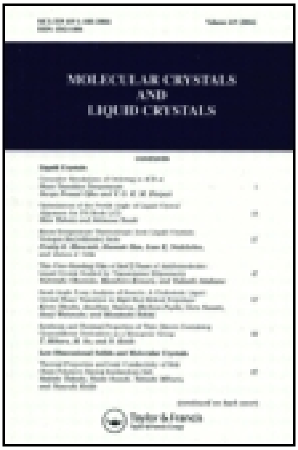

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A DFT and MD Study on the Interaction of Carbon Nano-Materials with Metal Ions

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The interaction of manganese (II) ion (Mn^{2+}) with graphene surfaces have been investigated by means of density functional theory (DFT). Also, the molecular dynamics (MD) calculations using molecular mechanics-2 (MM2) potential functions have been applied to the diffusion dynamics of Mn^{2+} on the graphene surface. Two graphene sheets ($n = 19$ and 52, where n means numbers of rings in each carbon cluster) were considered as models of graphene surface in the present study. The B3LYP/LANL2MB calculations showed that the Mn^{2+} ion is located in the ranges 2.28–2.46 Å from the graphene surface. Also, classical MD calculation was applied to diffusion processes of the Mn^{2+} on the graphene surface ($n = 52$). The classical MD calculations showed that the Mn^{2+} ion diffuses from bulk to edge region at 300–600 K and is trapped in the edge region. The nature of the interaction between the Mn^{2+} ion and the graphene sheet was discussed on the basis of theoretical results.

Keywords: DFT; diffusion; graphene; manganese (II) ion; MD calculation

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1. INTRODUCTION

Carbon nanomaterials, such as fullerrens, carbon nanotubes, and graphenes, have been widely studied and applied onto not only electronic and chemical fields but also biomedical and biochemical systems [1,2]. The structure of carbon nanomaterials can be regarded as a carbon capsule and they have been received much attention because the capsule has high chemical stability and the encapsulated materials such as metals and metal oxides are stable in air, water and acids. This nature may allow application to a new drug delivery system (DDS), contrast agent or tracer of biomedical imaging. For example, though Gd^{3+} and Mn^{2+} are well-known to effective contrast agents for magnetic resonance imaging (MRI), it is necessary to form a stable chelate for the agent [3,4]. Therefore, to elucidate quantum chemically the interaction of metal ion with carbon materials is important in order to develop new DDS's.

Recently, diffusion processes of metal atoms on graphene surfaces have been observed by high-resolution TEM. Gan *et al.* [5] observed diffusion of metal atoms (individual Au or Pt atoms) in layers consisting of one or two graphene planes in real time at high temperature by high-resolution TEM. They obtained information about the location of metal atoms in graphene. Also, they obtained diffusion coefficients in a range of values, $D = 6\text{–}20 \times 10^{-22}$ m^2/s for Au and $D = 4\text{–}10 \times 10^{-21}$ m^2/s for Pt at 900 K.

The elucidation of the diffusion processes of the metal and alkali ions on the graphene surfaces is one of the important themes in development of higher performance alkali ion secondary battery. However, works on the diffusion dynamics of the species are limited. Marquez carried out molecular dynamics (MD) simulations on lithium ion on graphite system with three layers [6]. Structural changes in bulk phases and at liquid-solid interfaces were evaluated on the basis of the MD calculation. Shimizu and Tachikawa investigated the electronic states and band structures of sodium ion (Na^+) trapped in graphite surfaces using the classical MD calculation and molecular orbital (MO) theory [7]. The theoretical features obtained by the MD calculation are in good agreement with experiments.

In previous papers [8–11], we investigated the Li^+ ion on the model surface of amorphous carbon to elucidate quantum chemically the diffusion dynamics. It was found that Li^+ ion diffuses along the node of highest occupied molecular orbital (HOMO) of carbon surface.

In the present paper, we applied DFT and classical MD methods to diffusion dynamics of the Mn^{2+} ion on the graphene surface to shed light on the mechanism of interaction and diffusion process from theoretical point of view.

2. METHOD OF CALCULATION

As graphene surfaces, two graphene sheets ($n = 19$ and 52, where n means numbers of hexagonal rings of carbon in each carbon cluster) were examined in the present study. First, one Mn^{2+} ion is put on the center-of-mass of the graphene surface, and then the structures of the Mn^{2+}-graphene systems were fully optimized at the B3LYP/LANL2DZ level of theory. The charge of the Mn^{2+} ion was calculated using natural bond population analysis (NPA) method at the B3LYP/6-311G(d,p)//B3LYP/LANL2DZ level. All density functional theory (DFT) calculation was carried out using Gaussian 03 program package [12].

Diffusion processes of Mn^{2+} ion on the graphene surface ($n = 52$) were investigated by means of classical MD method [7–11,13]. The total energy and energy gradient on the multi-dimensional potential energy surface of the system were calculated at each time step at the MM2 level of theory, and then classical equation of motion was full-dimensionally solved.

3. RESULTS

A. Binding Structures

As a model of graphene surface, we considered a hydrocarbon composed of 19 hexagonal rings ($n = 19$), as shown in Figure 1. Five binding sites of Mn^{2+} were examined in the calculation. The sites A-D, and E are hexagonal and bond center sites, respectively. The optimized structure of site-A calculated at the B3LYP/LANL2DZ level is illustrated in Figure 1. The Mn^{2+} ion can be trapped in the hexagonal site and the height of Mn^{2+} is calculated to be 2.4617 Å from the surface.

The relative energies of Mn^{2+} on several sites are given in Table 1. Sites A-D and site E are hexagonal and C-C bond center sites, respectively. The hexagonal sites B-D are $4.8 - 11.7$ kcal/mol higher in energy than the central hexagonal site A. The energy of site E is also higher than that of site A (+4.5 kcal/mol). These results indicate that the Mn^{2+} ion binds preferentially to the hexagonal site of graphene surface in case of small-sized graphene sheets.

B. Atomic Charges and Hyperfine Coupling Constants

The atomic charges of Mn^{2+}, calculated by means of natural population analysis (NPA), are summarized in Table 1. The charges on Mn^{2+} ion are slightly dependent on the trapping site: for example, charges on sites A and E are calculated to be +0.86 and +1.06,

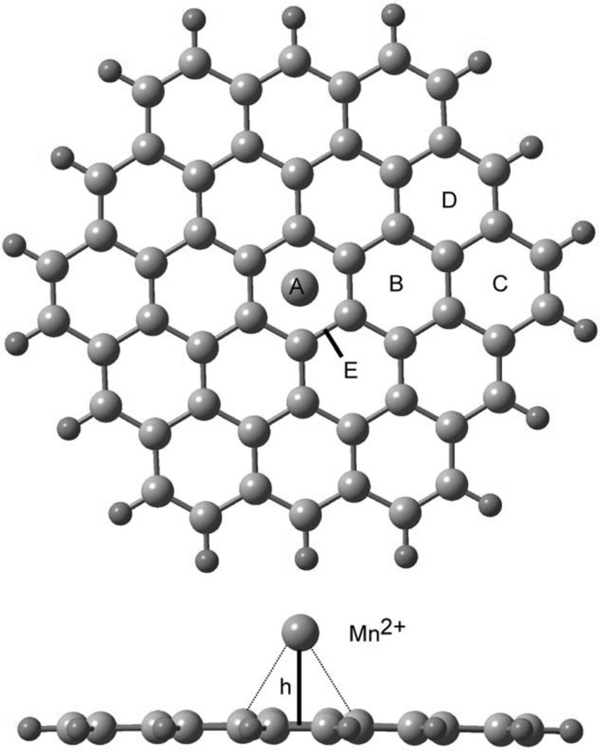

FIGURE 1 Optimized structure of Mn^{2+}-graphene interaction system (site A) calculated at the B3LYP/LANL2DZ level.

TABLE 1 Optimized Geometrical Parameters (h: Heights of Mn^{2+} Ion From the Graphene Surface in Å), Atomic Charges of Mn^{2+} Obtained by Natural Population Analysis (NPA), and Relative Energies (ΔE in kcal/mol). The Geometries were Optimized at the B3LYP/LANL2DZ and Electronic States were Calculated at the B3LYP/6-311G(d,p)// B3LYP/LANL2DZ Level

Site	h/Å	NPA	ΔE
A	2.4617	+0.86	0.0
B	2.3487	+1.07	11.7
C	2.3941	+0.96	11.0
D	2.3316	+1.08	4.8
E	2.2815	+1.06	4.5

respectively. These results indicate that the interaction between graphene and Mn^{2+} is composed of electron donation from graphene to Mn^{2+}.

The hyperfine coupling constants of Mn^{2+}, $a(Mn^{2+})$, are widely distributed. The values of hexagonal (A) and bond center (E) sites are calculated to be 1273.8 G and −413.8 G, respectively. Thus, the values are drastically changed by the binding site. This result indicates that one can detect the binding site from the measurement of hyperfine coupling constants of the Mn^{2+} ion in carbon system.

C. Diffusion of the Mn^{2+} Ion at 300–600 K

To elucidate the diffusion process of Mn^{2+} ion on the graphene surface, the classical MD calculations were carried out at 300 and 600 K. A sample trajectory for Mn^{2+} ion superimposed on the graphene surface at 300 K is given in Figure 2. The Mn^{2+} ion starting from the center-of-mass (site A) moves against to the edge region of the graphene. This is due to the fact the potential energy of Mn^{2+} in the edge region is lower than in the central region. The ion reaches the edge region at 0.5 ps, and then it is trapped. At 1.0 ps, the ion is still trapped in the edge region without deformation of graphene surface.

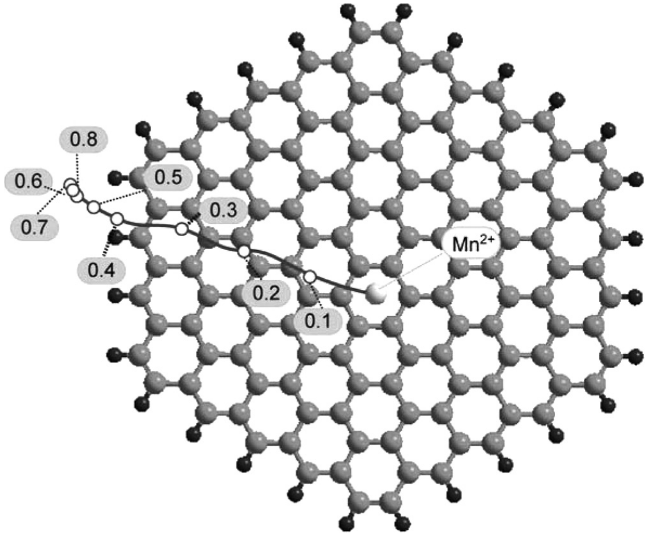

FIGURE 2 Sample trajectory of Mn^{2+} ion superimposed on the graphene ($n = 52$) at 300 K. Diffusion path is expressed by curve and the values in dots are elapsed time (in ps).

The trajectory at 600 K is illustrated in Figure 3 (upper figure). The Mn^{2+} ion moves directly to the edge region, and the trajectory shows a straight line from the center-of-mass to the edge region. The time scale from the center to the edge region is about 0.40 ps. The potential energy curve (PEC) for movement of the ion is plotted as a function of time and is given in Figure 3 (lower curve). Each potential minimum corresponds to a position of Mn^{2+} ion in the hexagonal site, whereas the maximum of PEC corresponds to the position between two hexagonal

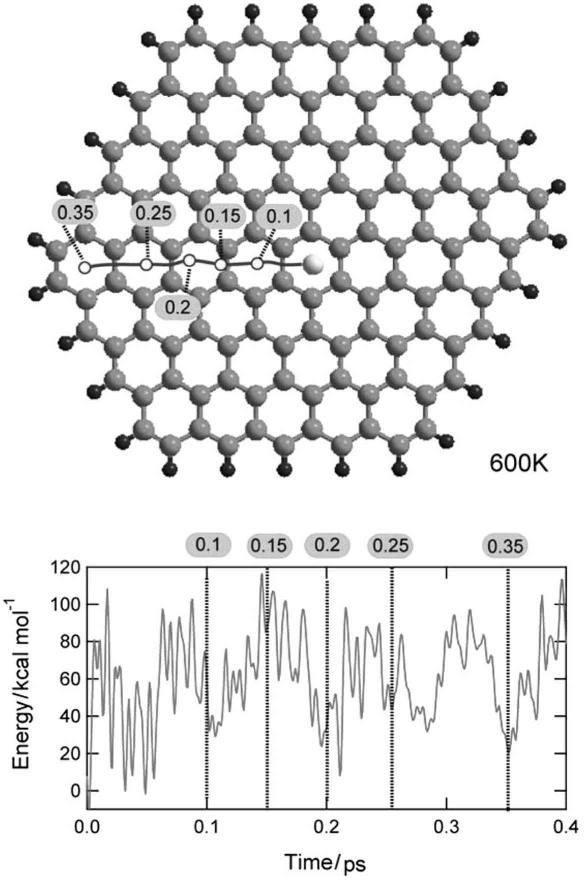

FIGURE 3 Sample trajectory of Mn^{2+} ion superimposed on the graphene ($n = 52$) at 600 K (upper), and potential energy of the system plotted as a function of time (lower). Diffusion path is expressed by curve and the values in dots are elapsed time (in ps). When Mn^{2+} is located in hexagonal site, the energy takes a minimum point.

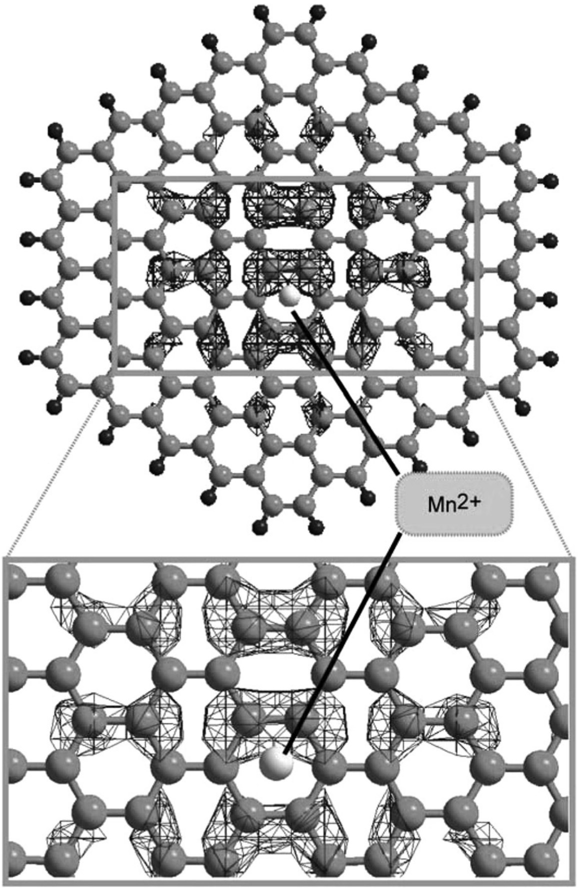

FIGURE 4 Spin density of Mn^{2+}-graphene interaction system calculated by extended Huckel method.

sites. Namely, the Mn^{2+} ion has a potential barrier at the C-C bond between two hexagonal sites.

Figure 4 shows the distribution of spin density of Mn^{2+} ion-graphene ($n = 52$) system. The unpaired electron is preferentially distributed around the Mn^{2+} ion. This feature is similar to the diffusion of Li atom on the graphene surfaces [7–11].

4. CONCLUSION

In the present study, density functional theory (DFT) calculations have been applied to the interaction system composed of graphene and the Mn^{2+} ion in order to elucidate the electronic states of materials for DDS. It was found that the Mn^{2+} ion can bind to hexagonal site of graphene sheet and a weak bond between Mn^{2+} and carbon atom is formed. The values of isotropic hyperfine coupling constant, $a(Mn^{2+})$, is drastically changed by the binding site.

The classical MD calculations showed that the Mn^{2+} ion diffuses freely on the surface from the center to edge region at room temperature.

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