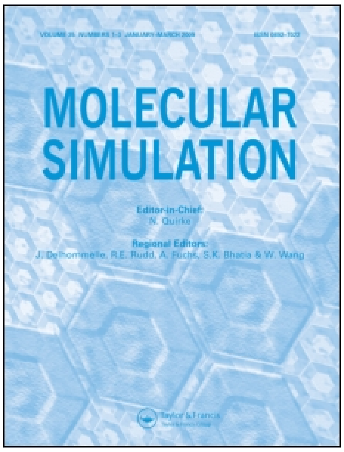

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Molecular-dynamics Studies on Hydrogen Atoms in Nanostructured Graphite

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We have investigated the effect of crystallization on the desorption of hydrogen atoms from nanostructured graphite by carrying out the hybrid molecular-dynamics simulation on model systems. It is shown by our simulation that the bond between hydrogen and carbon atoms becomes weaker due to the recrystallization of the nanostructured graphite and that the hydrogen dimer is formed with increasing temperature. We have thus found one possible mechanism of the hydrogen desorption from the nanostructured graphite.

Keywords: Hydrogen; Graphite; Hybrid molecular dynamics simulation; Carbon

INTRODUCTION

Recently much attention has been focused on the ability of the hydrogen storage of carbon-related materials with nanometer-scale, such as carbon nanotubes [1] and graphite nanofibers [2]. It is reported recently that there exists a hydrogen storage capacity of 7.4 wt.% ($CH_{0.95}$) for nanostructured graphite prepared by mechanical milling for 80 h under a hydrogen atmosphere [3]. It is suggested by the neutron diffraction experiment that hydrogen atoms exist in two kinds of states, one is the hydrogen–carbon covalent bond state and the other is the intercalated state between graphite layers [4]. As for the desorption of hydrogen molecule from the nanostructured graphite, two desorption peaks are observed in thermal desorption mass spectroscopy [5]. These peaks appear at about 750 and 1000 K, respectively, and it is suggested that the latter peak is related to the recrystallization of the nanostructured graphite.

In this paper, we consider the model system for the hydrogen-adsorbed nanostructured graphite, where four hydrogen atoms are trapped in the defective structure. We investigate particularly the effect of the recrystallization of the nanostructured graphite or disappearance of the defect on the bonding properties of hydrogen atoms. To clarify the bonding states of hydrogen atoms in nanostructured graphite theoretically, we have to treat quantum mechanically the bonding between the hydrogen and the carbon atoms of the nanostructured graphite and also employ a large system to take into account the nanometer-size of the ″nanostructured″ graphite. For these purposes, we employ the hybrid *ab initio*/classical molecular dynamics (MD) simulations proposed by Ogata *et al.* [6,7], in which the system is divided into a cluster region and an environmental region. The former region is embedded in the environmental region, and the cluster atoms are treated quantum mechanically by the density-functional theory (DFT), while atoms in the environmental region are described by the empirical interatomic potential.

METHOD OF CALCULATION

In our hybrid *ab initio*/classical MD method [6,7], the system (referred to as S in the following) is divided into a cluster region (referred to as C), where chemical reactions are assumed to occur, and an environmental region. Atoms in the total system are classified into three types; (i) atoms in the cluster region which are treated quantum mechanically;

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(ii) atoms in the environmental region which are described by an empirical interaction potential; and (iii) termination atoms which terminate the cluster atoms. The potential energy of the total system is defined as follows:

$$E(r_i \in \mathrm{S}) = E_{\mathrm{classical}}(r_i \in \mathrm{S}) - E_{\mathrm{classical}}(r_i \in \mathrm{C}) + E_{ab\ initio}(r_i \in \mathrm{C}), \quad (1)$$

where r_i is the coordinates of the *i*th atom, $E_{ab\ initio}$ is the potential energy obtained by the *ab initio* calculation based on the DFT and $E_{\mathrm{classical}}$ is the potential energy calculated using empirical potential. The potential energy of cluster atoms needs to be calculated by both DFT and empirical-potential calculations. In the *ab initio* calculation the termination atoms are introduced to terminate the dangling bond of the cluster and their coordinates are given as a function of atomic coordinates in both the cluster and the environmental regions.

Figure 1 shows the flowchart of the hybrid *ab initio*/classical MD simulation. The forces acting on the atoms in the cluster region are calculated by both *ab initio* DFT and the classical empirical potential methods, while those in the whole system are calculated by the classical method only.

In the *ab initio* DFT calculations, the generalized gradient approximation [8] is used for the exchange-correlation energy. The electronic wave functions and the charge density are expanded in plane waves with cutoff energies 20 and 180 RY., respectively. The energy function is minimized using an iterative scheme based on the preconditioned conjugate-gradient method [9,10]. The ultrasoft pseudopotential is used for interaction between valence electrons and ions [11]. The Poisson equation is solved with the real-space multigrid method [12] to obtain the Hartree potential, and the local pseudopotential is also calculated in the real space so as to avoid the interaction between the periodic replicas.

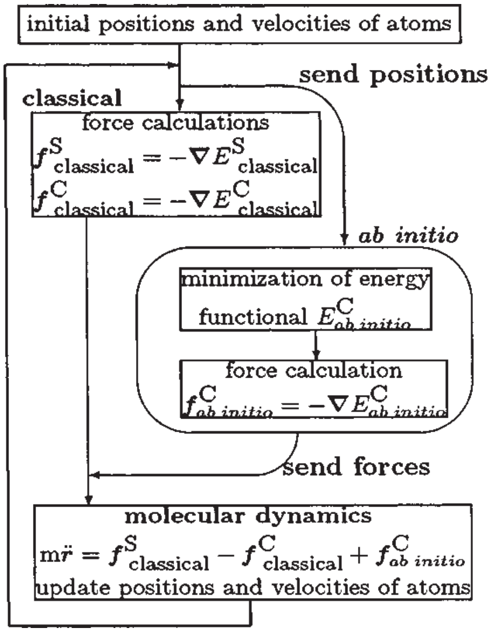


FIGURE 1 The flowchart of the hybrid *ab initio*/classical MD method. Symbols S and C denote the system and the cluster, respectively.

In the classical empirical-potential calculation, we use environment-dependent interaction potential (EDIP) proposed by Marks [13]. EDIP is represented as a sum of the pair potential and the three-body potential, and both of them are the function of not only the distance between two atoms and the angle formed by three atoms for three-body potential, but also the generalized coordination number of the atoms. The potential energy calculated by the EDIP depends on the local environment of the atoms through this generalized coordination number. EDIP has been applied to the liquid and the amorphous carbon and proved to be able to reproduce the static [13] and the dynamic [14] structures of them obtained by *ab initio* MD simulations, suggesting a very good transferability of the EDIP.

We have also confirmed the validity of our hybrid *ab initio*/classical MD method using EDIP by applying the hybrid method to the graphite sheet (graphen) for investigating the dynamic properties such as the heat transfer [14].

Figure 2 shows the model of nanostructured graphite on which the hydrogen atoms are absorbed. The model consists of five graphite layers and the central layer is divided into two separated graphite sheets with armchair edges in order to mimic a defective structure in the nanostructured graphite. Four hydrogen atoms are adsorbed at the edge of the left graphite sheet as shown in Fig. 2. The model system contains 1568 carbon atoms and four hydrogen atoms. The hydrogen atoms and the surrounding 32 carbon atoms are considered as the cluster region and are treated by *ab initio* DFT calculation.

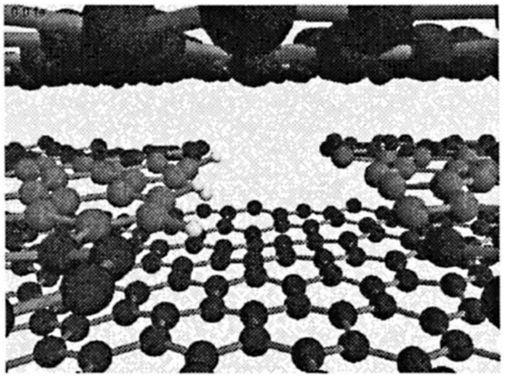


FIGURE 2 The atomic configuration obtained by the MD simulation for model I. The dark and light grey atoms are carbon atoms calculated using the EDIP and the DFT, respectively. The white atoms are hydrogen atoms.

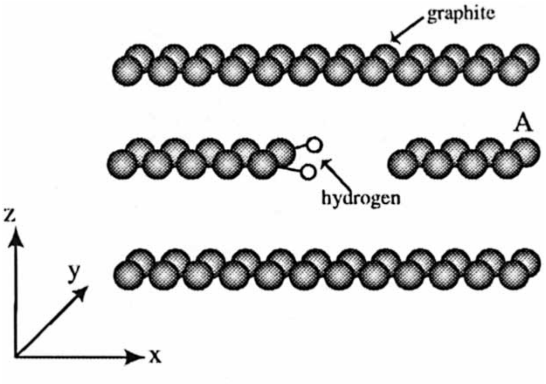


FIGURE 3 The schematic picture of the model system. The large grey atoms and the small white atoms denote the carbon and the hydrogen atoms, respectively.

Figure 3 shows the schematic picture of the system. On the y direction, we apply the periodic boundary condition. We consider two model systems. First, the gap between left and right graphite sheet is about 5 Å and there is no interaction between the hydrogen atoms and the right-hand carbon atoms. We carry out the hybrid MD simulation for this system (referred to as model I). The temperature of the system is 1000 K, which is the temperature corresponding to the second peak of the results of thermal desorption experiment [5]. Next, the sheet A is shifted to $-x$ direction artificially to mimic the recrystallization of the nanostructured graphite, so that the distance between two graphite sheets becomes about 1.5 Å, which is referred to as model II. We carry out the MD simulations for this model at 1000 K. Then, the temperature of the system is raised to 2000 K for carrying out further MD simulation. The time step of our MD simulations is 0.97 fs and the simulation is carried out at about 4.5 ps for these models.

RESULTS AND DISCUSSION

In the MD simulation for the model II, the recrystallization of graphite sheets occurs at 0.4 ps after we started the simulation. The recrystallization of graphite sheets means that two graphite sheets combine together to form a graphite sheet. Figure 4 shows the distance between two carbon atoms which bond together after the recrystallization. After 0.4 ps, the distance of two carbon atoms is about 1.5 Å, which corresponds to the C—C bond length of graphite. Due to the recrystallization, the hydrogen atoms are pushed by both sides of graphite sheets and move out of the sheet upward or downward.

To investigate the effects of recrystallization of graphite sheets on the dynamical properties of adsorbed hydrogen atoms, we calculate the Fourier transform of velocity autocorrelation functions (VAF) of hydrogen atoms, which is shown in Fig. 5. The peaks around 3000 and 1000 cm^{-1} correspond to the stretching mode of the C—H bond and the wagging motion of hydrogen atoms, respectively. It is seen that the frequency of the stretching mode shifts to lower frequency due to the recrystallization. Though the frequency of the wagging motion remains almost same, the relative strength of the stretching and wagging motion changes due to the recrystallization.

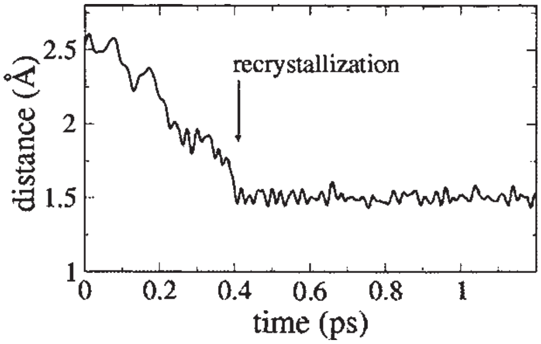


FIGURE 4 The distance between two carbon atoms of model II.

In Table I we show the bond lengths, the frequencies of C—H stretching mode and the bond angles related to the adsorbed hydrogen atoms before (model I) and after (model II) the recrystallization. As is shown in Table I, after the recrystallization, the C—H bond length becomes longer and the frequency of C—H stretching mode becomes lower, which suggest that the bonds between the hydrogen and carbon atoms become weaker. The local structure around the carbon atoms, which are connecting with hydrogen atoms, also change due to the recrystallization. After the recrystallization, the C—C bond length between the carbon atom,

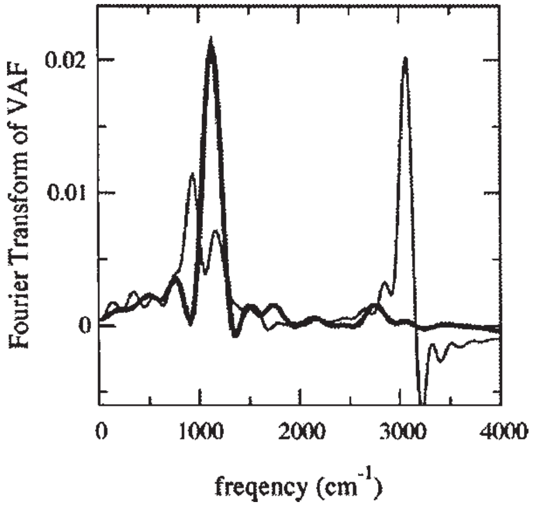
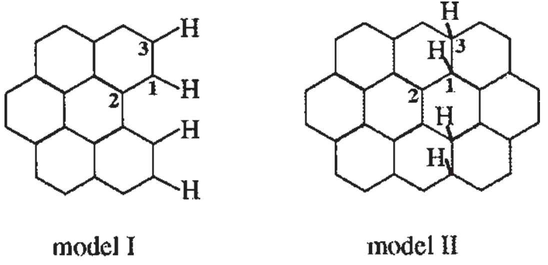


FIGURE 5 The Fourier transform of the velocity autocorrelation functions of hydrogen. The thin line and the thick line show the results obtained by the MD simulations for the model I and II, respectively.

TABLE I The bond lengths, the frequencies of C—H stretching mode and the bond angles around the carbon atoms which is bonding the hydrogen atoms

	Model I	*Model II*
Bond length (Å)		
C_1—H	1.11	1.13
C_1—C_2	1.41	1.55
Frequency (× 10^3 cm^{-1})		
C_1—H	3.05	2.76
Bond angle (°)		
H—C_1—C_2	119.6	101.1
C_2—C_1—C_3	119.5	116.0



which is bonding with the hydrogen atom, and the neighboring carbon atom becomes longer and the bond angle changes from about 120° (three-fold coordinates) to the smaller angle (four-fold coordinates). Note that the C—C bond length of model II is very close to that of the diamond, 1.54 Å.

After the MD simulation for the model II at 1000 K, we continue to carry out the MD calculation at the temperature of 2000 K for 4 ps. The wagging motion of the hydrogen atoms becomes more active than that at 1000 K, and after 0.5 ps, two hydrogen atoms form a hydrogen dimer. The dimer is stabilized and moves around between two graphite layers. Figure 6 shows the time dependence of the distance between two hydrogen atoms. The distance between the neighboring hydrogen atoms which are still bonding with carbon atoms is about 2.5 Å for the first 0.4 ps. At about 0.5 ps, these hydrogen atoms desorb from carbon atoms and form the hydrogen dimer. From 0.5 ps to 0.9 ps, the average bond length and frequency of H—H stretching mode are 0.89 Å and $3.7 \times 10^3\,cm^{-1}$, respectively. Note that the experimental value of the bond length and the frequency of an isolated H_2 molecule are 0.741 Å and $4.40 \times 10^3\,cm^{-1}$, respectively.

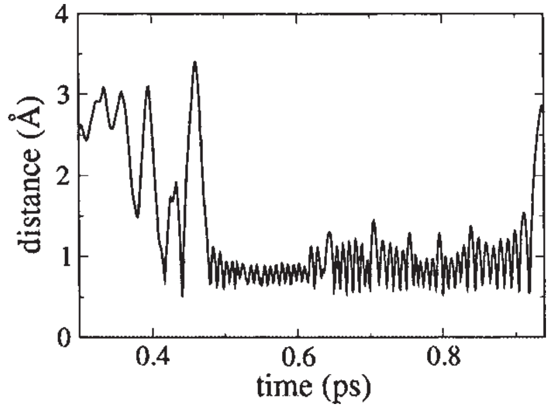


FIGURE 6 The time dependence of the distance between two hydrogen atoms which form the dimer.

CONCLUSION

We have applied the hybrid MD simulation to the model system for the nanostructured graphite with four adsorbed hydrogen atoms to investigate the effects of the recrystallization on the bonding states of hydrogen atoms. We have shown that the C—H bonds become weaker due to the recrystallization in the sense that the C—H bonds become longer and the frequency of C—H stretching mode becomes lower after the recrystallization. After that, when the temperature is increased to 2000 K, the C—H bond breaks and two hydrogen atoms bond together. The H—H bond is stable and the dimer diffuses between two graphite layers. Thus we have found that the recrystallization of graphite sheets together with increasing temperature is one of the possible mechanisms of the hydrogen desorption from the nanostructured graphite.

Acknowledgements

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