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Atomic structure and stability of elliptical carbon onion

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Abstract. Elliptical carbon onions were produced from amorphous carbon by electron beam irradiation. Atomic structure and structural stability of the onion were investigated by high-resolution electron microscopy, molecular mechanics calculation and molecular orbital calculation, and a structure model of C_{24}@C_{84} was proposed at the center of the elliptical onion.

PACS. 61.48.+c Fullerene and fullerene-related materials – 61.16.-d Electron, ion, and scanning probe microscopy – 31.15.Ct Semi-empirical and empirical calculations (differential overlap, Hünkel, PPP methods, etc.)

1 Introduction

Carbon nanostructures have been studied in recent years, since they have a high potential for many technological application [1-5]. They have various structures such as C_{60}, giant fullerenes, nanocapsules, onions, nanopolyhedra, cones, cubes and nanotubes. Cluster-included fullerene materials are especially interesting because they have applications such as nano-ball bearings and biotechnologies. The formation of carbon onions with sphere shape by electron-beam irradiation has been reported, which is a useful method for the in-situ synthesis [6–8].

The purpose of the present work is twofold. The first is to prepare a new onion structure. An electron-beam irradiation technique was used for the formation. The second purpose is to investigate the produced onion structures by high-resolution transmission electron microscopy (HREM) and theoretical calculations.

2 Experimental procedures

Amorphous carbon was fabricated by annealing polyvinyl alcohol at 400 °C in Ar [9]. The amorphous carbon was irradiated by an electron beam for 30 min under a beam current of 100 μA cm^{-2} at 1250 kV. This beam current is twenty times as large as that of ordinary observation by electron microscope [10,11]. To understand the formation mechanism of the cage structures, high-resolution electron microscopy was carried out for microstructure analysis. Theoretical calculations for structure stability were carried out by molecular mechanics calculations (MM2) and molecular orbital calculations (MOPAC).

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Table 1. Calculated values of C_{24} and C_{84}.

	C_{24}	C_{84}
Lateral size (nm)	0.463	0.947
Vertical size (nm)	0.333	0.674
Inter-atomic distance of the 5-membered rings (nm)	0.1523	0.1441
Inter-atomic distance of the 6-membered rings (nm)	0.1423	0.1424
Total steric energy (kcal/mole)	144	178
Heat of formation (kcal/mole)	776	990

3 Results and discussion

A HREM image of an elliptical onion with six carbon layers after electron-beam irradiation of amorphous carbon is shown in Fig. 1(a). The carbon vibration was also observed at the surface of the onion. There would be C_{24} and C_{84} cluster at the center of the elliptical onion from the sizes of 0.4 nm and 0.9 nm. The structure models of C_{24} and C_{24}@C_{84} are proposed, as shown in Figs. 1(b) and 1(c). The C_{24} and C_{84} structures are optimized by molecular orbital calculations using PM3. The inter-atomic distances of the carbon atoms are listed in Table 1. The inter-atomic distance of 5-membered rings of C_{24} is larger than that of C_{84}, which would be due to the adjacent 5-membered rings of C_{24} and the calculation results indicates that the C_{24} would be more stable than C_{84}. The C_{24}@C_{84} cluster is also optimized by molecular mechanics calculations (MM2), and the C_{84} cluster shrank slightly after the calculations. The lateral and vertical size of C_{24}@C_{84} are 0.926 nm and 0.782 nm, respectively. If outer clusters were calculated together, the size of the onion would

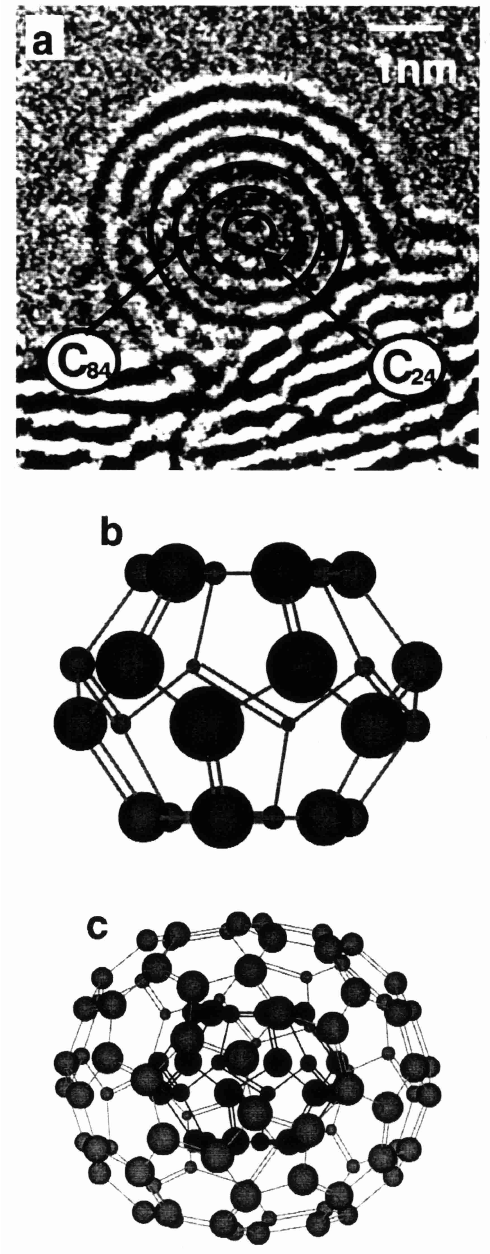

Fig. 1. (a) HREM image of the elliptical carbon onion. Structure models of (b) C_{24} and (c) $C_{24}@C_{84}$ clusters.

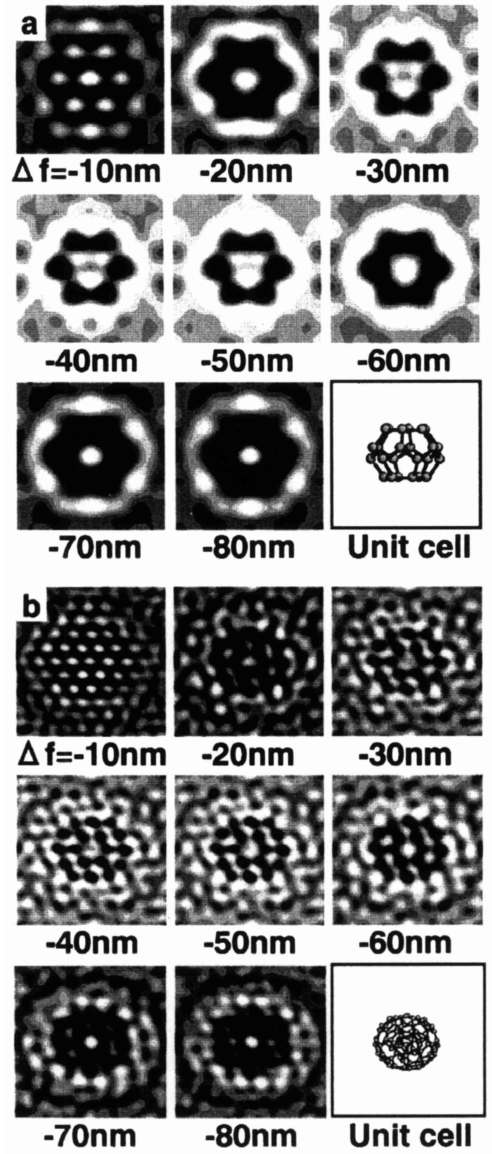

Fig. 2. Calculated HREM images of (a) C_{24} and (b) $C_{24}@C_{84}$ clusters as a function of defocus values.

additionally shrink and agree well with the observed image. HREM images of C_{24} and $C_{24}@C_{84}$ calculated along the [100] direction of the projected unit cell as a function of defocus values are shown in Figs. 2(a) and 2(b), respectively. The experimental data agree with HREM images calculated at the defocus value of 50 nm.

The onion would be formed from outside because C_{24} is too unstable to be fabricated, compared to C_{60} and related giant fullerenes. The most outside layer would be formed first time, and inside layers would be formed by gradation. In the end, the number of remaining carbon atoms is important to construct the structure at the center of the onion, so that C_{24} would be formed in the present work. Concerning the shape and the size of the onion, the center of the onion would be C_{24}, and the onion would have any effect from the carbon layer located outside.

4 Summary

The new elliptical-onion structure with 6 carbon layers was produced. HREM observation, image calculations, molecular mechanics calculations and molecular orbital calculation were performed for structure analysis. The structure model of C_{24} was proposed at the center of the elliptical onion, and the heat of formation was calculated to be 776 kcal/mole. The stability of $C_{24}@C_{84}$ were also calculated, which indicates they are stable. Image simulations of the $C_{24}@C_{84}$ clusters agree with the observed images of the elliptical onion.

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