Hydrogen Storage Mechanism in Sodium-Based Graphene Nanoflakes: A Density Functional Theory Study

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Abstract: Carbon materials, such as graphene nanoflakes, carbon nanotubes, and fullerene, can be widely used to store hydrogen, and doping these materials with lithium (Li) generally increases their H₂-storage densities. Unfortunately, Li is expensive; therefore, alternative metals are required to realize a hydrogen-based society. Sodium (Na) is an inexpensive element with chemical properties that are similar to those of lithium. In this study, we used density functional theory to systematically investigate how hydrogen molecules interact with Na-doped graphene nanoflakes. A graphene nanoflake (GR) was modeled by a large polycyclic aromatic hydrocarbon composed of 37 benzene rings, with GR-Na-(H₂)n and GR-Na⁺-(H₂)n (n = 0–12) clusters used as hydrogen storage systems. Data obtained for the Na system were compared with those of the Li system. The single-H₂ GR-Li and GR-Na systems (n = 1) exhibited binding energies (per H₂ molecule) of 3.83 and 2.72 kcal/mol, respectively, revealing that the Li system has a high hydrogen-storage ability. This relationship is reversed from n = 4 onwards; the Na systems exhibited larger or similar binding energies for n = 4–12 than the Li systems. The present study strongly suggests that Na can be used as an alternative metal to Li in H₂-storage applications. The H₂-storage mechanism in the Na system is also discussed based on the calculated results.

Keywords: DFT; binding energy; electronic states; coordination number

1. Introduction

Measures that counter climate change are of considerable international urgency [1–5]. Decarbonization is an effective method for reducing greenhouse gas emissions and achieving carbon neutrality [6–10]. In particular, the use of hydrogen energy is the key to carbonized fuel [11,12].

The establishment of appropriate transportation methods is an important factor when socially implementing hydrogen energy [13,14]. Carbon materials can safely store hydrogen [15,16]; in particular, lithium (Li)-doped graphene and carbon nanotubes (CNTs) have been used as effective storage materials [17,18]. Unfortunately, lithium is expensive because it is generally shipped from various international locations to China for processing into various products; therefore, alternative metals are required to realize a hydrogen-based society. In this regard, sodium (Na) is an inexpensive metal with chemical properties similar to those of Li.

Interactions between sodium with carbon materials have been investigated both theoretically and experimentally. Moon et al. used density functional theory (DFT) calculations to investigate the adsorption of Na by graphene and graphene oxide, which are used as anode materials in sodium-ion batteries [19]. The adsorption energy for Na on graphene was found to be −0.507 eV at hollow sites, which is indicative of favorable adsorption, while Na atoms were found to separately adsorb at the epoxide and hydroxyl functional areas.
groups of graphene oxide; indeed, Na is more strongly adsorbed at the epoxide sites of graphene oxide (adsorption energy: $-1.024$ eV) than on pristine graphene.

Zhu and Lu used DFT calculations to investigate the adsorptions of Li, Na, and K on graphene surfaces [20]; all three metal atoms were found to preferentially adsorb at hexagonal graphene sites, with Na more weakly bound than Li or K because the singly occupied molecular orbital (SOMO) of the Na atom lies exactly halfway in energy between the HOMO and the LUMO of the graphite layer.

Dimakis et al. investigated the multiple adsorption of Na onto a graphene surface using DFT calculations [21], which revealed that multiply adsorbed Na atoms are not stable on graphene at high coverages; however, the presence of defects on the graphene support was found to stabilize the adsorbed Na. Higher Na coverage results in metal nucleation that weakens adsorption. Consequently, alkali-metal-doped graphene nanoflakes have been extensively investigated.

H$_2$ adsorption onto Na-decorated materials has also been investigated. Kassaoui et al. used DFT calculations to investigate the adsorption of H$_2$ on Na-decorated tetragonal silicon carbide (t-SiC) [22] and found that Na-decoration enhances the hydrogen-storage properties of t-SiC.

Previously, we investigated the mechanism of hydrogen storage in a graphene nanoflake (GR) doped by a lithium atom or lithium ion (i.e., the GR-M-(H$_2$)$_n$ system, where M = Li or Li$^+$, and $n = 0$–10) by DFT [23]. The binding energies of H$_2$ to GR were calculated to be 3.83 kcal/mol (GR-Li) and 4.13 kcal/mol (GR-Li$^+$), which suggests that the GR-Li system can be used to store H$_2$. We showed that electron transfer from Li to graphene plays an important role in the adsorption of H$_2$. In addition, we demonstrated that the graphene–lithium system can effectively store molecular H$_2$. Analogously, the magnesium-based GR-Mg-H$_2$ system has reportedly been used in a reversible hydrogen-storage device [24].

In order to determine the hydrogen storage ability of GR-Na as an alternative metal-containing system, we used the DFT method in the present study to investigate interactions between molecular hydrogen and Na-doped graphene nanoflakes (GR-Na-(H$_2$)$_n$; $n = 1$–12). Elucidating the storage mechanisms of inexpensive metals is important for future hydrogen-transport applications; hence, we examined in detail whether or not sodium can be used as an alternative to lithium for this purpose.

2. Computational Methods

A graphene nanoflake composed of 37 benzene rings was used in this study and is referred to as “GR” hereafter. DFT calculations were performed using the CAM-B3LYP Coulomb-attenuating exchange-correlation energy functional [25] with the 6-311G(d,p) basis set [26], which is expressed as “CAM-B3LYP/6-311G(d,p)”. The structure of GR was first optimized, after which a sodium atom or ion was placed in the central region of the GR. The structures of GR-Na and GR-Na$^+$ were then fully optimized. The binding energy of the Na atom to GR is defined as follows:

$$-E_{\text{bind}} = E(\text{GR} - \text{Na}) - [E(\text{Na}) + E(\text{GR})] \quad (1)$$

where $E(X)$ is the total energy of X. The Na atom binds exothermally to the GR when $E_{\text{bind}}$(Na) is positive.

A total of 1–12 hydrogen molecules ($n = 1$–12) were added to GR-Na$^+$ or GR-Na to form the GR-Na-(H$_2$)$_n$ systems, with all atoms fully optimized without symmetry restriction. The binding energy of the $n$H$_2$ molecules to GR-Na was calculated as follows:

$$-E_{\text{bind}}(n, H_2) = [E(\text{GR} - \text{Na} - (H_2)_n) + nE(H_2) - E(\text{GR} - \text{Na})]/n \quad (2)$$

The addition of molecular hydrogen to GR-Li proceeds, and the H$_2 + \text{GR-Na} \rightarrow \text{H}_2\text{-GR-Na}$ addition reaction is exothermic when $E_{\text{bind}}$(H$_2$) is positive.

Atomic charges were calculated using the natural bond population analysis (NPA) algorithm [27]. All calculations were performed using the Gaussian 09 software package [28].
Additional calculations were carried out at the same level of theory for the lithium system. We previously investigated interactions between graphene and various molecules using DFT at the same level of theory [29–33]. A similar technique was used for the GR-Na-(H$_2$)$_n$ system in this study.

3. Results and Discussion

3.1. Structures of Na Doped-Graphene Nanoflakes

The optimized structures of GR-Na and GR-Na$^+$ are shown in Figure 1 and Figure S1 (see Supplementary Material, SI), respectively. Both Na and Na$^+$ are bound to hexagonal sites on the GR surface. The Na-surface distance, Na-GR binding energy, and NPA-determined atomic charge of Na are listed in Table 1 together with those of Na$^+$, Li, and Li$^+$. The distances between Na, Na$^+$, and the GR surface were calculated to be 2.247 and 2.288 Å, respectively; Na is slightly closer to the surface than Na$^+$. The binding mechanism is discussed in Section 3.3. The binding energies of Na and Na$^+$ were calculated to be 4.4 and 37.5 kcal/mol, respectively, which indicates that Na$^+$ is bound about nine times more strongly than Na.

![Figure 1. CAM-B3LYP/6-311G(d,p)—optimized structure of GR-Na (atom) with a GR composed of 37 benzene rings.](image)

Table 1. M-GR and M$^+$-GR binding energies ($E_{\text{bind}}$ in kcal/mol, M = Li, Na), M-GR-surface distances ($h$ in Å), and NPA-determined atomic charges for M on GR, calculated at the CAM-B3LYP/6-311G(d,p) level.

|       | $E_{\text{bind}}$ | Height ($h$) | NPA     |
|-------|------------------|--------------|---------|
| GR-Na | 4.4              | 2.247        | +0.978  |
| GR-Na$^+$ | 37.5           | 2.288        | +0.979  |
| GR-Li | 17.1             | 1.736        | +0.929  |
| GR-Li$^+$ | 52.8           | 1.771        | +0.937  |

The NPA-determined atomic charges on Na and Na$^+$ are +0.978 and +0.979, respectively; clearly, the net charge of Na is very similar to that of Na$^+$, which suggests that significant Na-to-GR electron transfer occurs during binding (0.98e). These features are in good agreement with the GR-Li and GR-Li$^+$ systems, as summarized in Table 1, where the NPA-determined atomic charges on Li and Li$^+$ are +0.929 and +0.937, respectively.
3.2. Structures of Molecular Hydrogen Bound to GR-Na

The geometries of the GR-Na-(H$_2$)$_n$ systems ($n = 1$–12) were fully optimized at the CAM-B3LYP/6-311G(d,p) level. Figure 2 shows the structures of H$_2$ bound to GR-Na ($n = 1$–6). H$_2$ is bound to Na with a side-on structure when $n = 1$, in which the two hydrogen atoms of H$_2$ are equivalently connected to Na (distances are almost identical: $R_1 = 2.445$, $R_1' = 2.415$ Å). The GR(X)-Na-H$_2$ (center-of-mass) angle is 113.2°, which indicates that the bond structure is bent. The distance ($b$) between Na and GR is 2.262 Å, which is slightly elongated from that observed for GR-Na devoid of H$_2$ ($b = 2.247$ Å; $n = 0$). The second H$_2$ molecule, (H$_2$)$_2$ is bound to Na with a similar side-on arrangement when $n = 2$, (H$_2$)$_1$ and (H$_2$)$_2$ are bound in a similar to each other. The third and fourth H$_2$ molecules are similarly bound to Na when $n = 3$ and 4. The average H$_2$-Na distances were calculated to be 2.262, 2.436, 2.456, and 2.502 Å for $n = 1$–4, respectively, which indicates that the distance increases slightly with increasing number of H$_2$ molecules ($n$). The fifth H$_2$ molecule, (H$_2$)$_5$, binds to Na in a manner orthogonal to the surface (vertical in Figure 2) when $n = 5$, with a distance of 2.833 Å, which is longer than those of (H$_2$)$_1$–4; clearly, the first coordination shell is saturated at $n = 4$. The sixth H$_2$ molecule interacts with a H$_2$ molecule in the first coordination shell and is not directly bound to Na (the distances between the sixth H$_2$ molecule and Na and the nearest H$_2$ molecule are 5.037 and 3.625 Å, respectively. Larger clusters ($n = 7$–12) were also optimized, the results of which are shown in Figure S2. Side-on coordination structures were observed in all cases.

![Figure 2. CAM-B3LYP/6-311G(d,p)-optimized structures of GR-Na (atom)-(H$_2$)$_n$ ($n = 1$–6).](image-url)
To understand these binding structures in more detail, the distances between the hydrogen atoms in H$_2$ and the Na atom, R(Na-H) are plotted as functions of the number of H$_2$ molecules (n) (Figure 3). The R(Na-H) distance is 2.445 Å (1st shell) when n = 1, and all hydrogen atoms are located at similar distances from Na up to n = 4, although the distance increased slightly with increasing n (2.415 Å for n = 1; 2.482 Å for n = 4). In contrast, the fifth H$_2$ (n = 5) is much further away from Na (2.833 Å) (2nd shell) compared to the others (n = 1–4; 2.45 Å), indicating that the first coordination shell is saturated by four hydrogen molecules (n = 4). The fifth H$_2$ binds to Na in an orthogonal direction and is located in a pocket composed of the other four H$_2$ molecules ((H$_2$)1–4). The second coordination shell is saturated at n = 5; hence, the sixth hydrogen molecule, (H$_2$)6, binds to GR-Na-(H$_2$)$_5$ as a ligand in the third coordination shell. The distances associated with n = 6–12 clearly reveal that the second coordination shell consists of only one H$_2$ molecule, (H$_2$)$_5$ and is saturated at n = 5, with the third coordination shell beginning at n = 6.

![Figure 3](image-url). CAM-B3LYP/6-311G(d,p)-calculated M-H interatomic distances in GR-M-(H$_2$)$_n$ (n = 1–12, M = Li, Li$^+$, Na, and Na$^+$) as functions of the number of H$_2$ molecules (n).

The analogous distances in GR-Li$^+$-(H$_2$)$_n$ (n = 1–12) are shown in Figure 3. The H$_2$ coordination structures in GR-Li-H$_2$ are different to those in GR-Na-H$_2$; when n = 4, the Na-H$_2$ distance results in a large binding energy for GR-Na-H$_2$.

3.3. Electronic States

The NPA-determined charges on Na, GR, and H$_2$ (summation of molecular charges over all H$_2$ molecules) are plotted in Figure 4 as functions of n. The Na and GR charges were calculated to be +0.978 and −0.978, respectively, when n = 0 (without any H$_2$ molecule), which indicates that the unpaired electron of Na is fully transferred to GR, and that the electronic state can be expressed as (Na)$^{+0.98}$-(GR)$^{-0.98}$. The charges on Na were determined by NPA to be 0.953, 0.834, 0.707, and 0.707 for n = 1, 3, 5, and 6, respectively, which indicates that the charge decreases linearly to n = 5 and is then saturated. In contrast, the (H$_2$)$_n$ charge was observed to increase to n = 5 and saturate. The electrons of H$_2$ are gradually transferred into Na when H$_2$ is added to GR-Na in a stepwise manner (to n = 5). A similar electron-transfer trend was observed for GR-Li to n = 3. The first coordination shells of Na
and Li contain four and three $\text{H}_2$ molecules, respectively, and electron transfer from $\text{H}_2$ to Na (or Li) occurs only in the first coordination shell.

![Figure 4](image)

**Figure 4.** NPA-determined atomic charges of Li, Na, and GR as functions of $n$. Summed $\text{H}_2$ charges are also plotted. Calculations were performed at the CAM-B3LYP/6-311G(d,p) level.

Distance ($h$) between Na and the GR surface are plotted in Figure 5 as functions of $n$; $h$ was observed to increase with increasing $n$ for both Na and Na$^+$ to the second shell ($n = 5$) and became saturated at 2.35 Å (Na) and 2.42 Å (Na$^+$). For lithium, the saturated distances were determined to be 1.85 Å (Li) and 1.89 Å (Li$^+$) (from $n = 5$).

![Figure 5](image)

**Figure 5.** Distances between M and the GR surface (in Å) as functions of $n$ (M = Li, Li$^+$, Na, and Na$^+$).

The Na and Li atoms are always closer to the surface than their corresponding ions (Na$^+$ and Li$^+$). Electrons are transferred from M to GR to form separate M(+1.0)-GR(−1.0) electronic states in the GR-M (atom) systems. Significant attractive interactions (positive-negative) operate in these GR-M systems that result in shorter M($h$) distances.
3.4. \( \text{H}_2 \) Binding Energies to GR-Na

The binding energy of \( \text{H}_2 \) to GR-Na (per \( \text{H}_2 \) molecule) is plotted in Figure 6 as a function of \( n \). The binding energy associated with the addition of the first \( \text{H}_2 \) molecule to GR-Na was calculated to be 2.72 kcal/mol (\( n = 1 \)), which gradually decreased with increasing \( n \); binding energies of 2.67, 2.50, 2.34, and 2.01 kcal/mol were calculated for \( n = 2 \)–5, respectively. On the other hand, binding energies of 3.83, 3.29, 2.85, 2.20, and 1.83 kcal/mol were calculated for Li (\( n = 1 \)–5, respectively), which reveals that GR-Li interacts more strongly with \( \text{H}_2 \) than GR-Na for \( n = 1 \)–3, while the interactions are comparable for both Li and Na at \( n = 4 \). GR-Na interacts slightly more strongly with \( \text{H}_2 \) in the larger systems (\( n = 5 \)–12). Thus, GR-Na appears to have a higher \( \text{H}_2 \)-storage ability than GR-Li.

![Figure 6. CAM-B3LYP/6-311G(d,p)-calculated \( \text{H}_2 \)-GR-M binding energies (per \( \text{H}_2 \) molecule) plotted as functions of \( n \) (M = Li, Li\(^+\), Na, and Na\(^+\)).](image)

The abovementioned trends strongly suggest that GR-Na can be used as an \( \text{H}_2 \)-storage material; this system can store \( \text{H}_2 \) up to the second coordination shell (\( n = 12 \)) when a threshold binding energy of 1.0 kcal/mol is assumed. The GR-Na\(^+\)-(\( \text{H}_2 \))\(_n\) system exhibited similar features. Since the Na-(\( \text{H}_2 \))\(_n\) binding energy is close to zero in the absence of GR, GR clearly enhances binding through electron transfer from Na to GR: GR + Na \( \rightarrow \) (GR)\(^-\)-Na\(^+\).

\( \text{H}_2 \)-GR-Na\(^+\) and \( \text{H}_2 \)-GR-Li\(^+\) binding energies are compared in Figure 6. The binding energy of the first addition of \( \text{H}_2 \) to GR-Li was calculated to be 2.99 kcal/mol (\( n = 1 \)), and gradually decreased with increasing \( n \), with values of 2.58, 2.12, and 1.60 kcal/mol determined for \( n = 3, 5, \) and 7, respectively, for the GR-Na\(^+\)-\( \text{H}_2 \) system, and 2.58, 2.12, and 1.00 kcal/mol for the GR-Li\(^+\)-\( \text{H}_2 \) system, respectively.

These results suggest that GR-Na is a suitable candidate for the efficient storage of hydrogen gas for various applications. The effectivity in GR-Na is originated from the number of first coordination shell of \( \text{H}_2 \); the first coordination shell in GR-Na is saturated by \( n = 4 \), which is larger than GR-Li (\( n = 3 \)). Hence, GR-Na binds strongly to \( \text{H}_2 \) as average.

3.5. Effect of the Functional on Binding Energy

The effect of the DFT functional on the binding energy is examined in this section, with the PW91PW91 functional [34] used for the GR-Na, GR-Na\(^+\), GR-Li, and GR-Li\(^+\) systems. The binding energies of \( \text{H}_2 \) to these systems are plotted as functions of \( n \), the results of which are shown in Figure 7. \( \text{H}_2 \) is bound more strongly to the GR-Li and GR-Li\(^+\) systems than the Na systems in the \( n = 1 \)–4 range using the PW91PW91 functional, whereas the opposite trend was observed for \( n = 5 \). These features are in excellent agreement with those
observed using the CAM-B3LYP functional, suggesting that the present system shows only minor functional dependence.

![Figure 7](image-url)

**Figure 7.** Functional dependency of the $\text{H}_2$-GR-Li$^+$ (Na$^+$) binding energy (per $\text{H}_2$ molecule). Calculations were performed at the PW91PW91/6-311G(d,p) level.

The present calculations were performed using GR composed of 37 benzene rings throughout. The binding energies were calculated using a smaller sized graphene composed of 19 benzene rings to check the size dependency. As clearly seen in Figure S3, the size dependency on the binding energy of $\text{H}_2$ to GR-Na is negligibly small. Also, in order to elucidate the effects of van der Waals term on the binding energy, the wB97XD functional [35] was applied to GR-Na-H$_2$ system. The result was given in Figure S4. The tendency of binding energy was in excellent agreement with those observed using the CAM-B3LYP functional.

### 4. Conclusions

The abilities of sodium atoms and ions to store hydrogen were examined using DFT calculations in this study, with GR-Na and GR-Na$^+$ (GR-M-(H$_2$)$_n$; M = Na and Na$^+$, $n = 1$–12) exhibiting similar $\text{H}_2$-binding energies. The binding energies for the $n = 1$ Li- and Na-systems were calculated to be 3.83 and 2.72 kcal/mol, respectively, which indicates that the Li-system is more capable of storing hydrogen at lower coverages ($n = 1$–3). However, the opposite relationship was observed at $n = 4$; $E_{\text{bind}} = 2.20$ kcal/mol (Li) and 2.34 kcal/mol (Na), suggesting that the Na system binds $\text{H}_2$ slightly more strongly than the Li system. $E_{\text{bind}}$ values of 1.43 kcal/mol (Li) and 1.53 kcal/mol (Na) were obtained at $n = 7$. These results strongly suggest that GR-Na is a suitable candidate for the efficient storage of hydrogen gas for various applications in the hydrogen economy, and that sodium is an alternative to lithium for that purpose.

**Supplementary Materials:** The following supporting information can be downloaded at: [https://www.mdpi.com/article/10.3390/hydrogen3010003/s1](https://www.mdpi.com/article/10.3390/hydrogen3010003/s1). The optimized structures of GR-Na$^+$ (ion), GR-Na (atom)-(H$_2$)$_n$ ($n = 7$–12), GR-Na$^+$ (ion)-(H$_2$)$_n$ ($n = 1$–12), and size and functional dependency of binding energy are provided in the SI.
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