: top (T), down (D), hollow (H) and bridge (B). Adsorption energy of H_2 molecule (E_A), H_2 -germanene distance (β), and Voronoi charge excess on the molecule (Q_V).

Orientation	Site	E_A (eV)	β (Å)	$Q_V(e)$
Vertical	T	0.180	3.310	0.032
	D	0.188	3.975	0.029
	H	0.206	3.807	0.046
	B	0.187	3.657	0.034
Horizontal	T	0.180	3.325	0.032
	D	0.187	3.960	0.029
	H	0.193	3.707	0.050
	B	0.188	3.337	0.034

For a further exploration of the interaction between pristine germanene and H_2 molecules, we calculate charge density difference (CDD) plots in our models using the next expression:

$$\Delta\rho(\mathbf{r}) = \rho_{\text{H/Ger}}(\mathbf{r}) - \rho_{\text{Ge}}(\mathbf{r}) - \rho_{\text{H}}(\mathbf{r}), \quad (2)$$

where $\rho_{\text{H/Ger}}$ is the electronic charge density of the system as whole, and ρ_{H} and ρ_{Ge} are the electronic charge densities of isolated H and Ge atoms, respectively, located at the same positions as they are in the system as a whole. The CDD plots are shown in Fig. 2, the cyan region represents charge accumulation [positive values of $\Delta\rho(\mathbf{r})$], while the purple region represents charge reduction [negative values of $\Delta\rho(\mathbf{r})$], both in reference to the charge density of isolated atoms.

The amount of charge transfer between the H_2 molecule and germanene is obtained by Voronoi electronic population analysis. Magnitudes of this transfer for all systems are presented in Table 1. For all cases the H_2 molecule can be considered an electron donor, however, the magnitude of the transfer is too small in comparison to a true chemical bond.

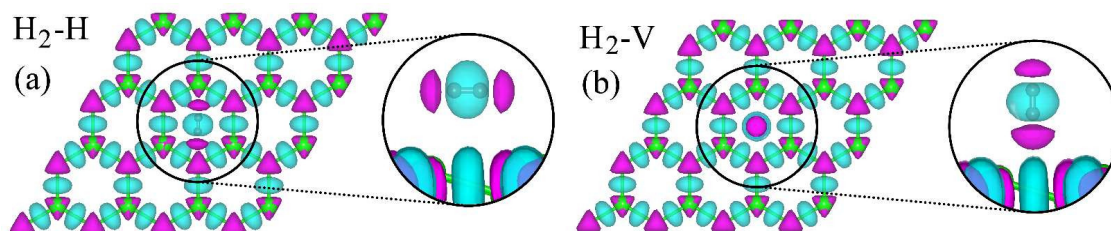


Figure 2. CDD plots for (a) horizontal and (b) vertical H_2 -adsorption on pristine germanene, in both systems on the H site. Cyan regions represent the charge accumulation, while purple regions represent the charge depletion.

The CDD for the most favorable site, in both molecule orientations, is shown on Fig. 2. The H_2 molecule is not dissociated by its interaction with germanene, and there is no accumulation of charge that suggests a strong chemical bond with germanene atoms. The molecule favors the H site, at the center of the hexagon of the honeycomb lattice, where electronic density is less concentrated, and the repulsion between electronic clouds is weaker. Two zones of charge reduction can be seen close to the hydrogen atoms, and in the vertically oriented case, the zone closer to the germanene monolayer is slightly bigger, which may suggest that some of the electronic density from the hydrogen atom was transferred to the monolayer. This may account for the relatively larger adsorption energy in this case.

3.2. Adsorption of alkali atoms on germanene

In this section, we investigate the adsorption of alkali metal atoms on germanene. We explore the possible sites for the adsorption of the metallic atoms in the same way we did for the hydrogen molecule. The metal atom is placed in each of the possible places—top (T), down (D), hollow (H) and bridge (B)—and the supercell is geometrically optimized. The binding energy, as well as metal-germanene distance, charge transfer and CDD plots are calculated.

The resulting characteristic bonding geometry of the metal atoms in germanene is shown in Fig. 3. Upon full geometry optimization all Li, Na and K atoms favor the H site of the germanene. The adsorption of the metal atoms does not yield any significant distortion or stress on the germanene lattice. For all cases, the down site is the next favorable site.

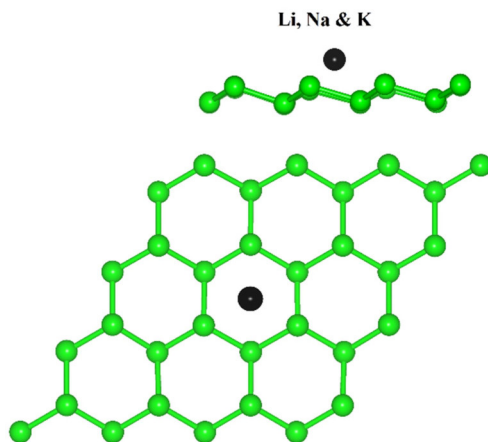


Figure 3. Side and top view for the most favorable adsorption geometry for metal atoms on germanene.

For all optimized metal-decorated germanene structures, we define the binding energy as:

$$E_B = E_{\text{alk}} + E_{\text{ger}} - E_{\text{alk/ger}} + \Delta_{\text{BSSE}}, \quad (3)$$

where, E_{alk} is the total energy of an isolated alkali metal atom, E_{ger} is the total energy of the pristine germanene supercell and $E_{\text{alk/ger}}$ is the total energy of the metal-decorated germanene supercell. Δ_{BSSE} refers to the basis set superposition error correction. All models are calculated using same-sized supercells. The results of binding energy, as well as metal-germanene distance and charge transfer, are listed in Table 2.

The results show that once again the H site is the most energetically favorable. The calculated values of binding energy of metal atoms in the present work go from 2.08 to 2.64 eV. These energies are stronger than reported results for graphene (silicene), i.e., 1.1(2.4) eV for Li, 0.5(1.9) eV for Na and 0.8(2.1) eV for K, respectively [52]. The magnitude of the binding energy is well in the chemisorption range, and the magnitude of the Voronoi population suggests that the metals lose much larger electronic density to the monolayer than the case of H_2 adsorption. These results point towards the creation of a chemical bond between the metals and the monolayer.

Table 2. Calculated values of adatom adsorption on germanene. The adsorption sites are: top (T), down (D), hollow (H) and bridge (B). Binding energy of metal atom on germanene (E_B), adatom-germanene distance (β), and Voronoi charge excess on the metal atom (Q_V).

Metal atom	Site	E_B (eV)	β (Å)	$Q_V(e)$
Li	T	2.64	2.69	0.273
	D	2.31	2.71	0.360
	H	2.64	2.83	0.273
	B	2.64	2.83	0.273
Na	T	2.30	2.98	0.411
	D	2.08	2.99	0.466
	H	2.30	3.16	0.410
	B	2.08	3.04	0.466
K	T	2.37	3.35	0.514
	D	2.23	3.41	0.551
	H	2.37	3.57	0.512
	B	2.37	3.57	0.513

The calculated binding energies per atom of alkali atoms adsorbed on germanene, the corresponding binding energies of alkali atoms adsorbed on silicene [25] and cohesive energies of the respective alkali atoms [53] are shown in Fig. 4. For all metals, the binding energy for germanene is greater than for silicene. The binding energies for germanene are typically ~ 1 eV over the experimental cohesive energy of the bulk metals. This suggests that a metal adatom favors adsorption on the H site rather than binding with other metal atoms. Therefore, metal atoms do not tend to clusterize on the germanene monolayer. Clusterization would cause reduction of the metal's capacity to adsorb H_2 molecules.

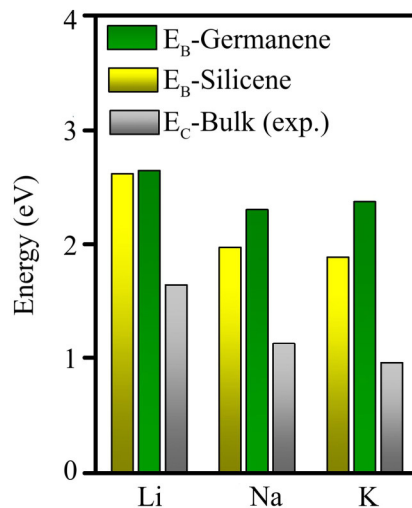


Figure 4. Calculated metal atom binding energies on germanene (E_B -Germanene), binding energies on silicene (E_B -Silicene), and corresponding experimental cohesive energies of the bulk metals (E_C -Bulk experimental).

The CDD plots corresponding to the adsorption of metals are calculated using Eq. (2), with the electronic charge density of an isolated metal atom instead of the density of a hydrogen atom. The CDD plots are shown in Fig. 5.

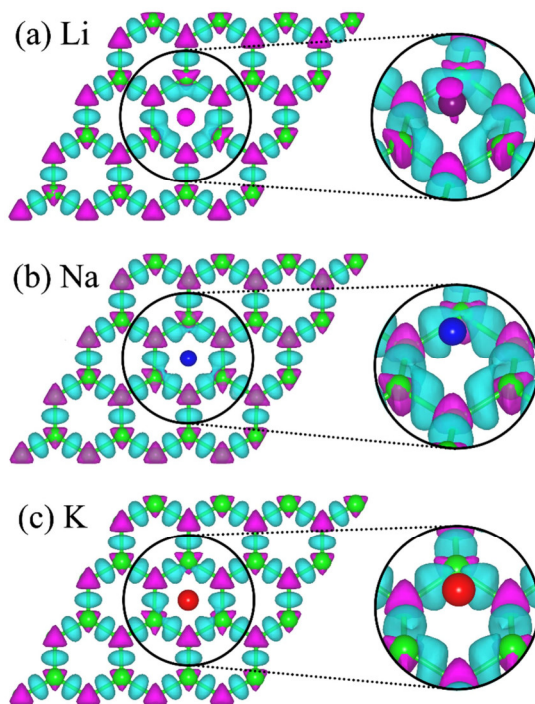


Figure 5. Charge density difference of (a) Li-, (b) Na- and (c) K-adsorption on pristine germanene, in the three systems on the hollow site.

There is an accumulation of electrons between two Ge first neighbors only in the hexagon where the metal is adsorbed. This accumulation may be electronic density that was transferred from the metal atom to the germanium lattice. As can be seen in the zoomed areas of Fig. 5, the accumulation on the Ge bonds diminishes from Li to K. There is a small surface of charge reduction around the Li. This suggests that Li transfers more electronic density to the monolayer, followed by Na and K. This tendency matches the calculated Voronoi charge on the metal (less charge on Li, more charge on K), the metal-germanene distance (increasing from Li to K) and the ability of the alkali metals to

lose electrons, as given by their ionization energies and electropositivity. This electronic density redistribution, more noticeable than on the case of H₂ adsorption, points towards a chemical bond between the germanene lattice and the metal adatom.

3.3. Adsorption of H₂ molecules on alkali metal decorated germanene

On the basis of the above investigation of alkali metal decorated germanene systems, in the following, we turn to the discussion on the adsorption of H₂ molecules on these systems. The adsorption of several hydrogen molecules is calculated using the next equation:

$$E_A = NE_H + E_{\text{alk/ger}} - E_{\text{H/alk/ger}} + \Delta_{\text{BSSE}}, \quad (3)$$

where E_H , $E_{\text{alk/ger}}$ and $E_{\text{H/alk/ger}}$ are the total energies of an isolated H₂ molecule, metal-decorated germanene and metal-decorated germanene after adsorbing an N number of molecules. Δ_{BSSE} refers to the basis set superposition error correction. Positive adsorption energies signify that H₂ molecules tend to be adsorbed by the metal-decorated germanene

In these models, an increasing number of H₂ molecules were placed around the metal atom, at a distance of ~ 1 Å and on a symmetric configuration, on the geometrically optimized metal-decorated germanene. The models with the H₂ molecules were then geometrically optimized again. Fig. 6 shows the optimized structures of metal-decorated germanene with the maximum number of H₂ molecules it can adsorb: Li can adsorb 3, while Na and K can adsorb up to 7 H₂ molecules. The results of adsorption energy per H molecule and its average distance from metal-decorated germanene are listed in Table 3.

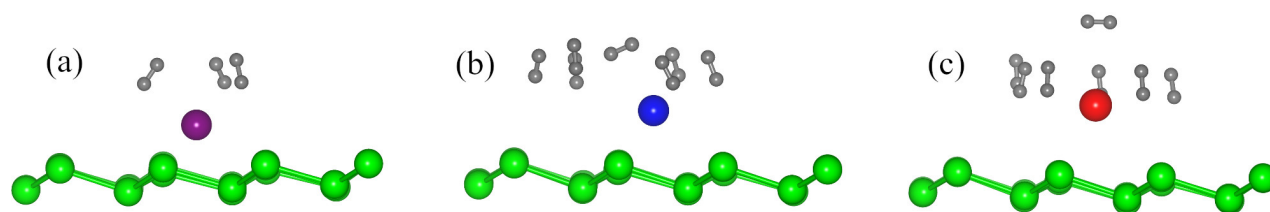


Figure 6. Optimized structures of Li-, Na-, and K-decorated germanene with the maximum number of H₂ molecules they can adsorb.

Table 3 shows the adsorption energy per H₂ molecule. If we compare the adsorption energy with and without metal atoms, it can be seen that only Li improves the adsorption strength. The magnitude of the adsorption energy of H₂ on pristine germanene has a value between the adsorption with Li and with Na. All values are still in the range of physisorption, which is favorable for hydrogen storage applications, as it means that the energy required for desorbing the molecules is not as much as the needed to dissociate H—metal chemical bonds. Note that the H—H bonds never break, their bond length is consistently 0.79 eV.

Table 3. Adsorption energy per H_2 molecule (E_A) on metal-decorated germanene, molecules-metal atom average distance (α), average Voronoi H_2 charge excess (Q_V), and average $H-H$ bond distance (β).

Atom	Number of H_2 molecules	E_A (eV)	α (Å)	Q_V (e)	β (Å)
Li	1	0.28	1.965	0.170	0.79
	2	0.23	2.017	0.105	0.79
	3	0.21	2.030	0.087	0.79
Na	1	0.18	2.335	0.176	0.79
	2	0.19	2.355	0.121	0.79
	3	0.19	2.358	0.104	0.79
	4	0.18	2.388	0.081	0.79
	5	0.16	2.511	0.065	0.79
	6	0.15	2.524	0.055	0.79
	7	0.14	2.940	0.051	0.79
K	1	0.13	2.700	0.195	0.79
	2	0.18	2.682	0.135	0.79
	3	0.18	2.688	0.116	0.79
	4	0.18	2.693	0.105	0.79
	5	0.18	2.690	0.088	0.79
	6	0.18	2.705	0.074	0.79
	7	0.16	3.032	0.066	0.79

In Fig. 7 the adsorption energies obtained in the present work are compared with theoretical data obtained in other works. The case with lithium, is compared with silicene (red) [25], SiC monolayer (black) [54], and Li-coated B_{80} buckyballs (magenta) [55]. Except for the case of one molecule, the values are very similar. The case with sodium is compared with silicene (red) [25], Na-coated B_{80} buckyballs (magenta) [55], and graphene (blue) [51]. The graphene has values considerably different to the other materials, but silicene and germanene are very similar, and adsorb the same number of molecules. Na-coated buckyballs have also similar values but can adsorb only one molecule. The case with potassium is compared with silicene (red) [25], K-coated B_{80} buckyballs (magenta) [55], and germanene (dark green) [24]. K-coated B_{80} buckyballs have very low values and can only adsorb one molecule. Silicene is again very close to our results. Values for K-decorated germanene are available in the literature, which are in very good agreement with ours, except for a constant difference in magnitude which can be attributed to the exchange-correlation functional used.

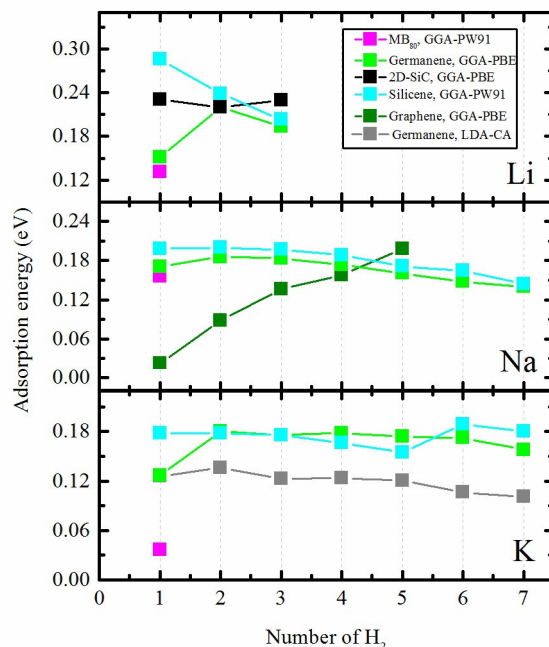


Figure 7. Adsorption energy per H_2 molecule for Li-, Na-, and K-adsorbed on germanene (light green), compared with other nanomaterials: silicene (GGA-PW91) (cyan), 2D-SiC (GGA-PBE) (black) sheet, MB_{60} (GGA-PW91) (magenta), graphene (GGA-PBE) (green), and germanene (LDA-CA) (gray).

Conclusions

In summary, we have investigated metal-decorated germanene as a hydrogen storage nanostructure using first-principles calculations. The results show that pristine germanene does not have high storage capacity to H_2 , as it can adsorb only one hydrogen molecule per site. Adsorption energies of hydrogen on pristine and metal-decorated germanene are comparable, but Li-decorated germanene can store up to 3 molecules, while the Na and K cases can store up to 7 molecules.

It was also found that the binding energy of the metal adatoms to the hollow site on the germanene monolayer is too strong to allow the clustering of the metal adatoms, as has been predicted on graphene or other carbon-based nanostructures as a hydrogen storage material. The values of adsorption energy and capacity are very close to the reported results for silicene monolayers. The results of binding of alkali atoms on some sites on germanene may be significant in the exploration of potential applications of germanene not only in hydrogen-related technologies, but also in electrodes for alkali-ion batteries.

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References

- [1] Schlapbach L, Züttel A. Hydrogen-storage materials for mobile applications. *Nature*. 2001 Nov 15;414:353.
- [2] Gaudernack B, Lynam S. Hydrogen from natural gas without release of CO_2 to the atmosphere. *Int J Hydrogen Energy*. 1998;23(12):1087–93.

- [3] Garland NL, Papageorgopoulos DC, Stanford JM. Hydrogen and Fuel Cell Technology: Progress, Challenges, and Future Directions. *Energy Procedia* . 2012;28:2–11.
- [4] Zhou L. Progress and problems in hydrogen storage methods. *Renew Sustain Energy Rev*. 2005;9(4):395–408.
- [5] Ding F, Jakobson BI. Challenges in hydrogen adsorptions: from physisorption to chemisorption. *Front Phys*. 2011;6(2):142–50.
- [6] B. Arboleda N, Nobuhara K, Kasai H, A. Diño W, Nakanishi H. First Principles Studies for the Interaction of Hydrogen with a Li(100) Surface. *J Phys Soc Japan*. 2005;74(1):478–82.
- [7] Kobayashi H, Yoshida S, Kato H, Fukui K, Tarama K. Theoretical studies of hydrogen molecule adsorption on flat and stepped platinum surfaces. *Surf Sci* . 1979;79(1):189–204.
- [8] Granja A, Alonso JA, Cabria I, López MJ. Competition between molecular and dissociative adsorption of hydrogen on palladium clusters deposited on defective graphene. *RSC Adv* . 2015;5(59):47945–53.
- [9] Dürr M, Höfer U. Dissociative adsorption of molecular hydrogen on silicon surfaces. *Surf Sci Rep*. 2006;61(12):465–526.
- [10] Henry DJ, Yarovsky I. Dissociative Adsorption of Hydrogen Molecule on Aluminum Clusters: Effect of Charge and Doping. *J Phys Chem A* . 2009;113(11):2565–71.
- [11] Novoselov KS, Geim AK, Morozov S V, Jiang D, Zhang Y, Dubonos S V, et al. Electric Field Effect in Atomically Thin Carbon Films. *Science*. 2004;306(5696):666 LP-669.
- [12] Gallouze M, Kellou A, Drir M. Electronic and magnetic properties of adsorbed H₂ on graphene with atomic defects: Ab initio study. *Phys E Low-dimensional Syst Nanostructures*. 2013;52:127–35.
- [13] Lee CH, Chen SC, Su WS, Chen RB, Lin MF. Tuning the electronic properties of monolayer graphene by the periodic aligned graphene nanoribbons. *Synth Met*. 2011;161(5):489–95.
- [14] Enriquez JIG, Villagrancia ARC. Hydrogen adsorption on pristine, defected, and 3d-block transition metal-doped penta-graphene. *Int J Hydrogen Energy*. 2016;41(28):12157–66.
- [15] Geim AK, Novoselov KS. The rise of graphene. *Nat Mater*. 2007;6:183.
- [16] Castro Neto AH, Guinea F, Peres NMR, Novoselov KS, Geim AK. The electronic properties of graphene. *Rev Mod Phys*. 2009;81(1):109–62.
- [17] Cho JH, Yang SJ, Lee K, Park CR. Si-doping effect on the enhanced hydrogen storage of single walled carbon nanotubes and graphene. *Int J Hydrogen Energy*. 2011;36(19):12286–95.
- [18] Denis PA, Huelmo CP, Iribarne F. Theoretical characterization of sulfur and nitrogen dual-doped graphene. *Comput Theor Chem*. 2014;1049:13–9.
- [19] Sun Q, Wang Q, Jena P, Kawazoe Y. Clustering of Ti on a C₆₀ Surface and Its Effect on Hydrogen Storage. *J Am Chem Soc*. 2005;127(42):14582–3.
- [20] Faye O, Eduok U, Szpunar J, Szpunar B, Samoura A, Beye A. Hydrogen storage on bare Cu atom and Cu-functionalized boron-doped graphene: A first principles study. *Int J Hydrogen Energy*. 2017;42(7):4233–43.
- [21] Cahangirov S, Topsakal M, Aktürk E, Şahin H, Ciraci S. Two- and One-Dimensional Honeycomb Structures of Silicon and Germanium. *Phys Rev Lett*. 2009;102(23):236804.
- [22] Houssa M, Scalise E, Sankaran K, Pourtois G, Afanas'ev V V, Stesmans A. Electronic properties of hydrogenated silicene and germanene. *Appl Phys Lett* 2011 May 30;98(22):223107.
- [23] Li F, Zhang C, Luan H, Wang P. First-principles study of hydrogen storage on Li-decorated silicene. *J Nanoparticle Res*. 2013;15(10):1972.
- [24] Rojas KIM, Villagrancia ARC, Moreno JL, David M, Arboleda NB. Ca and K decorated germanene as hydrogen storage: An ab initio study. *Int J Hydrogen Energy*.

2018;43(9):4393–400.

- [25] Wang Y, Zheng R, Gao H, Zhang J, Xu B, Sun Q, et al. Metal adatoms-decorated silicene as hydrogen storage media. *Int J Hydrogen Energy*. 2014;39(26):14027–32.
- [26] Lay MED and LX and SC and AR and G Le. Germanene: a novel two-dimensional germanium allotrope akin to graphene and silicene. *New J Phys*. 2014;16(9):95002.
- [27] Li L, Lu SZ, Pan J, Qin Z, Wang YQ, Wang Y, et al. Buckled germanene formation on Pt(111). *Adv Mater*. 2014;26(28):4820–4.
- [28] Bampoulis P, Zhang L, Safaei A, Van Gastel R, Poelsema B, Zandvliet HJW. Germanene termination of Ge₂Pt crystals on Ge(110). *J Phys Condens Matter*. 2014;26(44).
- [29] D'Acapito F, Torrenco S, Xenogiannopoulou E, Tsipas P, Marquez Velasco J, Tsoutsou D, et al. Evidence for Germanene growth on epitaxial hexagonal (h)-AlN on Ag(1 1 1). *J Phys Condens Matter*. 2016;28(4).
- [30] Derivaz M, Dentel D, Stephan R, Hanf M-C, Mehdaoui A, Sonnet P, et al. Continuous Germanene Layer on Al(111). *Nano Lett*. 2015;15(4):2510–6.
- [31] Bianco E, Butler S, Jiang S, Restrepo OD, Windl W, Goldberger JE. Stability and Exfoliation of Germanene: A Germanium Graphene Analogue. *ACS Nano*. 2013;7(5):4414–21.
- [32] van den Broek B, Houssa M, Scalise E, Pourtois G, Afanas'ev V V, Stesmans A. First-principles electronic functionalization of silicene and germanene by adatom chemisorption. *Appl Surf Sci*. 2014;291:104–8.
- [33] Ye M, Quhe R, Zheng J, Ni Z, Wang Y, Yuan Y, et al. Tunable band gap in germanene by surface adsorption. *Phys E Low-dimensional Syst Nanostructures*. 2014;59:60–5.
- [34] Pang Q, Zhang C, Li L, Fu Z, Wei X, Song Y. Adsorption of alkali metal atoms on germanene: A first-principles study. *Appl Surf Sci*. 2014;314:15–20.
- [35] Zhang X, Tang C, Jiang Q. Electric field induced enhancement of hydrogen storage capacity for Li atom decorated graphene with Stone-Wales defects. *Int J Hydrogen Energy*. 2016;41(25):10776–85.
- [36] Hussain T, Pathak B, Adit Maark T, Moyses Araujo C, Scheicher RH, Ahuja R. Ab initio study of lithium-doped graphane for hydrogen storage. *EPL*. 2011;96(2):27013.
- [37] Hohenberg P, Kohn W. Inhomogeneous Electron Gas. *Phys Rev*. 1964;136(3B):B864–71.
- [38] Kohn W, Sham LJ. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys Rev*. 1965;140(4A):A1133–8.
- [39] Sánchez-Portal JMS and EA and JDG and AG and JJ and PO and D. The SIESTA method for ab initio order- N materials simulation. *J Phys Condens Matter*. 2002;14(11):2745.
- [40] Perdew JP, Burke K, Ernzerhof M. Generalized Gradient Approximation Made Simple. *Phys Rev Lett*. 1996 (18):3865–8.
- [41] Artacho E, Sánchez-Portal D, Ordejón P, García A, Soler JM. Linear-Scaling ab-initio Calculations for Large and Complex Systems. *Phys status solidi*. 1999;215(1):809–17.
- [42] Junquera J, Paz Ó, Sánchez-Portal D, Artacho E. Numerical atomic orbitals for linear-scaling calculations. *Phys Rev B*. 2001;64(23):235111.
- [43] Troullier N, Martins JL. Efficient pseudopotentials for plane-wave calculations. *Phys Rev B*. 1991 ;43(3):1993–2006.
- [44] Kleinman L, Bylander DM. Efficacious Form for Model Pseudopotentials. *Phys Rev Lett*. 1982;48(20):1425–8.
- [45] Grimme S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J Comput Chem*. 2006;27(15):1787–99.
- [46] Monkhorst HJ, Pack JD. Special points for Brillouin-zone integrations. *Phys Rev B [Internet]*. 1976;13(12):5188–92.

- [47] Gupta SK, Singh D, Rajput K, Sonvane Y. Germanene: a new electronic gas sensing material. *RSC Adv.* 2016;6(104):102264–71.
- [48] Hussain T, Kaewmaraya T, Chakraborty S, Vovusha H, Amornkitbamrung V, Ahuja R. Defected and Functionalized Germanene-based Nanosensors under Sulfur Comprising Gas Exposure. *ACS Sensors.* 2018;3(4):867–74.
- [49] Fonseca Guerra C, Handgraaf J-W, Baerends EJ, Bickelhaupt FM. Voronoi deformation density (VDD) charges: Assessment of the Mulliken, Bader, Hirshfeld, Weinhold, and VDD methods for charge analysis. *J Comput Chem.* 2004;25(2):189–210.
- [50] Boys SF, Bernardi F. The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors. *Mol Phys.* 1970;19(4):553–66.
- [51] Pantha N, Belbase K, Adhikari NP. First-principles study of the interaction of hydrogen molecular on Na-adsorbed graphene. *Appl Nanosci.* 2015;5(4):393–402.
- [52] Sahin H, Peeters FM. Adsorption of alkali, alkaline-earth, and 3d transition metal atoms on silicene. *Phys Rev B.* 2013;87(8):85423.
- [53] Kittel C. *Introduction to Solid State Physics.* Wiley; 2004.
- [54] Song N, Wang Y, Zheng Y, Zhang J, Xu B, Sun Q, et al. New template for Li and Ca decoration and hydrogen adsorption on graphene-like SiC: A first-principles study. *Comput Mater Sci.* 2015;99:150–5.
- [55] Wu G, Wang J, Zhang X, Zhu L. Hydrogen Storage on Metal-Coated B80 Buckyballs with Density Functional Theory. *J Phys Chem C.* 2009;113(17):7052–7.