Large Scale Simulations for Carbon Nanotubes

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CARBON NANOTUBE RESEARCH GROUP
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Nano carbon materials as nanotube and fullerene have a potential for applications to the advanced industries. For nano carbon materials, it has been recognized that large-scale simulation is a powerful and efficient tool to find and create new functional nano carbon materials.

Aiming at conducting the productive simulation for nano-materials, we have developed the large-scale simulation models such as tight-binding molecular dynamic model, *ab-initio* density functional theory (DFT), and time-dependent DFT model.

In this term, by utilizing these models effectively, we have studied various physical properties of nano-carbon and applications such as (1) Novel Functions of Mackay Crystal, (2) Structural relaxation of Nano Diamond, (3) Large-scale Simulation on Electron Conduction in Carbon Nanotubes at Finite Temperature, (4) Application of time-dependent density functional theory for irradiation of strong optical field on nano-carbons. Along these works, we have realized that the Earth Simulator is a very powerful tool for large-scale nano-material simulations.

Keywords: Large scale simulation, TB theory, ab initio theory, Time-dependent DFT, Carbon Nanotube, Fullerenes, Green energy, solar cell, photoelectric material

1. Introduction

Nano-carbon materials have been expected to bring breakthrough to material science and nanotechnology. A lot of potential applications of nanotube and fullerene to electronic devices have been attracted to scientists and engineers.

In the present days, large-scale numerical simulation by using supercomputer's computational performance has turned to be a very efficient tool and leverage for investigating their novel material properties. It now allows us to simulate complex nano-structures with more than ten thousand atom of carbon.

Aiming at using large-scale simulations on the Earth Simulator, we have developed an application package of *ab initio* DFT theory and parameterized tight-binding (TB) models. Especially, the TB model shows that it is very suitable for the very large systems even if it has a lack of symmetrical arrangement.

In this term, we have carried out simulation studies, in which there are three primary objectives as (1) design of innovative nonmaterial with the required properties; (2) obtain fundamental properties in nano-scale matter, and (3) develop new applications.

2. Physical studies on nano materials

2.1 Novel Functions of Mackay Crystal [1]

The comprehensive simulation has been conducted so far on properties of the Mackay crystal, focusing on synthesis process through atomic arrangement of GSW and mechanical properties as stiffness, etc.. As Mackay crystals, it is well known that there are three different sizes and types. The crystal is classified as P, D, G-types, by the atomistic bonding configuration of hexagon or octagon on the surface curvature of the unit cell.

In this term, focusing P type crystal, the dependency of

energy band gap on the crystal size has been investigated though simulating the electronic band structure by DFT model.

This result indicates that Mackay crystal has a potential for highly efficient photoelectric material for solar cell. The energy band structures and electron density distribution are shown in Figs. 1-3. These show that the band gaps are ranged from 0.05eV to 0.94 eV and the electron density depends on the size of atomic unit cell. The peak of electron density appears at octagon bonding and the lowest at hexagon in the direction to (111). It is the reason why the intrinsic electron density

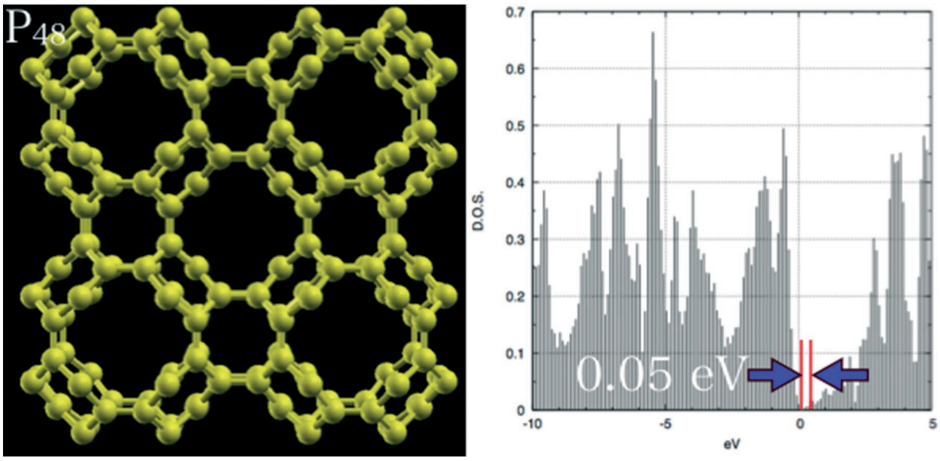

Fig. 1 Energetically optimized structure of P48 zigzag Mackay crystal and energy band structure.

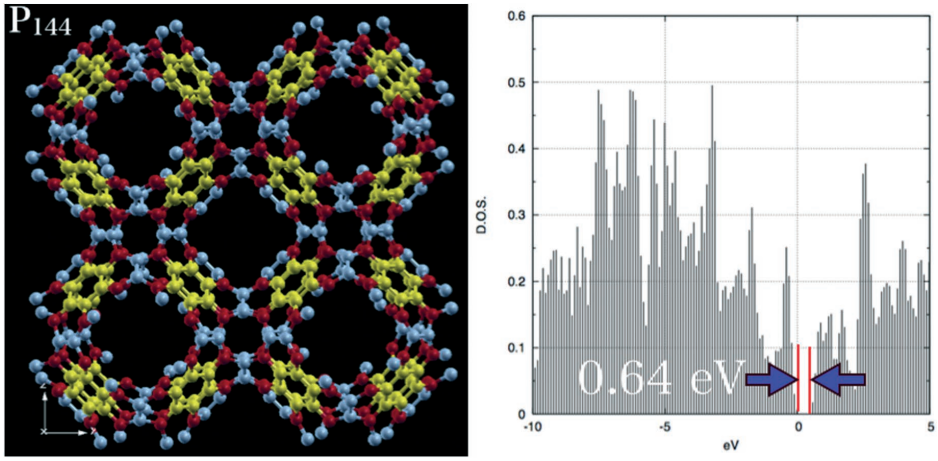

Fig. 2 Energetically optimized structure of P144 zigzag Mackay crystal and energy band structure. The color represents number of electrons, which decreases in the order of yellow and red.

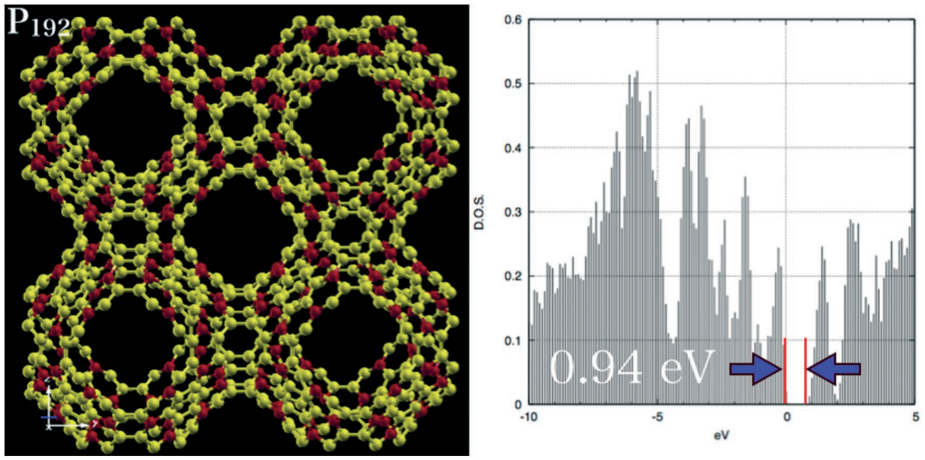

Fig. 3 Energetically optimized structure of P192 armchair Mackay crystal and energy band structure. The color represents number of electrons, which decreases in the order of yellow, red and aqua.

distribution and band gap are due to the existence of octagon forming the negative curvature of Mackey crystal.

Absorbable wavelengths of sun light depend on the energy band gap of the photo-electric material. By stacking Mackey crystal films with the different size, a tandem-type solar cell has been designed conceptually, which would be able to absorb the sun light with near infrared light. As the next step, the feasibility study of Mackey crystals for solar cell will be made by large-scale simulations.

2.2 Structural relaxation of Nano Diamond

Recently the fragment-diamond transformed into carbon-onions, so called as nano-diamond, was synthesized experimentally. Some researches & developments have been made by modifying the nano-diamond chemically to disperse or gel in solution for a drug delivery system. Presently there is no information on the characteristics of the surface of nano-diamond that leads us to select the adequate molecules to chemical modification.

For reliable and accurate simulations, DFT simulations have been carried out to describe the properties on size, temperature and pressure dependence. The relaxation simulation has made on two sizes of nano-diamond by using DFT model. The initial structure is set in truncated octahedron and the number of atoms is 147 and 413 .

The structure of before- and after- relaxation are shown in Figs. 4 and 5 for C_{147} and C_{413} , respectively. It shows that the surface layer of the (111) is graphitized with sp^2 bond. The area of graphite layer increases as the size of the nano-diamond increases. The direction (100) consists of the diamond structure with sp^3 bond. The mixing state of sp^2 and sp^3 bonds is expected to generate the polarized electric fields with functional elements.

The polarized nano-diamond might be one of the functional elements for the drug delivery system or some fields. As a next step, large-scale simulation will be carried out on nano-diamond with thousand atoms.

2.3 Large-scale Simulation on Electron Conduction in Carbon Nanotubes at Finite Temperature [2]

According to Moore's law, which states that the number of transistors in integrated circuit (IC) will double every 18 months, the rapid development of ICs has to a large extent

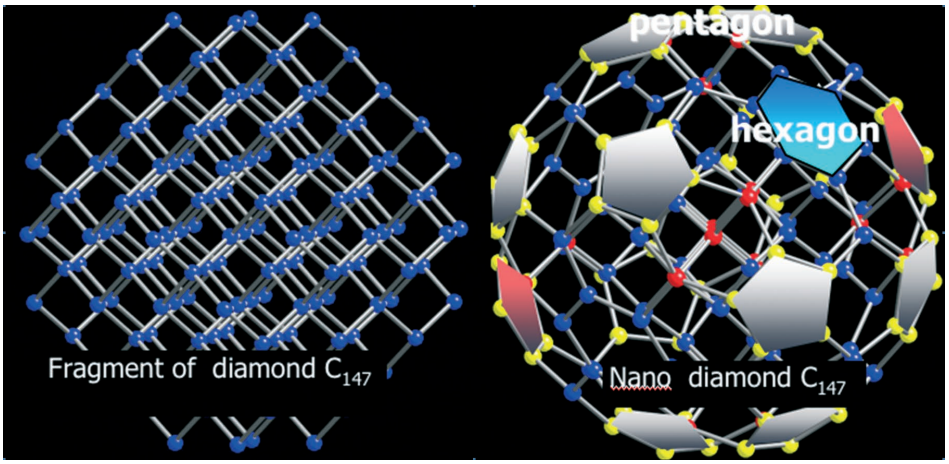

Fig. 4 C_{147} octahedral nanodiamond structure before (left) and after (right) the relaxation simulation.

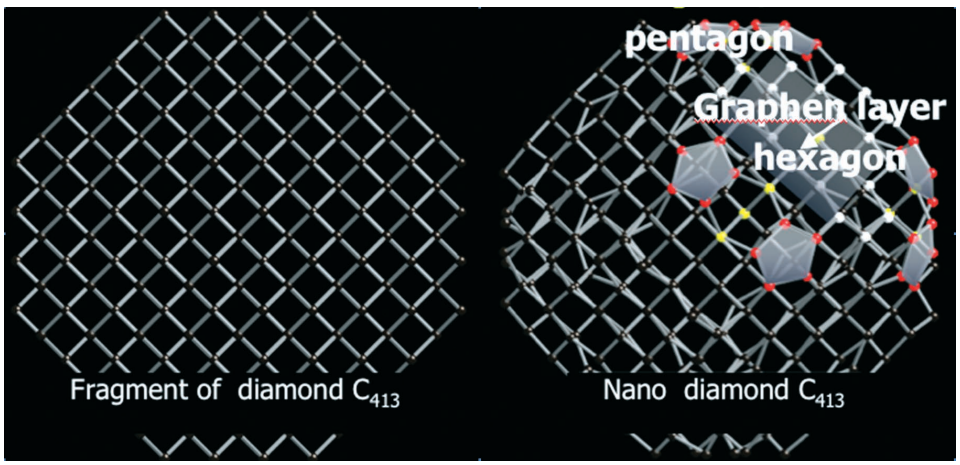

Fig. 5 C_{413} octahedral nanodiamond structure before (left) and after (right) the relaxation simulation.

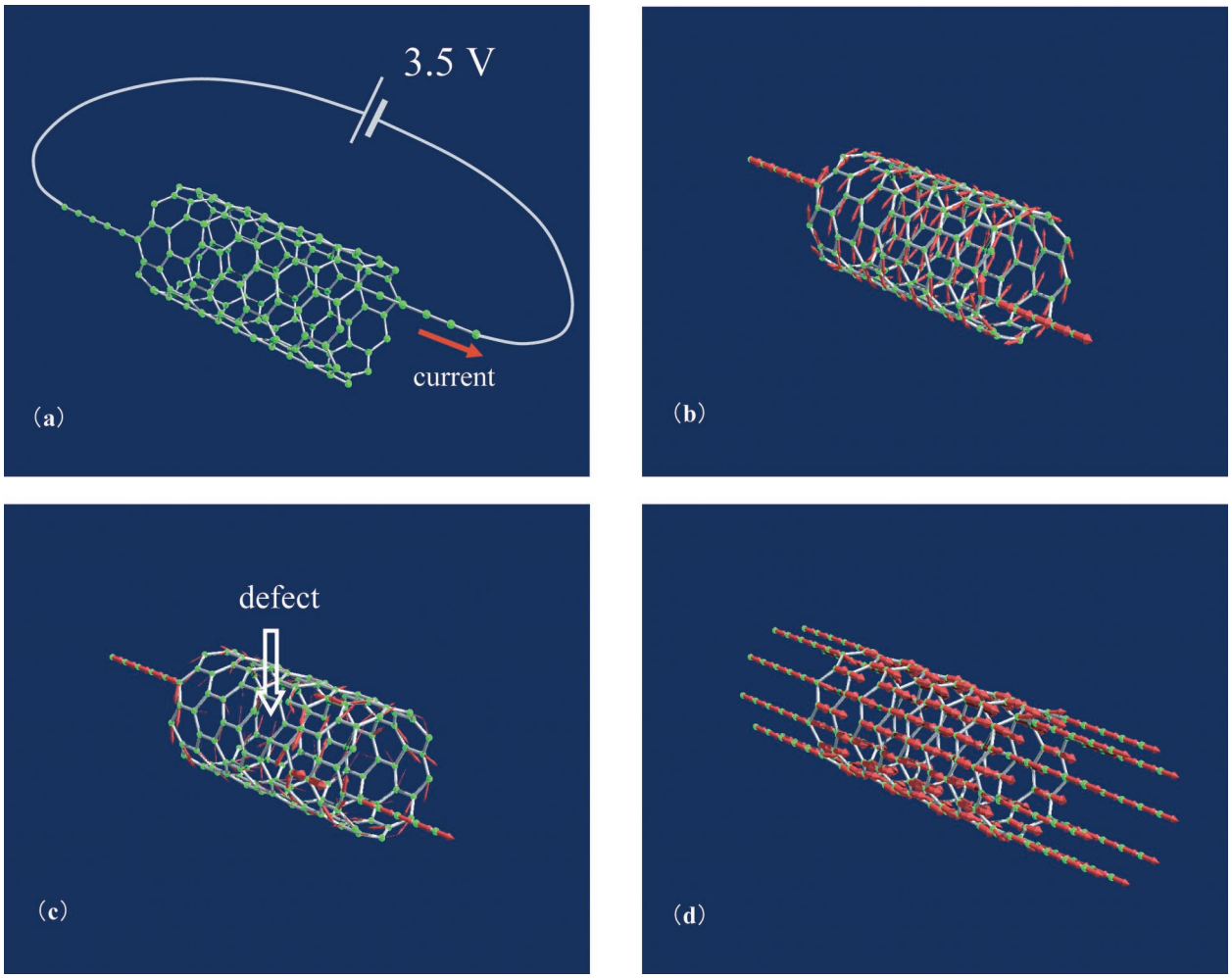

Fig. 6 (a) shows a schematic view of the system under consideration. Figures 1 (b), (c), and (d) show our simulation results under three different conditions: (b) The line connecting two electrode-junctions is not parallel to the axis of CNT. (c) Under the identical condition as Fig. (a) except for the existence of a defect in the CNT. (d) Many electrodes are attached on the CNT.

been enabled due to the improvement of a transistor design based on Silicon. By scaling down dimensions, the silicon-based technologies have been pushed close to its physical limits as soon as the end of this decade. Therefore it becomes crucial to develop technologies that will enable continued implementation of increasingly higher performance devices.

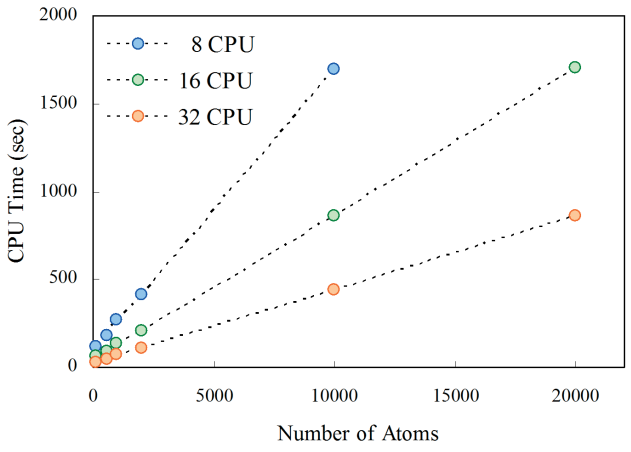

Fig. 7 CPU time versus the number of carbon atoms

Carbon nanotubes (CNTs) are considered attractive candidates for new technologies that could take the place of the silicon-based electronic.

It is still difficult, however, to manipulate CNTs experimentally; and besides the macroscopic Ohm's law breaks down due to the various effects caused by the microscopic size effect. In this context, it is necessary to study the transport behavior of CNTs using a quantum mechanical simulation. We have developed a simulation code by which electron transport simulations of nano- and meso-scale CNTs can be performed. We focused on the system under consisting of two semi-infinite electrodes and a scattering region sandwiched between these electrodes (see Fig. 6 (a)).

Using non-equilibrium Green's function (NEGF) technique, we obtain the following expression for electron current from j_1 site to j_2 site.

$$J_{j_1\to j_2}=\frac{e}{\pi}\sum_{\xi_1\xi_2}t_{j_2\xi_2 j_1\xi_1}(\{R\})\int\{f(\omega-\mu R)-f(\omega-\mu L)\}$$
$$\times\sum_{\sigma}\mathrm{Re}[G^{r}_{CC}(\omega)\{-i\Gamma_L(\omega)\}G^{a}_{CC}(\omega)]_{(j_1,\xi_1,\sigma)(j_2,\xi_2,\sigma)}d\omega,$$

with $-i\Gamma_L(\omega) = \Sigma^{r}_{L}(\omega) - \Sigma^{a}_{L}(\omega)$,

$$G_{CC}(z) = \frac{I_{CC}}{zI_{CC} - H_{CC} - \Sigma_L(z) - \Sigma_R(z)},$$

$$\Sigma_L(z) = H_{CL}\,\frac{1}{z - H_{LL}}\,H_{LC},$$

$$\Sigma_R(z) = H_{CR}\,\frac{1}{z - H_{RR}}\,H_{RC}.$$

Here Hcc is the matrix describing the scattering region sandwiched between electrodes. Σ_L is the self-energy of the left-hand side electrode, and Σ_R the self-energy of the right-hand side. In this scheme, the large-dimensional matrix inversion to calculate the Green's function in the scattering region becomes the most heavy part of the model computationally. An embedding potential algorithm is implemented to obtain the equilibrium and non-equilibrium Green's functions.

Since the NEGF technique is also applicable to calculate the density of electrons, we determined NEGF self-consistently together with Poisson equation. The substitute charge method is considered to be a simple and effective method to solve the Poisson equation. The positions of substitute charges, however, are empirically determined. Therefore, in our solution method, both the positions and the values of charges are determined so that the differences of the potentials on boundary are least in a sense of the least square method. In this case, the implementation of least square method is made with Davidon-Fletcher-Powell algorithm.

These figures 6 (b), (c), and (d) show our simulation results at 300 (K). The arrows represent the electron current in CNTs

From figures 6 (b), (c), and (d), one can find the following results: When the line connecting two electrode-junctions is not parallel to the axis of the CNT, circular current occurs. On the other hand, under the same condition except for the existence a defect in the CNT, circular current decreases. When many electrodes are attached on the CNT, current flows along the axis of the CNT and circular current does not occur.

Finally, CPU time versus the number of carbon atoms is shown in Fig. 7. One can see that our simulation code achieves the order (N) algorithm with respect to the size of the system. The sustained performance of 13 Tera flops was achieved, and the computing efficiency was seventeen percent of the peak performance.

2.4 Application of time-dependent density functional theory for irradiation of strong optical field on nano-carbons [3]

In this term, we discovered field enhancement inside nanotube and pulse-laser induced exfoliation of graphene from graphite surfaces. These phenomena suggested the possibility of efficient photo-fabrication of nano-carbons with controlled manners. This term, we further investigated these two subjects.

As for the exfoliation of graphene from graphite surface, we searched more efficient process, i.e., faster exfoliation with lower energy cost of laser-shot, by tuning the shape of pulse laser in the time-axis. Last year, the assumed wavelength of the laser was 800 nm, and pulse width was 45 fs. In this year, we just shorten the pulse width as 10 fs and compared the dynamics shown in Fig. 1.

When we further shorten the pulse width, nothing happened on the surface. Therefore, we believe that the pulse width as 10 fs is optimized for graphene exfoliation which should be tested by experiments in future.

As for the photochemistry of molecule inside carbon nanotube, we rely on experience of last year which was the enhancement of the electric field (E-field) inside semiconducting

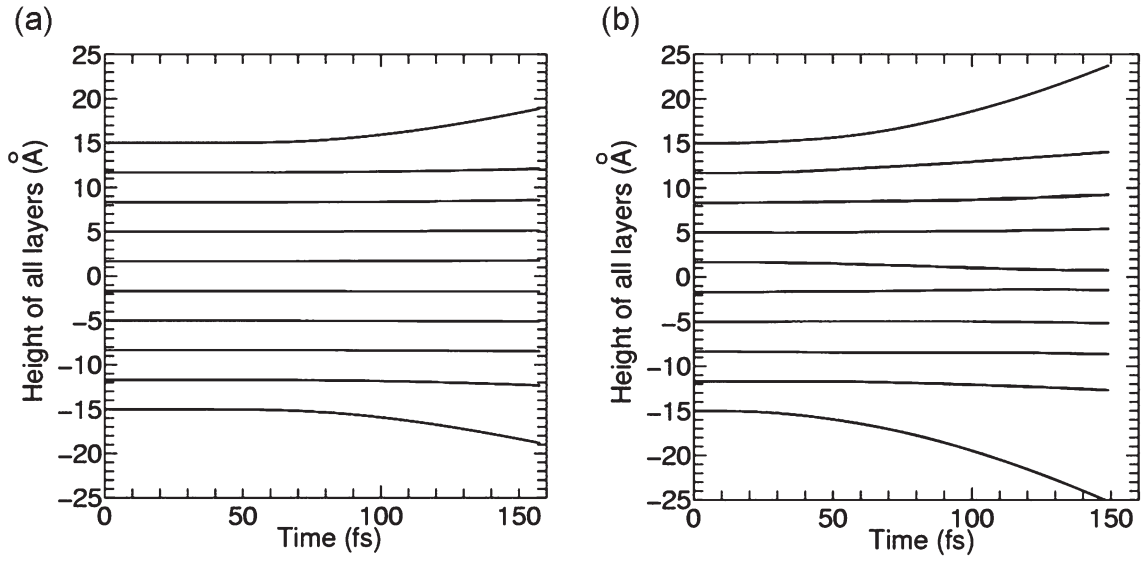

Fig. 8 Time evolution of heights of graphene layers (10-layer slab model having two surfaces on top and bottom) after irradiation of laser shot (a) with wavelength 800 nm, pulse width = 45 fs, and power per shot is about 87.9 mJ/cm^2, (b)with the same wavelength, pulse width 15 fs, and power 20 mJ/cm^2.

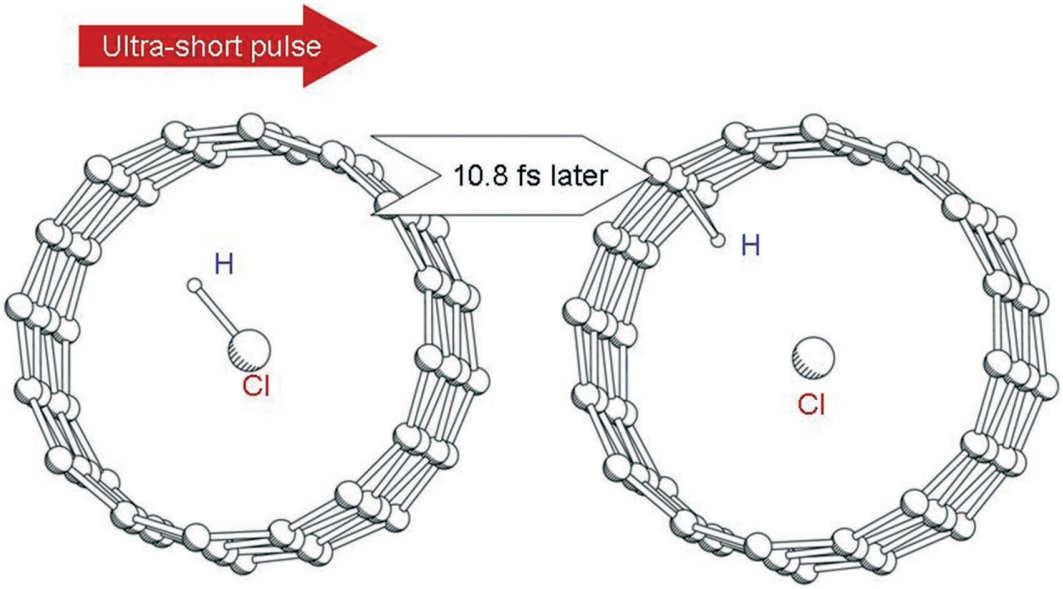

Fig. 9 Disintegration of an HCl molecule inside an (8,0) nanotube induced by very short pulse.

nanotube. We thus expect that trapping molecule inside semiconducting nanotube can make light illumination to molecule more efficient. We tested photo-induced disintegration of an HCl molecule inside an (8,0) nanotube.

Figure 9 shows the geometrical time-evolution of an HCl molecule inside an (8,0) nanotube after giving very short pulse shot with wavelength 800 nm, pulse width is 1 fs and maximum intensity of E-field is 12 V//Å. (Such an extremely high E-field is available only at such very short pulse.) One can note spontaneous disintegration of HCl molecule and an ejected H atom is sticking nanotube wall, so the H atom is expected to reflect from the wall. According to our preliminary test, the nanotube itself is sustainable under such short pulse with the same field-intensity, but show significant shaking motion. We therefore think further simulation is needed to check whether the nanotube can remain and to check trajectory of reflected H atom. We believe this simulation will design efficient photo-chemical processes using encapsulation of molecules inside carbon nanotubes.

3. SUMMARY

Large-scale simulations have been carried out on nonmaterial by using *ab initio* density functional theory and the parameterized tight-binding models. These optimized models allowed us to simulate the properties with excellent performance on the Earth Simulator. It enables us to come across discoveries of novel phenomena in nano scale and find out some useful materials for clean energies.

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カーボンナノチューブの特性に関する大規模シミュレーション

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1. 研究目的

優れた物性が予想されナノテクの基本材であるナノ炭素類（カーボンナノチューブ（CNT）、フラーレン、グラフェン）の電子・機械特性を従来不可能だった大規模シミュレーションにより推定し、科学技術及び産業界に提供すると共に、応用として特性の優れた新構造を発見し、基本材の拡充に寄与する目的で実施された。

2. 成果

これまで、我が国のナノチューブ研究で当面する課題解決に向けた応用シミュレーションを実施した。本年度さらに、グリーンエネルギーに関するシミュレーションを推進した。得られた結果を以下に示す。

(1) これまでマッカイ結晶の包括的な特性把握のために、合成法、機械特性などのシミュレーションを実施してきた。本年度は、電子構造特性のシミュレーションにより、マッカイ結晶が太陽電池材料としての可能性があることが示せた。サイズが異なる単位セルにそれぞれ 48、144、192 個の炭素をもつ P 型マッカイ結晶のエネルギーバンド構造を第一原理計算で調べたところ、0.05eV から 0.94eV のエネルギーギャップを持つこと、原子が中性電荷からずれていることが明らかとなった。これらの理由は、マッカイ結晶がもつ負のガウス曲面を維持するために基本となる 6 員環構造に 8 員環が混じり、特殊な電荷ポテンシャルが生じたためである。異なるバンドギャップをもつ積層半導体マッカイ結晶は、応用として、広範囲の波長の光吸収を可能とする、高効率太陽が期待される。

(2) タマネギ型構造をもち表面が活性で特徴的性質をもつナノダイヤモンドが合成されゲル状の分散が可能となった事から、ドラックデリバリーシステムなどへの応用も進められている。この構造体はダイヤモンドクラスターの構造最適化により得られるが、分子化学修飾が可能な表面の性質は未だ詳細に得られていない。DFT 計算手法により、ナノダイヤモンドのサイズ依存性を、147、413 原子について調べた。その結果、(111) 方向は sp^2 結合による黒鉛化し、(100) 方向は sp^3 結合によるダイヤモンド構造であることが明らかとなった。サイズが大きくなると黒鉛層が大きくなる。sp^2 と sp^3 の混在により、ナノダイヤモンドの電荷偏極が発生していると予測される。電荷偏極したナノダイヤモンドはドラックデリバリーシステム等への機能材料の一つと期待される。さらに大きなナノダイヤモンドの特性把握シミュレーションを予定している。

(3) 電子デバイスとしてシリコンを使った微細加工は限界に達している。カーボンナノチューブは次世代の電子デバイスとして期待されている。しかし、未だカーボンナノチューブを実験で操作することは困難であるが、オームの法則からなずれなどの量子効果が観測されている。ナノスケールの伝導特性を把握する事は重要である。非平衡グリーン関数法により、各原子から原子への電子の流れの計算手法を開発した。代用電荷法でポアソン方程式の電荷分布を再現した。カーボンナノチューブに流れる電流の微細な様子はワーヤー電極の着ける位置、本数で代わり、条件によっては渦電流の発生が確認された。また、不純物効果も扱う事もできた。コード性能評価により、計算量は原子数に比例するオーダー N であり、大規模計算が可能である事を確認した。

(4) 次世代電子材料として期待されるグラフェンの製造方法に関する知見をシミュレーションから得た。グラフェンの純度を損なわないように、化学物質の天下は行わず、グラファイト表面にフェムト秒レーザー照射を行うことにより、表面からの原子一 層分のグラフェンをはがせることが、第一原理計算より判明した。

キーワード:大規模シミュレーション, タイトバインディング理論, 時間依存密度汎関数法, オーダー N 法,
カーボンナノチューブ, マッカイ構造, ナノダイヤモンド, 量子伝導, グラファイト加工技術