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Ab-Initio and MD Studies on the Interaction of Carbon Nano-Materials with Alkali Ion and Atom

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The structures and electronic states of sodium atom (Na) trapped on the graphene surfaces have been investigated by means of density functional theory (DFT) calculation to elucidate the nature of interaction between Na and the graphenes. In addition, direct molecular orbital-molecular dynamics (MO-MD) calculation [Tachikawa, J. Phys. Chem. C, 112 (2008) 10193] was applied to diffusion processes of the Na atom on graphene surfaces. Seven graphenes ($n = 7$, 14, 19, 29, 37, 44 and 52, where n means numbers of rings in each carbon cluster) were examined in the present study. The B3LYP/LANL2MB calculation showed that the sodium atom is located at ca. 3.0 Å from the graphene surfaces. The direct MO-MD calculation showed that diffusion of Na atom is slower than that of Na^+ ion on graphene surface. The nature of the interaction between Na atom and the carbon clusters was discussed on the basis of theoretical results.

Keywords: ab-initio MD; charge distribution; diffusion dynamics; graphene; sodium atom

1. INTRODUCTION

Carbon materials have potential to interact a variety of chemical species on both surface and edge regions of the carbon sheet [1–7]. In particular, the interaction of the carbon with alkali metal ion and atom

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are much important in the field of secondary rechargeable batteries. In case of lithium ion (Li^+) and graphite, a theoretical maximum capacity of normal graphite material for lithium ion (LiC_6) is 372 mAh/g. If the carbon material is changed from graphite to amorphous carbon, it is known that capacity increases up to 500–1100 mAh/g. The characteristics are originated from non-layer structure where Li atom and ion are stored in the edge region of the carbon sheet. Therefore, several investigations for the interaction between carbon surface and alkali metals have been carried out from both experimental and theoretical points of view.

The elucidation of the diffusion processes of the alkali atom and ion on the graphene is one of the important themes in development of higher performance secondary battery. However, the dynamics feature of the diffusion of the species is scarcely known due to a lack of theoretical method to treat the diffusion dynamics in quantum mechanical level of theory. Recently, we have developed a dynamics method to calculate the trajectory on the full dimensional potential energy surface obtained by ab-initio and semi-empirical molecular orbital (MO) methods [8–13]. This method, called direct ab-initio molecular orbital-molecular dynamics (MO-MD) method, has been applied to chemical reactions, dynamics of molecular clusters, and diffusions of atoms and ions in materials. In previous papers [8–13], 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 direct MO-MD methods to a diffusion dynamics of the alkali atom on the model surfaces of graphene to shed light on the mechanism of diffusion of alkali metal atom from quantum mechanical point of view. In particular, we focus our attention on interaction of Na atom with the graphenes. In previous paper [14], we investigated preliminary the electronic states of Na^+ ion adsorbed on graphene surface using DFT and direct MO-MD calculations. It was found that the Na^+ ion is preferentially bound to a hexagonal site of graphene surface. The similar technique will be applied to the Na atom -graphene system in the present work.

2. METHOD OF CALCULATION

The structures of Na atom on the graphenes were fully optimized at the B3LYP/LANL2MB and AM1 levels of theory. One Na atom was put on the center-of-mass of the graphene, and then the structures of the Na- graphene were fully optimized. Seven graphenes ($n = 7$, 14, 19, 29, 37, 44 and 52, where n means numbers of rings in each carbon cluster) were examined in the present study. For comparison, the interaction system of Na^+–graphenes were investigated with the same manner. All density functional theory (DFT) calculation was carried out using Gaussian 03 program package [15].

Diffusion processes of Na atom on the graphene ($n = 37$) were investigated by means of direct molecular orbital-molecular dynamics (MO-MD) method [16–19]. The total energy and energy gradient on the multi-dimensional potential energy surface of the Na-graphene were calculated at each time step at the AM1-MO level of theory, and then classical equation of motion was full-dimensionally solved. Therefore, charges and electronic states of the Na atom and all atoms were exactly treated within the level of theory by the calculations at each time step. This point is much different from usual classical molecular dynamics (MD) calculation where the charges of all atoms are constant during the diffusion. Hence, one can obtain details of the diffusion processes of Na atom on amorphous carbon using direct MO-MD method.

3. RESULTS

A. Binding Structures of the Na Atom on Several Sized Graphenes

The structures of the Na atom-graphene systems ($n = 7, 14, 19, 29, 37, 44$ and 52) are fully optimized at the B3LYP/LANL2MB level. The results for $n = 29$ and 52 are illustrated in Figure 1 for example, while the optimized parameters are given in Table 1. The Na atoms are located in the ranges 2.98–3.09 Å from the surface of graphenes. The distances of Na atom are significantly longer than those of Na^+ ion (2.24–2.26 Å).

The atomic charges of Na atom, obtained by natural population analysis (NPA), are plotted as a function of number of hexagonal rings (n) and the result is given in Figure 2. The charge of Na atom increases with increasing n and is saturated around $n = 44$–52. As well as atomic charge, the spin density of Na atom is strongly dependent on n, but the spin density decreases with increasing n. The charge and spin density of Na atom at $n = 52$ are calculate to be $+0.46$ and 0.52, respectively. This result indicates that the electron transfer from the Na atom to the graphene is important in the interaction. The size dependency is caused by change of electron affinities of grapheme surfaces.

The charges of Na^+ ion adsorbed on the graphenes are plotted for comparison. The Na^+ charge is not dependent on n and has a constant value ($+0.98$). This is much different from that of Na atom. This is due to the fact that electrostatic interaction is dominant in case of Na^+.

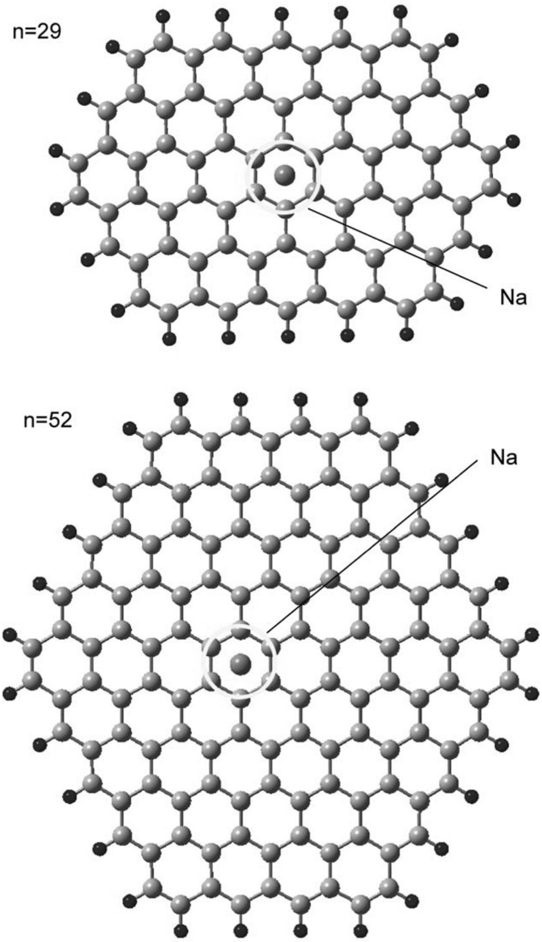

FIGURE 1 Optimized structures of Na atom-graphenes obtained at the B3LYP/LANL2MB calculation. Only two sized graphenes with $n = 29$ and 52 are illustrated.

B. Diffusion of the Na Atom at 1100 K

The Na atom can move on the graphene surface by thermal activation. A trajectory for the Na atom superimposed on the graphene surface at 1100 K is illustrated in Figure 3 (upper). For comparison, a trajectory of Na^+ ion is also calculated with the same manner Figure 3 (lower). The Na atom and Na^+ ion move gradually at 1100 K. The Na^+ ion diffuses widely on the graphene surface, whereas region of the Na atom is

TABLE 1 Optimized Geometrical Parameters (Heights of Na/Na^+ from the Graphene Surface in Å) and NPA Atomic Charges of Na Atom and Na^+ Ion on Several Graphene Surfaces Calculated at the B3LYP/6–31G* Level of Theory. Spin Densities of the Na Atom are Given in Parenthesis. The Geometries are Calculated at the B3LYP/LANN2MB Level

	Na		Na^+	
n	Distance/Å	NPA charge	Distance[a]/Å	NPA charge
7	3.010	−0.011 (1.002)	2.258	+0.975
14	2.939	+0.233 (0.747)	2.249	+0.975
19	2.912	+0.194 (0.793)	2.243	+0.976
29	3.057	+0.493 (0.491)	2.232	+0.976
37	2.981	+0.318 (0.668)	2.231	+0.975
44	3.085	+0.432 (0.553)	2.224	+0.975
52	3.088	+0.461 (0.524)	2.224	+0.975

[a] Distance of Na^+ ion from surface are cited from our previous paper [Ref. 14].

significantly narrow. The diffusion coefficients estimated from these trajectories are $D(Na) = 8 \times 10^{-7}\,m^2/s$ and $D(Na^+) = 2 \times 10^{-6}\,m^2/s$. This result indicates that the Na^+ ion can move more easily on the graphene surface at 1100 K than Na atom.

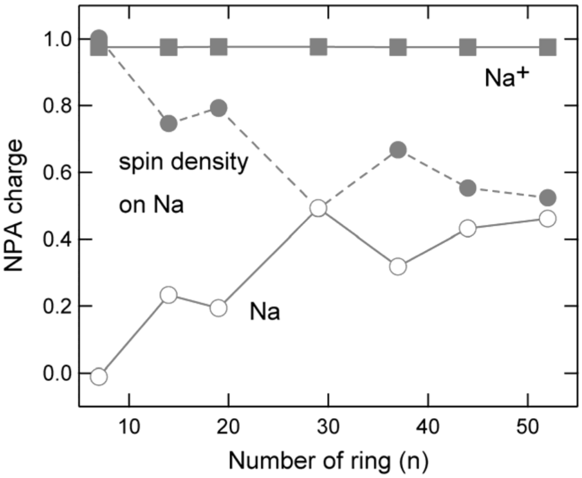

FIGURE 2 Atomic charges of Na atom and Na^+ ion adsorbed on several sized graphenes plotted as a function of number of hexagonal rings of graphenes. Spin densities on the Na atom are also plotted. The values are calculated at the B3LYP/6-31G(d)//B3LYP/LANL2MB level.

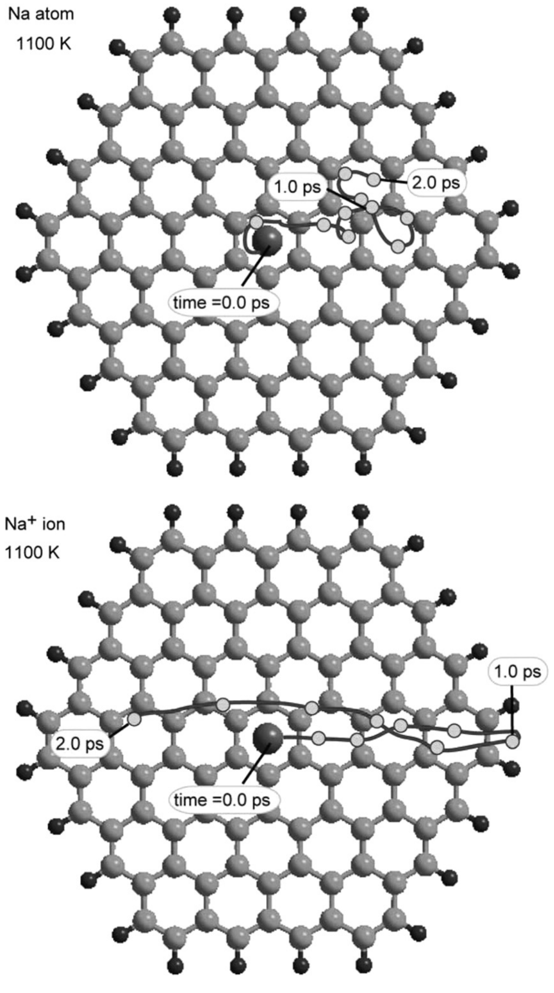

FIGURE 3 Trajectories of Na atom and Na^+ ion superimposed on graphene surface ($n = 37$) at 1100 K. The Na atom and Na^+ ion are started from the center-of-mass of the graphene.

C. Conclusion

In the present study, first, DFT calculation has been carried out for the Na atom-graphene system to elucidate the nature of Na-graphene interaction. Seven cluster models ($n = 7$, 14, 19, 29, 37, 44 and 52, where n means numbers of rings in the carbon cluster models) were considered in the present study. The charge of Na atom is strongly dependent on number of hexagonal ring of graphene (n). Magnitude of electron transfer is saturated around $n = 50$. The interaction between Na atom and graphene is composed of electron transfer from Na atom to graphene. The direct MO-MD calculations showed that diffusion rate of Na is slower than that of Na^+ ion.

REFERENCES

[1] For a review article: Inagaki, M. (1989). *J. Mater. Res.*, *4*, 1560.

[2] Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., Grigorieva, I. V., & Firsov, A. A. (2004). *Science*, *306*, 666.

[3] Wu, J., Pisula, W., Multen, K. (2007). *Chem. Rev., 107*, 718.

[4] Inagaki, M., Tachikawa, H., Nakahashi, T., Konno, H., & Hishiyama, Y. (1998). *Carbon*, *36*, 1021.

[5] Konno, H., Oka, H., Shiba, K., Tachikawa, H., & Inagaki, M. (1999). *Carbon, 37*, 887.

[6] Shimizu, A., Inagaki, M., & Tachikawa, H. (1999). *J. Phys. Chem. Solid*, *60*, 1811.

[7] Konno, H., Shiba, K., Tachikawa, H., Nakahashi, T., Oka, H., & Inagaki, M. (2001). *Synth. Metals*, *125*, 189.

[8] Shimizu, A. & Tachikawa, H., (2003). *J. Phys. Chem. Solds*, *64*, 2397.

[9] Tachikawa, H. (2008). *J. Phys. Chem. C.*, *112*, 10193.

[10] Tachikawa, H. (2007). *J. Phys. Chem. C.*, *111*, 13087.

[11] Tachikawa, H. & Shimizu, A. (2006). *J. Phys. Chem. B*, *110*, 20445.

[12] Tachikawa, H. & Shimizu, A. (2005). *J. Phys. Chem. B*, *109*, 13255.

[13] Tachikawa, H., Kawabata, H., Miyamoto, R., Nakayama, K., & Yokoyama, M. (2005). *J. Phys. Chem. B*, *109*, 3139.

[14] Iyama, T., Kawabata, H., & Tachikawa, H. (2008). *Thin Solid Films*, *516*, 2611.

[15] Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Montgomery, J. A., Jr., Vreven, T., Kudin, K. N., Burant, J. C., Millam, J. M., Iyengar, S. S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G. A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J. E., Hratchian, H. P., Cross, J. B., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Ayala, P. Y., Morokuma, K., Voth, G. A., Salvador, P., Dannenberg, J. J., Zakrzewski, V. G., Dapprich, S., Daniels, A. D., Strain, M. C., Farkas, O., Malick, D. K., Rabuck, A. D., Raghavachari, K., Foresman, J. B., Ortiz, J. V., Cui, Q., Baboul, A. G., Clifford, S., Cioslowski, J., Stefanov, B. B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R. L., Fox, D. J., Keith, T., Al-Laham, M. A., Peng, C. Y., Nanayakkara, A., Challacombe, M., Gill, P. M. W., Johnson, B., Chen, W., Wong, M. W., Gonzalez, C., & Pople, J. A. (2003). *Ab-Initio MO Calculation Program: Gaussian 03, Revision B.04*, Gaussian, Inc.: Pittsburgh, PA.

[16] Tachikawa, H. (2006). *J. Phys. Chem. A*, *110*, 153.

[17] Tachikawa, H. (2006). *J. Chem. Phys.*, *125*, 133119.

[18] Tachikawa, H. (2006). *J. Chem. Phys.*, *125*, 144307.

[19] Tachikawa, H. & Kawabata, H. (2008). *J. Phys. Chem. B*, *112*, 7315.