Molecular Design of a Reversible Hydrogen Storage Device Composed of the Graphene Nanoflake–Magnesium–H₂ System

Hiroto Tachikawa,* Yoshiki Izumi, Tetsuji Iyama, and Kazuhisa Azumi

ABSTRACT: Carbon materials such as graphene nanoflakes (GRs), carbon nanotubes, and fullerene can be widely used for hydrogen storage. In general, metal doping of these materials leads to an increase in their H₂ storage density. In the present study, the binding energies of H₂ to Mg species on GRs, GR–Mg⁺ⁿ⁺ (n = 0–2), were calculated using density functional theory calculations. Mg has a wide range of atomic charges. In the case of GR–Mg (m = 0, Mg atom), the binding energy of one H₂ molecule is close to 0, whereas those for m = 1 (Mg⁺) and 2 (Mg⁺⁺) are 0.23 and 13.2 kcal/mol (n = 1), respectively. These features suggest that GR–Mg⁺⁺ has a strong binding affinity toward H₂, whereas GR–Mg⁺ has a weak binding energy. In addition, it was found that the first coordination shell is saturated by four H₂ molecules, GR–Mg⁺⁺–(H₂)₄ (n = 4). Next, direct ab initio molecular dynamics calculations were carried out for the electron-capture process of GR–Mg⁺⁺–(H₂)₄ and a hole-capture process of GR–Mg⁺⁺–(H₂)₄ (n = 4). After electron capture, the H₂ molecules left and dissociated from GR–Mg⁺⁺: GR–Mg⁺⁺–(H₂)₄ + e⁻ → GR–Mg⁺⁺ + (H₂)₄ (H₂ is released into the gas phase). In contrast, the H₂ molecules were bound again to GR–Mg⁺⁺ after the hole capture of GR–Mg⁺⁺: GR–Mg⁺⁺ + (H₂)₄ (gas phase) + hole → GR–Mg⁺⁺–(H₂)₄. On the basis of these calculations, a model device with reversible H₂ adsorption–desorption properties was designed. These results strongly suggest that the GR–Mg system is capable of H₂ adsorption–desorption reversible storage.

1. INTRODUCTION

The hydrogen molecule (H₂) is the ultimate clean energy source. In order to realize a hydrogen energy system, technological development related to hydrogen storage and transportation is required. Currently, hydrogen is stored as compressed gas or liquefied hydrogen, and safety issues remain unresolved. Hence, the development of a safer chemical hydrogen storage system is highly stable and great potential as a hydrogen storage material. However, the efficiency of bare carbon materials is still low for hydrogen storage. For example, pure carbon nanotubes (CNTs) can store only ca. 7.7 wt % hydrogen molecules.

This drawback is greatly improved by introducing transition and alkali metals into carbon materials. In the case of a transition metal (M) on a graphene surface, H₂ can adsorb M on the graphene surface owing to the fact that electron transfer occurs from sigma electrons of H₂ to the least unoccupied molecular orbital of M. Sigal et al. reported that the introduction of Ni atoms to the graphene surface results in H₂ adsorption on Ni. Sun et al. introduced two Ti atoms into fullerenes and reported that five H₂ molecules were adsorbed. However, it is known that Ti forms clusters on fullerenes, thus reducing the hydrogen storage performance.

Froudakis applied a mixed quantum mechanics/molecular mechanics method to molecular hydrogen adsorption in pure and alkali–metal-doped CNTs. He demonstrated that the charge transfer (CT) from the alkali metal to the CNTs polarizes the H₂ molecule and that this charge-induced dipole interaction is responsible for the higher hydrogen uptake of the doped CNTs. Kolmann et al. calculated the binding energy of H₂ molecules to Li atoms adsorbed on benzene molecules (Bz–Li–H₂ system). The binding energy was calculated to be 4.7 kcal/mol. D’Arcy et al. investigated the Bz–Li–(H₂)n system (n = 1, 2) using quantum Monte Carlo simulations and obtained binding energies of 4.5 (n = 1) and 3.2 kcal/mol (n = 2). Zhang and Cheng investigated hydrogen adsorption to pure graphene nanoribbons and Li-doped ones using density functional theory (DFT) calculations. They showed that the adsorption energy is enhanced by Li atom doping.

More recently, DFT calculations have shown that Li doping in graphene nanoflakes (GRs) leads to an increase in their hydrogen storage capacity. Electron transfer occurs from Li atoms to graphene, resulting in Li⁺ ions and increased hydrogen adsorption energy. H₂ molecules bind to Li⁺ ions via the CT interaction. Thus, it was clarified that the CT interaction of the doped atom with H₂ greatly contributes to
hydrogen storage. However, there is no work on the molecular design of hydrogen storage with reversible H$_2$ adsorption–desorption properties. In addition, the theoretical design of such molecular devices is challenging.

In this study, we theoretically designed a hydrogen storage device with reversible H$_2$ adsorption–desorption properties using a graphene–Mg system on the basis of direct ab initio molecular dynamics (AIMD) calculations. Mg has a wide range of charges (Mg atom, Mg$^+$, and Mg$^{2+}$). Therefore, high hydrogen storage capacity is expected owing to flexible CT.

2. RESULTS

2.1. Structures of Mg-Doped GRs. The optimized structures of GR–Mg$^{m+}$ ($m = 2$) and ($m = 0$ and 1) are shown in Figures 1, S1, and S2, respectively. The binding energies of systems with $m = 0$, 1, and 2 were calculated to be 0.3, 39.9, and 159.8 kcal/mol, respectively, indicating that the binding energy is strongly dependent on the charge of Mg. The GR–Mg$^{2+}$ bonding is 4 times stronger than that of GR–Mg$^+$. The Mg species were bound to the hexagonal sites of the GRs. The distances of Mg$^{m+}$ ($m = 0$, 1, and 2) from the GR surface ($h$) were calculated to be 4.339, 2.214, and 1.806 Å, respectively. The binding distance of Mg$^{2+}$ was shorter than that of Mg$^+$, and the Mg atom could not bind to the GR surface. Notably, the hexagonal site is more stable in energy than the other binding sites, viz., the on-top and C–C bond center sites.

The natural bond population analysis (NPA) atomic charges on the Mg species were $-0.001$ ($m = 0$), $+0.960$ ($m = 1$), and $+1.882$ ($m = 2$), suggesting that slight electron transfer occurs from GR to Mg$^{m+}$ ($m = 1$ and 2) after binding.

2.2. Binding Structures of Hydrogen Molecules to GR–Mg$^{2+}$. The binding structures of H$_2$ to GR–Mg$^{m+}$ ($m = 2$) are shown in Figure 2. The geometries of the GR–Mg$^{2+}$–(H$_2$)$_n$ systems ($n = 1–6$) were fully optimized at the CAM-B3LYP/6-311G(d,p) level. For $n = 1$, the distances of H1 and H1’ in (H$_2$)$_1$ from Mg (R1 and R1’, respectively) were calculated to be 2.087 and 2.088 Å, respectively. The positions of both H1 and H1’ atoms relative to Mg$^{2+}$ were equivalent, suggesting that the H$_2$ molecule binds to Mg$^{2+}$ with a side-on structure. For $n = 2$, the distances R1, R1’, R2, and R2’ were 2.107, 2.108, 2.133, and 2.136 Å, respectively, indicating that the binding structure is side-on, similar to that seen in the $n = 1$ case. The addition of a second hydrogen molecule, (H$_2$)$_2$, affected the bond distance of (H$_2$)$_1$, where it was slightly increased by the addition of H$_2$ (2.09 vs 2.11 Å).

For $n = 3$, the binding structure remained side-on. The R1, R2, and R3 distances were 2.146, 2.147, and 2.147 Å, respectively, indicating that the three hydrogen molecules are nearly equivalent. For $n = 4$, H$_2$ binds to Mg$^{2+}$ with a side-on structure. The distance of H$_2$ from Mg$^{2+}$ gradually increased...
after the hydrogen molecule addition (2.09–2.24 Å), although the distance increase was small.

For n = 5, the distances R1, R2, R3, R4, and R5 were 2.195, 2.194, 2.217, 2.217, and 3.335 Å, respectively. The additional hydrogen molecule [i.e., the fifth hydrogen molecule, (H2)S] is located far from Mg2+ (3.335 Å), indicating that the first coordination shell is fulfilled in n = 4. The fifth hydrogen molecule is located in the second shell.

2.2.1. Stick Diagram. To clearly express the bonding structures of H2 molecules in more detail, the distances of the hydrogen atoms in H2 from the Mg2+ ion, R(Mg−H), are represented in the form of a stick diagram in Figure 3. For n = 1, the R(Mg−H) distances are both 2.087 Å (doubly degenerate). Until n = 4, all hydrogen atoms were located at similar distances from Mg2+. In contrast, the distance between the fifth H2 in n = 5 and Mg2+ (3.335 Å) was greater compared to those in n = 1−3 (2.10–2.15 Å), indicating that the first coordination shell is saturated by four hydrogen molecules (n = 4). Thus, the fifth H2 molecule, (H2)S, binds to GR−Mg2+−(H2)4 as a ligand in the second coordination shell.

The sixth H2 molecule was located in the third shell where the distance was R6 = 4.332 Å and R6′ = 4.429 Å. From the distance distributions of n = 4−6, it is clear that the first coordination shell is saturated at n = 4.

2.3. Binding Structures of Hydrogen Molecules to GR−Mg+. The binding structures of H2 to GR−Mg+ (m = 1) were calculated in the same manner, and the optimized structures of GR−Mg2+−(H2)m (n = 1−6) are shown in Figure S3. Similar binding structures were obtained for Mg+, where the H2 molecules bind to GR−Mg+ in the side-on form. However, the distances of H2 from Mg+ on GR were significantly greater than those of H2 from Mg2+, as shown in Figure S4 (stick diagram). The distance of H2 from Mg+ on GR for n = 1 was 3.572 Å, while the average distance of H2 was 3.744 Å for n = 4. In the case of GR−Mg2+−(H2)m the average distance was 2.240 Å, indicating that the locations of H2 from Mg+ in GR−Mg+ are far from those in GR−Mg2+.

In addition to these forms with considerable GR−Mg+ distances (stable forms), metastable forms with shorter GR−Mg+ distances were obtained for n = 2, 3, and 6. The geometrical configurations are shown in Figure S5. The distances of Mg+ from GRs for n = 2, 3, and 6 were 1.793, 1.839, and 1.874 Å, respectively, in the metastable form. The corresponding values in the stable forms were 2.232, 2.239, and 2.247 Å, respectively. In the case of n = 4 and 5, there is also a metastable form. However, the structures of the metastable form gradually varied to the stable forms after geometry optimization. The energies of the metastable forms were 37–48 kcal/mol higher than those of the stable forms. In the metastable and stable forms, the unpaired electron is localized on GR and Mg+, respectively, in GR−Mg2+−(H2)m.

2.4. Binding Energy of H2 to GR−Mg+ (m = 1 and 2).

The binding energy of H2 to GR−Mg+ (per H2 molecule) is plotted in Figure 4 as a function of n. The binding energy of the first addition of H2 to GR−Mg+ was calculated to be 13.22 kcal/mol (n = 1), which gradually decreased as a function of n. The binding energies of the system with n = 3, 5, and 7 were 9.99, 6.79, and 5.03 kcal/mol, respectively. In contrast, the binding energies of GR−Mg+−(H2)α (m = 1) were significantly lower than those for m = 2. The binding energies with n = 1, 3, 5, and 7 were 0.31, 0.28, 0.26, and 0.24 kcal/mol, respectively. These trends strongly indicate that GR−Mg+ can be used as a H2 storage material, whereas the ability of GR−Mg+ to absorb H2 is significantly low. Thus, the H2 absorption ability of the GR−Mg+ system was significantly changed by the charge of GR. The adsorption–desorption is controlled by the molecular charge in the GR−Mg+−(H2)α system (m).

For comparison, the binding energy of H2 to larger GRs composed of 37 benzene rings, GR37−Mg2++(H2)n → GR37−Mg2+−(H2)n is plotted in Figure 4 (dashed line) as a function of n. The binding energy of the first addition of H2 to GR37−Mg2+ was calculated to be 11.21 kcal/mol (n = 1), which is close to that of GR−Mg+. The shape of the energy curve for GR37 is qualitatively similar to that of GR. For n = 4,
the binding energies were 8.10 kcal/mol (GR) and 7.18 kcal/mol (GR37), indicating that the difference becomes smaller as the size increases.

The binding energies of GR$-\text{Mg}^+$ and GR37$-\text{Mg}^+$ were significantly close to each other: the binding energies of GR$-\text{Mg}^+$ for $n = 1, 3, 5$, and $7$ were 0.31, 0.28, 0.26, and 0.24 kcal/mol, respectively, while those of GR37$-\text{Mg}^+$ were 0.78, 0.29, 0.29, and 0.24 kcal/mol, respectively. These trends strongly indicate that the size of GRs is secondary in the GR$-\text{Mg}^+$ system. The binding structures of $\text{H}_2$ to GR37 (interatomic distances) were close to those of GR, as shown in Figures S6 and S7.

2.5. Electron-Capture Dynamics of GR$-\text{Mg}^+\text{H}_2$. The structure of the GR$-\text{Mg}^+\text{H}_2$ system is largely dependent on the charge of Mg. This specific property makes GR$-\text{Mg}^+\text{H}_2$ suitable for use as a $\text{H}_2$ storage device with adsorption−desorption reversible properties. In the following sections, direct AIMD calculations for the electron- and hole-capture processes of the GR$-\text{Mg}^+\text{H}_2$ system are described.

Figure 5 shows the electron-capture dynamics of GR$-\text{Mg}^{2+}\text{H}_2$ ($m = 2$). Snapshots and potential energies of GR$-\text{Mg}^{2+}\text{H}_2$ are shown in Figure S5A,B, respectively. At time zero, the optimized structure of GR$-\text{Mg}^{2+}\text{H}_2$ was chosen as the initial structure. The average distance between the Mg and H$_2$ molecules was $\langle R \rangle = 2.253$ Å at time = 0 fs (before electron capture). The distance between Mg and the GR surface was $h = 1.908$ Å. After electron capture, the charge on Mg suddenly changed (Mg$^{2+}$ to Mg$^+$). The distance of H$_2$ from Mg$^+$ was slightly increased to $\langle R \rangle = 2.327$ Å, and the distance between Mg$^+$ and the GR surface was slightly decreased ($h = 1.820$ Å) at 51.7 fs. The potential energy of the system is plotted as a function of time in Figure 5B. The zero level corresponds to the total energy of GR$-\text{Mg}^{2+}\text{H}_2$ at the vertical electron-capture point (time = 0 fs). After the electron capture, the energy was slightly decreased at time = 0−50 fs because a slight structural deformation occurred in this time region. Namely, the metastable form of GR$-\text{Mg}^{2+}\text{H}_2$ was formed, and this structure was maintained up to 51.7 fs. After 51.7 fs, the energy decreased suddenly up to $-45$ kcal/mol because the metastable form was broken and changed to a stable form. The elongation of the GR$-\text{Mg}^+$ bond and release of H$_2$ from Mg$^+$ occur. The geometry was changed from metastable to stable forms of GR$-\text{Mg}^+\text{H}_2$. At 85.9 fs, H$_2$ molecules moved away from Mg$^+$, where the average distance was $\langle R \rangle = 3.034$ Å. At the final stage of the reaction (100 fs), H$_2$ molecules were released from GR$-\text{Mg}^+$ to the gas phase, $\langle R \rangle = 4.014$ Å. The interaction of H$_2$ with Mg$^+$ was negligible in this region. Thus, the electron capture of GR$-\text{Mg}^{2+}\text{H}_2$ results in the dissociation of H$_2$ from GR$-\text{Mg}^{2+}\text{H}_2$ and the time scale of the dissociation is very fast (ca. 100 fs). The reaction is expressed as follows

\[
\text{GR} - \text{Mg}^{2+} - (\text{H}_2)_n + e^- \rightarrow \text{GR} - \text{Mg}^+ - (\text{H}_2)_n \quad (\text{H}_2 \text{ in the gas phase})
\]
Thus, H₂ molecules are released into the gas phase after the electron capture.

The time evolution of the spin densities on Mg and GR in GR⁻Mg⁺···(H₂)₄ is shown in Figure S8. Initially, the spin densities on Mg and GR were 0.033 and 1.002, respectively, indicating that the unpaired electron is localized on the GR. These spin densities were crossed and reversed at 75 fs. At 100 fs, the spin densities on Mg and GR were 0.946 and 0.030, respectively. These results suggested that the unpaired electron is occupied on GR in the metastable state and is transferred to Mg⁺ at the final stage.

2.6. Hole-Capture Dynamics of the Dissociation System. Figure 6 shows the hole-capture dynamics of GR⁻Mg⁺⁻⁻(H₂)₄ (m = 1). At time zero, one of the dissociation structures of GR⁻Mg⁺⁻⁻(H₂)₄ is selected as the initial structure at time zero. The geometry at the selected point is shown in Figure 5 by an arrow. The average distance between the Mg and H₂ molecules was ⟨R⟩ = 3.704 Å at time = 0 fs. The height of Mg⁺ was h = 2.472 Å. After hole capture, the charge on Mg changed from Mg⁺ to Mg²⁺, and Mg²⁺ approached GR: h = 1.786 Å at 40.2 fs. The potential energy decreased gradually from 0 to −39.0 kcal/mol (time = 0–40.2 fs), as shown in Figure 6B. At 57.7 fs, Mg²⁺ collided with the GR surface (h = 1.451 Å). At the final stage of the hole-capture process (86.6 fs), the distance of Mg from the GR surface was h = 2.787 Å.

The H₂ molecules gradually approached Mg²⁺ after hole capture: ⟨R⟩ = 3.704 Å (time = 0 fs), 3.636 Å (40.2 fs), 3.540 Å (57.7 fs), and 2.787 Å (86.6 fs). At 86.6 fs, the H₂ molecules were fully bound to Mg²⁺, and the structure was recovered by the addition of H₂ to GR⁻Mg²⁺: the average distance was ⟨R⟩ = 2.787 Å and the distances of H₂ were in the range of 2.197–2.978 Å, indicating that the reverse reaction is completed at ∼90 fs. The reaction is expressed as follows

\[
GR - Mg^+ + (H_2)_n \text{ (gas phase) } + \text{ hole} \\
\rightarrow GR - Mg^{2+} - (H_2)_n
\]

These results strongly indicate that the charge switching of GR⁻Mg can control the adsorption–desorption reversible reaction of H₂.

2.7. Effects of Initial Geometries on Reaction Dynamics. Similar dynamics calculations were carried out for electron- and hole-capture processes from several initial structures. First, the structure of GR⁻Mg²⁺⁻⁻(H₂)₄ fluctuated at 10 K. Second, seven geometries were selected from the geometries generated at 10 K, and then, the trajectories of GR⁻Mg⁺⁻⁻(H₂)₄ following the electron capture of GR⁻Mg⁺⁻⁻(H₂)₄ were run. The results are shown in Figure 7. All trajectories gave similar results: the following reaction proceeded.
The electronic states are negligibly small in the present system. The binding energies of H2 to GR

\[
\text{GR} - \text{Mg}^{2+} - (\text{H}_2)_n (\text{adsorption}) + e^- \\
\rightarrow \text{GR} - \text{Mg}^{2+} - (\text{H}_2)_n (\text{gas phase})
\]

follows (wB87XD), indicating that the e

\[
12.6 \text{ kcal/mol (M062X)}, 11.3 \text{ kcal/mol}
\]

The binding energies of H2 to GR

results are shown in Figure S9. The adsorption structure was generated at 10 K simulation of GR

structure of GR

capture process from the geometries around the optimized structure. Figure S9 shows an example of a molecular device comprising a GR−Mg system. The injection of electrons or holes can control the H2 adsorption−desorption process.

3.2. Comparison with the GR−Li−H2 System. In a previous paper,20 we calculated the binding energies of H2 to a GR−Li−H2 system. In case of one H2 molecule, the binding energies were calculated to be 3.71 kcal/mol (Li atom) and 4.03 kcal/mol (Li+ ion), which are about one-third of those associated with GR−Mg. Therefore, the ability of the GR−Mg system to store H2 is larger than that of the GR−Li system.

3.3. Summary. In this study, the binding energies of H2 to Mg(n) = 0 (Mg atom), the binding energy of one H2 molecule is close to 0, whereas those for n = 1 and 2 are 0.31 and 13.22 kcal/mol (n = 1), respectively. These features suggest that GR−Mg2+ has a strong binding affinity toward H2, whereas GR−Mg+ has a weak binding energy. In addition, it was found that the first coordination shell was saturated by four H2 molecules (n = 4).

Next, direct AIMD calculations were carried out for the electron-capture process of GR−Mg2+−(H2)4 and hole-capture processes of GR−Mg−(H2)4 and GR−Mg+−(H2)4 (gas phase). After electron capture in GR−Mg2+−(H2)4, the H2 molecules left and dissociated from GR−Mg+ to the gas phase. In contrast, the H2 molecules returned to GR−Mg2+ after the hole capture of GR−Mg2+.

Based on the results of direct AIMD calculations, a model device of H2 storage with an adsorption−desorption reversible device was proposed (Figures 8 and S12). The H2 molecules in GR−Mg2+−H2 are dissociated by electron capture: GR−Mg2+−(H2)n + e− → GR−Mg+(H2)n (H2 in the gas phase). On the other hand, GR−Mg+ can capture H2 molecules again after hole capture: GR−Mg+(H2)n (gas phase) + hole → GR−Mg2+−(H2)n (adsorption). These results strongly suggest that the GR−Mg system has the potential to be used as a H2 adsorption−desorption reversible device.

**3. DISCUSSION AND CONCLUSIONS**

3.1. Model of the H2 Adsorption−Desorption Reversible Material. Based on the present theoretical results, a model of the H2 adsorption−desorption reversible device is proposed in this section. Figure 8 shows a schematic of the proposed device model. The GR−Mg2+ system (GR−Mg2+) plays a strong role in H2 storage, where H2 can bind to GR−Mg2+ with a binding energy of 8−13 kcal/mol (n = 1−4). When electron capture takes place in GR−Mg2+−(H2)n, the H2 molecules leave GR−Mg+ and release into the gas phase, as expressed by GR−Mg2+−(H2)n (gas phase). In contrast, once a hole capture occurs in GR−Mg+(H2)n (gas phase), the H2 molecules return to GR−Mg2+ again due to the strongly bound nature of GR−Mg2+−H2 as expressed by GR−Mg2+−(H2)n → GR−Mg2+−(H2)n. Thus, the GR−Mg system can be used as an efficient H2 adsorption−desorption reversible device. Figure S11 shows an example of a molecular device comprising a GR−Mg−H2 system. The injection of electrons or holes can control the H2 adsorption−desorption process.
4. COMPUTATIONAL METHODS

4.1. Binding of Mg\(^{n+}\) (n = 0–2) to GRs. A GR composed of seven benzene rings was used in this study. DFT calculations were performed using a Coulomb-attenuating exchange–correlation energy functional (CAM-B3LYP)\(^{24}\) with a 6-311G(d,p) basis set,\(^{25}\) which is expressed as CAM-B3LYP/6-311G(d,p).

First, the structure of GRs was optimized, and the Mg species were placed in the central region of the GRs. The structures of GR–Mg were fully optimized. The binding energy of the Mg species to the GR is defined as follows

\[
-E_{\text{bind}} = E(\text{GR} - \text{Mg}) - [E(\text{Mg}) + E(\text{GR})]
\]

where \(E(X)\) is the total energy of X. If \(E_{\text{bind}}(\text{Mg})\) is positive, Mg binds exothermically to GRs.

4.2. Binding of \(\text{H}_2\) to GR–Mg. In the GR–Mg–hydrogen system, expressed as \(\text{GR} - \text{Mg} - (\text{H}_2)_n\), 1–7 hydrogen molecules \((n = 1–7)\) were added to GR–Mg, while all atoms in GR–Mg–(\(\text{H}_2\))\(_n\) were fully optimized without straining the structure. The binding energy of the \(n\text{H}_2\) molecules to GR–Mg was calculated as follows

\[
-E_{\text{bind}}(n, \text{H}_2) = [E(\text{GR} - \text{Mg} - (\text{H}_2)_n) - nE(\text{H}_2)] - E(\text{GR} - \text{Mg})/n
\]

If \(E_{\text{bind}}(\text{H}_2)\) is positive, the addition of \(\text{H}_2\) to GR–Mg proceeds, and the addition reaction, \(\text{H}_2 + \text{GR} - \text{Mg} \rightarrow \text{H}_2 - \text{GR} - \text{Mg}\), is exothermic.

The atomic charges were calculated using NPA.\(^{26}\) All calculations were performed using the Gaussian 09 software package.\(^{27}\) In previous studies,\(^{28–30}\) we investigated the interaction between graphene and various molecules using DFT at the same level of theory. A similar technique was applied to the GR–Mg–(\(\text{H}_2\))\(_n\) system in this study.

4.3. Effects of Size of GRs. To investigate the influence of the size of graphene on the relevant electronic states and binding energies, a GR composed of 37 benzene rings, denoted as GR37, and the 6-311G(d,p) basis set were examined. The structure of GR37 is shown in Figure S13 in the Supporting Information. It should be noted that the effects of GR size on the electronic states and binding energies were small in this system, as discussed in Section 4.2.

4.4. Direct AIMD Calculations. The trajectories of GR–Mg\(^{n+}\)–(\(\text{H}_2\))\(_n\) following the vertical electron capture of GR–Mg\(^{n+}\)–(\(\text{H}_2\))\(_n\) were calculated at the CAM-B3LYP/6-31G(d) level. The forward reaction (electron capture) is expressed as follows

\[
\text{GR} - \text{Mg}^{n+} - (\text{H}_2)_n + \text{e}^- \rightarrow [\text{GR} - \text{Mg}^{n+} - (\text{H}_2)n]_{\text{ver}} \rightarrow \text{product}
\]

where \([\text{GR} - \text{Mg}^{n+} - (\text{H}_2)n]_{\text{ver}}\) is the species at the vertical electron-capture point. The reverse reaction (hole capture) is expressed as follows

\[
\text{GR} - \text{Mg}^{+} \cdots (\text{H}_2)_n \text{ (gas phase)} + \text{hole} \rightarrow [\text{GR} - \text{Mg}^{+} \cdots (\text{H}_2)n]_{\text{ver}} \rightarrow \text{product}
\]

where \([\text{GR} - \text{Mg}^{n+} \cdots (\text{H}_2)n]_{\text{ver}}\) is the species at the vertical hole-capture point. As reverse reactions, the geometries of the optimized structure and around the optimized structure were also examined. The reaction is expressed as follows

\[
\text{GR} - \text{Mg}^{+} - (\text{H}_2)_n + \text{hole} \rightarrow [\text{GR} - \text{Mg}^{+} - (\text{H}_2)n]_{\text{ver}} \rightarrow \text{product}
\]

The geometries around the optimized structures were generated at 10 K.

In the trajectory calculation, the velocity Verlet algorithm was used with a time step of 0.05 fs to solve the equation of motion of the system. The drifts of total energies in all trajectory calculations were less than 0.01 kcal/mol, where the trajectory was based on a constant total energy. Direct AIMD calculations were performed using our in-house code.\(^{31,32}\)

To generate the geometries around the equilibrium point at time zero, direct AIMD calculations of GR–Mg\(^{n+}\)–(\(\text{H}_2\))\(_n\) and GR–Mg\(^{n+}\)–(\(\text{H}_2\))\(_n\) were carried out under constant temperature conditions. The Nosé–Hoover algorithm was used to maintain a constant temperature within each trajectory; the simulation temperature was set to 10 K. From the geometries generated at 10 K, 5–8 geometries were sampled, and then direct AIMD calculations were carried out after electron or hole capture in the GR–Mg\(^{n+}\)–(\(\text{H}_2\))\(_n\) systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00243.

Optimized structures of GR37 composed of 37 benzene rings, GR–Mg (atom), GR–Mg\(^{+}\) (ion), and GR–Mg\(^{+}\)–(\(\text{H}_2\))\(_n\) (with metastable \((n = 2, 3, 6)\), calculated at the CAM-B3LYP/6-311G(d) level; stick diagrams of interatomic distances between the Mg\(^{+}\) ion and hydrogen atoms of \(\text{H}_2\) in GR–Mg\(^{+}\)–(\(\text{H}_2\))\(_n\) (n = 1–6), GR37–Mg\(^{+}\)–(\(\text{H}_2\))\(_n\) (n = 1–12), and GR37–Mg\(^{+}\)–(\(\text{H}_2\))\(_n\) (n = 1–12); and effects of initial geometries on time evolution of potential energies of GR–Mg\(^{+}\)–(\(\text{H}_2\))\(_n\) following the hole capture of GR–Mg\(^{+}\)–(\(\text{H}_2\))\(_n\) (gas phase), and of GR–Mg\(^{+}\)–(\(\text{H}_2\))\(_n\), following the hole capture of GR–Mg\(^{+}\)–(\(\text{H}_2\))\(_n\) (PDF)

AUTHOR INFORMATION

Corresponding Author

Hiroto Tachikawa — Division of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan; orcid.org/0000-0002-7883-2865; Email: hiroto@eng.hokudai.ac.jp

Authors

Yoshiki Izumi — Division of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan
Tetsuji Iyama — Division of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan
Kazuhisa Azumi — Division of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c00243
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