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Se atom incorporation in fullerenes by using nuclear recoil and *ab initio* molecular dynamics simulation

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The formation of Se-atom-incorporated fullerenes has been investigated by using radionuclides produced by nuclear reactions. From the trace of radioactivities of ^{75}Se after high-performance liquid chromatography, it was found that the formation of endohedral fullerenes or heterofullerenes is possible by a recoil process following the nuclear reactions. To confirm the produced materials, *ab initio* molecular-dynamics simulations based on an all-electron mixed-basis approach were carried out. We found that the insertion of a Se atom into C_{60} cage is much easier than that of As and Ge atoms. The result indicates that an electron affinity of doping atoms seems to be important in the formation of foreign-atom-doped fullerenes.

Fullerenes have been presented a new type of carbon compounds and show very interesting physical and chemical properties since the discovery and the synthesis of a large amount of fullerenes.[1,2] Especially, the chemical interaction between C_{60} and a variety of atoms is becoming a very new field of cluster research. So far, numerous experimental studies for endohedrally doped[3-13] or exohedrally doped[14-16] fullerenes with foreign atoms have been undertaken by resorting to arc-desorption or laser-vaporization techniques. On the other hand, it has become possible to synthesize the heterofullerenes, where the foreign atom is incorporated into the carbon cage. Experimentally, heterofullerenes doped with foreign atoms, such as boron[17,18] (B), nitrogen[19,20] (N), and silicon[21,22] (Si) have been reported. In our previous studies, we have studied not only the endohedral doping of Be (Ref. 23), Kr, and Xe (Ref. 24) but also the substitutional doping of ^{11}C (Ref. 25), ^{13}N (Ref. 26), ^{69}Ge, and ^{72}As (Ref. 27) by a recoil-implantation process following nuclear reactions. In spite of the intense research, only partial facts for the formation process and the produced materials have been unveiled on the nature of the chemical interaction between a foreign atom and a fullerene cage. Therefore, it is important and intriguing to synthesize new complexes, such as several foreign-atom-incorporated fullerenes, and to investigate their properties so that knowledge about how to produce a large amount of these complexes is gained.

In this paper, we show evidence of Se-atom-incorporated fullerenes on the collision between a C_{60} cage and an Se atom, which was generated from a recoil process following nuclear reactions. We performed *ab initio* molecular-dynamics (MD) simulations to see whether the Se atom can be incorporated in the fullerene with the endohedral doping: Se@C_{60}. Furthermore, the chemical nature of the Se atom in a fullerene is compared with that of the Ge and As atoms.

In order to produce Se atom-incorporated fullerenes, about 10 mg of C_{60} fullerene powder was mixed homogeneously with 10 mg of As_2S_3 (200 meshes) and used to the target material. Deuteron irradiation with beam energy of 16 MeV was performed at the Cyclotron Radio-Isotope Center

(CYRIC), Tohoku University. Radioisotopes of ^{75}Se can be produced by ^{75}As$(d,2n)^{75}$Se reactions. The beam current was typically 5 μA and the irradiation time was about 1 h. The sample was cooled with He gas during irradiation. After the irradiation, the samples were left for 1 day to cool down the several kinds of short-lived radioactivities of byproducts. After the 1-day cooling, radioactivities, such as ^{11}C or ^{13}N, e.g., ^{11}C decays to ^{11}B with $T_{1/2}=20$ min, the radioactivities of ^{75}Se could be measured with its characteristic γ rays. The typical γ ray and the half-life ($T_{1/2}$) of ^{75}Se are 136 keV (and 265 keV), 120 days,[28] respectively.

The fullerene samples were dissolved in *o*-dichlorobenzene after being filtrated to remove insoluble materials through a membrane filter (pore size=0.2 μm). The soluble fraction was injected into a high-performance liquid chromatograph (HPLC) equipped with a 5PBB (silica bonded with the pentabromobenzyl group) column of 10 mm (inner diameter)$\times$250 mm (length), at a flow rate of 3 ml/min. The eluted solution was passed through a UV detector, the wavelength of which was adjusted to 290 nm in order to measure the amount of fullerenes and their derivatives. The fraction was collected at 30-sec intervals, and the γ-ray activities of each fraction were measured with a Ge detector. Therefore, the existence of ^{75}Se could be confirmed by their characteristic γ rays.

The elution curve shown by solid line in Fig. 1 indicates the absorbances monitored continuously by a UV detector for the irradiated samples of $C_{60}+As_2S_3$. The horizontal axis indicates the retention time after injection into the HPLC, and vertical one indicates the absorption intensity of the UV and the γ counting rate of the ^{75}Se radionuclide produced by the ^{75}As$(d,2n)^{75}$Se reaction. A strong absorption peak was observed at the retention time of 4.2–5.2 min in the elution curve (solid line) which was measured by the UV detector. This peak position corresponds to the retention time of C_{60} which was confirmed by the calibration run using the C_{60} sample before the irradiation. Following the first peak, two peaks at around 6.5–7.2 min and 10–15 min were consecu-
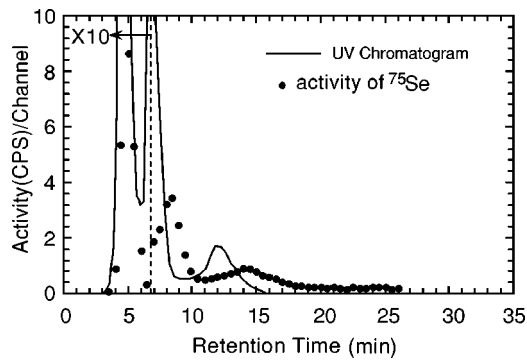
FIG. 1. HPLC elution curves of the soluble portion of the crude extracted in the deuteron-irradiated sample of C_{60} mixed with As_2S_3. The horizontal axis indicates retention time, while the vertical axis represents the counting rate of the radioactivities of [75]Se (solid circles) measured with a Ge detector and the absorbance of a UV chromatogram of C_{60} (solid line).

FIG. 2. Simulation of Se hitting the center of the uppermost six-membered ring (u-C_6) of C_{60} with a kinetic energy of 40 eV. Here, the local skeleton disappears from the figure when the bond length is elongated to more than by 1.5 Å .

tively observed in the UV chromatogram. This fact indicates that the second and smaller third peaks can be assigned to C_{60} dimers and C_{60} trimers, respectively, with resorting to TOFMAS measurements. These materials can be produced by the interaction between C_{60}'s in coalescence reactions after ionization by the incident or produced charged particles. Three peaks appeared in the curve of the ^{75}Se radioactivities in the radiochromatogram. Aside from a slight delay, the first peak (5.0 min) corresponds to the C_{60} UV absorption peak. The second and the relatively broad third peaks were observed at the retention time of 7–10 min and 11–18 min, respectively. Though there is a delay in the elution peaks of the radioactivities against that of the UV absorption peaks, it seems that the elution behavior is similar. This result indicates that the radioactive fullerene monomers and their polymers (dimers and trimers) labeled with ^{75}Se possibly exist in the final fractions.

In order to understand the present experimental results, *ab initio* molecular-dynamics simulations were carried out. The method, which is used here, is based on the all-electron mixed-basis approach[29–31] using both plane waves (PW's) and atomic orbitals (AO's) as a basis set within the framework of the local density approximation (LDA). In the present study, all the core atomic orbitals are determined numerically by a standard atomic calculation based on the Herman-Skillman framework with logarithmic radial meshes. We use the Ceperley-Alder fitting form for the LDA.[32] For the present system, we use 318 numerical AO's and 4169 PW's corresponding to a 7-Ry cutoff energy. For dynamics, we assume the adiabatic approximation where the electronic structure is always in the ground state. We utilize a supercell composed of $64 \times 64 \times 64$ meshes, where one mesh corresponds to 0.196 Å . We set the basic time step as $\Delta t = 0.1$ fs and perform five steepest descent (SD) iterations after each updation of atomic positions. We do not impose any velocity control, so that the system is almost microcanonical with a little energy dissipation from the SD algorithm.

First, we show the results of the following simulation: an Se atom with a kinetic energies (KE) 40 eV hits vertically the
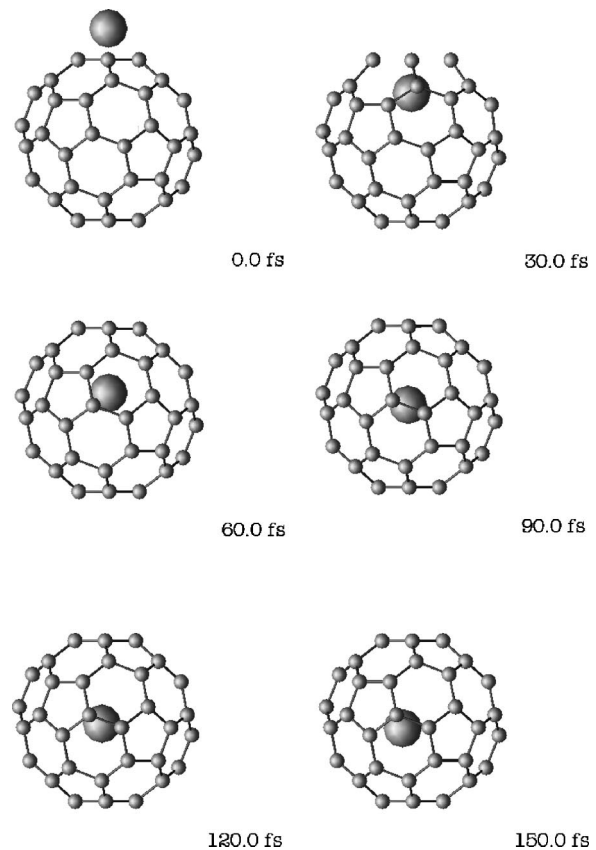
center of the uppermost six-membered ring (hereafter we call it u-C_6) of C_{60}. From the simulation, we found that an Se atom can penetrate into C_{60} easily when its initial speed is 40 eV and stop at the inside of the C_{60} cage (see Fig. 2), although an Se atom goes out again from the opposite side of the cage when its initial speed is greater than 100 eV. For an interaction with the KE lower than 40 eV, the Se atom first touches u-C_6 and carbon atoms are pushed to open u-C_6, but the u-C_6 soon recovers its initial configuration. Similar simulations were performed for the case of As.[27] In this case, we found that an As atom can penetrate into C_{60} if its KE is greater than 70 eV, although an As atom goes out again from the opposite side of the cage when its initial energy is greater than 160 eV. Comparing Se and As, we found that the formation of Se@C_{60} seems to be easier than that of As@C_{60}, because the energy range of the insertion for the Se atom is relatively lower than that for the As atom.

Second, we put additionally one Se atom on the radial axis by 1.39 Å inward from the original C position of C_{60}, and then start the simulation with zero initial velocity. Then we found that there is a force acting on the Se atom to accelerate it inward, and finally the Se atom stops at around the center of C_{60}. Thus the Se-encapsulated fullerene, Se@C_{60}, is reproduced. Similarly, when we put additionally one As atom on the same radial axis by 1.39 Å inward from the original C position of C_{60}, on the contrary, there is a strong

force acting on the As atom to accelerate it outward and, as a result, to repel the outward C atom. Finally, the As atom[27] stops at 0.50 Å from the cage sphere. Thus, it seems that the As atom put inside the cage is relatively unstable and has a strong tendency to repel the closest C atom of C_{60}, and is stabilized slightly outside the cage sphere after the removal (emission) of the closest C atom. Therefore, a hetero-fullerene, such as AsC_{59}, may exist stably under realistic conditions. It should be noted that similar results for the case of a Si atom have been reported by Pellarin and co-workers[21,22] (however, the possibility for endohedral doping, $As@C_{60}$, cannot be completely ruled out at present; there seems to be a local stable point inside the cage).

Radiochromatograms of ^{69}Ge, ^{72}As and ^{75}Se are shown in Figs. 3(a) and 3(b), respectively. The area ratios, the peak area assigned by A and B in Figs. 3(a) and 3(b), are shown in Fig. 3(c) for Ge, As and Se atoms, respectively. It is interesting and important to note that the area ratio A/B (monomer/dimer) in the radiochromatogram of ^{75}Se is much larger than that in the radiochromatogram of ^{72}As (and further much larger than that in the radiochromatogram of ^{69}Ge). This trend indicates that the shock caused by a collision with higher KE (e.g., ~ 70 eV, for an As atom) most probably induced the cage to create dimers with a higher rate.

The difference can be due mainly to the nature of the covalent bonding between the C atom and the 4B–6B (Ge–Se) atoms. An electron affinity of the Se atom is greater than that of Ge and As atoms. It seems that a hall of u-C_6 at the collision between Se and C_{60} comes to be larger due to the occurrence of a few-electron transfer from the u-C_6 to Se atom. Therefore, the penetrability of the Se atom into C_{60} may increase, compared with that of As and Ge atoms.

In this study, the formation of atom-incorporated fullerenes has been investigated by the trace of radioactivities of ^{75}Se produced by nuclear reactions. It was found that a 6B element, like Se, remained in the final C_{60} portion after a HPLC process. This fact suggests that the formation of ^{75}Se atom-incorporated fullerenes can be possible by a recoil process following nuclear reactions. Carrying out *ab initio* MD simulations on the basis of the all-electron mixed-basis approach, we showed possibility of the formation of endohedral fullerenes for Se atoms. In comparison with 4B–6B (Ge–Se) atoms, we found that the insertion of a Se atom into a C_{60} cage is much easier than that of As and Ge atoms.
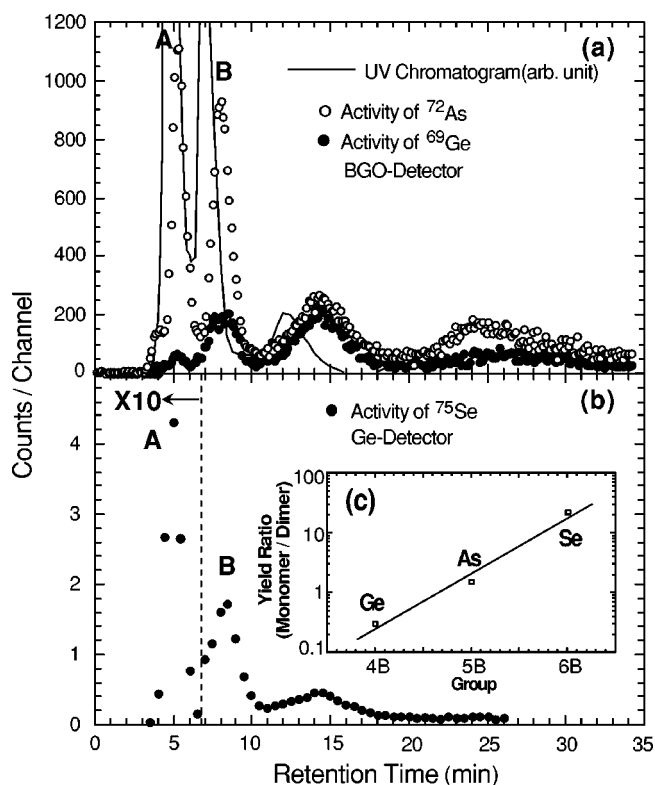

FIG. 3. (a) HPLC elution curves of the soluble portion of the crude extracted in the deuteron-irradiated sample for the production of ^{69}Ge and ^{72}As taken from Ref. 24. The horizontal and vertical axes are same as Fig. 1, but for ^{69}Ge and ^{72}As. (b) Same as (a), but for ^{75}Se for comparison with the ^{69}Ge and ^{72}As cases. The difference in vertical scale between (a) and (b) is due to the efficiency of the BGO and Ge detectors. (c) Area ratio, monomer/dimer indicated by peaks A and B in (a) and (b), in the radiochromatogram of 4B–6B (Ge–Se) atoms.

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