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Formation of carbon onions with Pd clusters in a high-resolution electron microscope

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Carbon onions have been produced in a transmission electron microscope by electron irradiation of amorphous carbon in the presence of Pd clusters. High-resolution electron microscopy revealed structural changes of the onion surface, and atom clouds were observed at the pentagonal vertices. In some onions, Pd atoms were intercalated between the graphite onion sheets, and a structural model for the intercalation has been proposed. The present work indicates that electron-beam irradiation of amorphous carbon in the presence of Pd clusters is an effective method for the formation of intercalated onions.

1 Introduction

Carbon exhibits various hollow cage structures such as C_{60}, giant fullerenes, nanocapsules, onions, nanopolyhedra, cones, cubes and nanotubes.[1–7] These structures display different physical properties, and show potential for studying materials of low dimensionality within an isolated environment. Nanoclusters encapsulated within these carbon hollow cage structures are intriguing for both scientific research and future device applications such as cluster protection, nano-ball-bearings, nano-optical-magnetic devices, catalysis and biotechnology.[8–11]

Carbon onions are formed from carbon soot or diamond by electron-beam irradiation or annealing at elevated temperatures.[3,12–15] These carbon onions have spherical concentric graphite shells with the innermost shell *ca.* 0.7 nm in diameter, which can be regarded as C_{60}. The stability of such onions (polyhedral structures) has been calculated theoretically.[16–19] Large fullerenes show less strain because of nearly sp^2 bonding in the connecting of carbon atoms. The observed spherical structures would be due to inclusion of defects such as heptagonal bonding.

Carbon onions filled with Au and LaC_2 have been reported.[20] Various types of carbon nanocapsules incorporating clusters (Co, Fe, Ni, Cu, CrC_x, MoC_x, MoO_3, WC_x, WO_3, TiC, SiC *etc.*) have also been reported.[4,7–11,21–27] The arc discharge method[28] is a traditional method for the formation of hollow cage structures. However, it is hard to separate these cages from carbon soot, and an understanding of the formation processes are difficult because of the coexistence of various carbon products and of high-temperature annealing. The formation of carbon onions with cage structures by electron-beam irradiation has also been reported,[3,12–15] which is a useful method for the investigation of the formation mechanism by direct *in situ* observation.

The purpose of the present work was to produce carbon onions in an electron microscope by electron-beam irradiation. Pd clusters were mixed with amorphous carbon to induce onion formation. It is known that Pd clusters have catalytic effects,[29] which will induce the formation of carbon onions from amorphous carbon. In addition, the size of the Pd clusters used is very small and controllable.[29] To understand the formation mechanism of carbon onions, *in situ* observation and microstructure analysis were carried out by high-resolution electron microscopy (HREM). These studies give visible information on the formation mechanism of carbon onions with Pd clusters.

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2 Experimental

Pd clusters were prepared by the reduction of H_2PdCl_4 with trisodium citrate, and stabilized by *p*-$H_2NC_6H_4SO_3Na$.[29–31] The Pd colloidal particles were isolated in the solid state on an amorphous carbon support.

Samples for HREM observation were prepared by dispersing the materials on holey carbon grids. HREM was performed with a 200 kV electron microscope (JEM-2010) having a point-to-point resolution of 0.194 nm. The electron microscope is equipped with the TEM-IP system (PIXsysTEM) and imaging plates with the benefit of a large detection area and digital data were used to record the observed images. The detection area of the IP is 102 × 77 mm with a pixel size of 25 µm × 25 µm and an image depth of 0–16 383 gray scale. The digital data were saved *via* digital data storage (DDS) by Digital Micro-Luminography (Fuji Film Co. Ltd.). For image processing and analysis of the observed HREM images, Image Gauge, L process (Fuji Film Co. Ltd.), Digital Micrograph (Gatan Inc.) and Adobe Photoshop software were used.

3 Results

A typical HREM image of as-prepared Pd clusters in a carbon matrix is shown in Fig. 1(a). The Pd clusters which have higher atomic number *cf.* carbon show dark contrast in the carbon matrix. The cluster size is 2.5 nm with a size distribution of ±0.5 nm, which indicates the core structure is a five-to-six shell structure. Lattice fringes with a separation of 0.23 nm which corresponds to the distance of the {111} planes of fcc Pd are observed in the clusters. From the HREM image the carbon matrix is found to have an amorphous structure.

The same region was irradiated with an electron beam for 5 min with a beam current of 150 pA cm^{-2} at 200 kV, as shown in Fig. 1(b). This beam current is *ca.* 20 times higher compared to that used for ordinary observation by electron microscopy. Graphitization of amorphous carbon is observed, which is confirmed by the lattice fringes of graphite layers with a spacing of *ca.* 0.34 nm. In addition, Pd clusters combined to form Pd nanoparticles of size *ca.* 4 nm. After electron irradiation for 20 min, graphitization of the carbon matrix progresses as shown in Fig. 1(c). Graphite shells with onion and half-onion structures are observed as indicated by arrows A and B, respectively. Fig. 1(d) is an HREM image of the

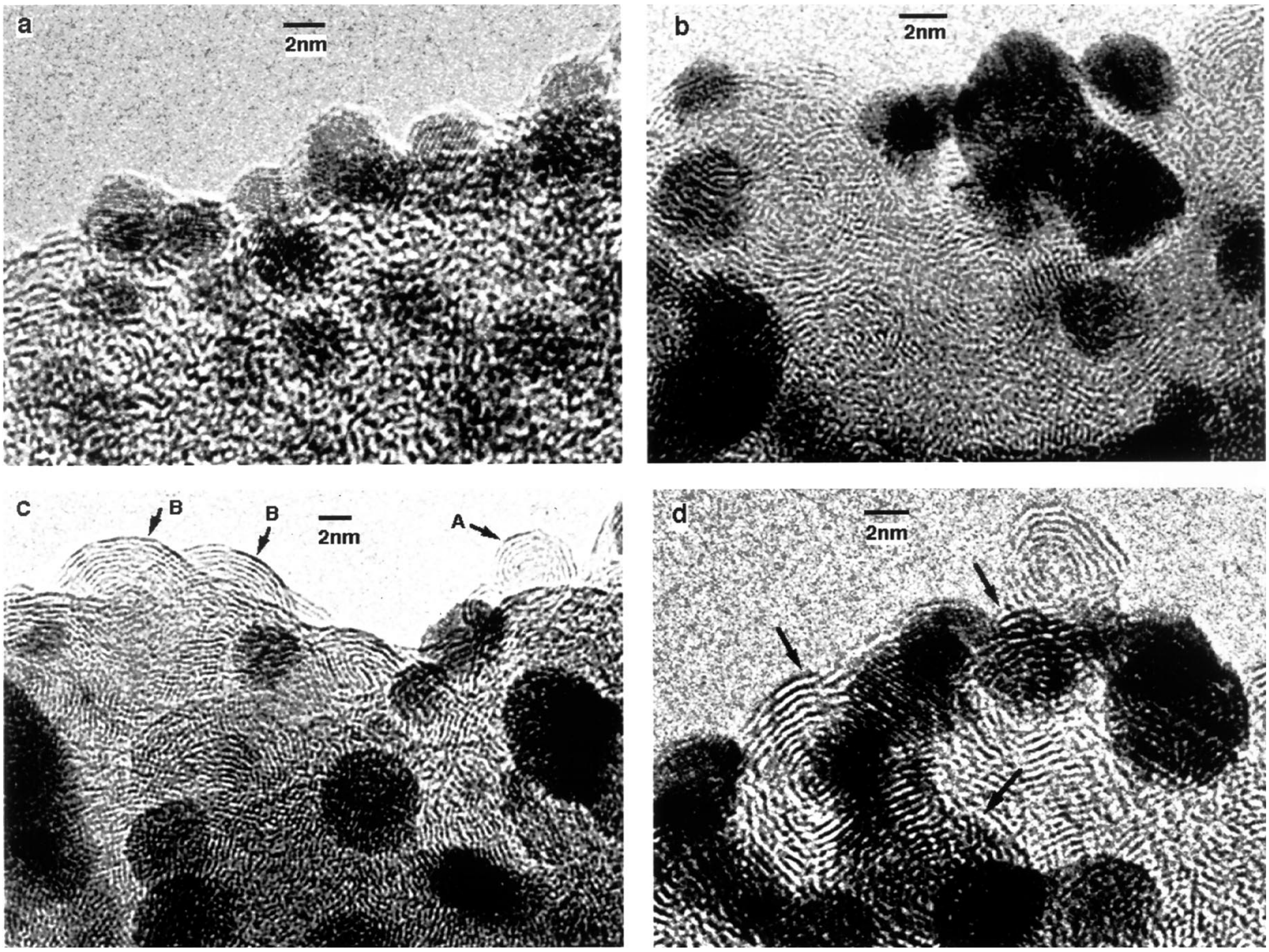

Fig. 1 (a) HREM image of as-prepared Pd clusters in a carbon matrix. HREM images at the same region after electron-beam irradiation for (b) 5 min, (c) 20 min and (d) 60 min

same region after electron-beam irradiation for 60 min. A distorted onion is observed at the surface, and a onion structure is also observed in the carbon matrix. In some onions, black contrast is observed inside the lattice fringes of the onion layers as indicated by arrows.

An enlarged HREM image of the seven-layered onion structure in Fig. 1(c) is shown in Fig. 2(a). The number of carbon atoms on the outside of the onion is calculated to be 2940 from the relation $60n^2$ where n is the shell number. At the center of the onion, lies C_{60}. The lattice fringes of the graphite {002} planes are smeared at the edges of the onions with pentagonal carbon bonding, as indicated by arrows. 'Atom clouds',[32] which have an indistinct contrast, are observed at the vertices of the onion edges. Carbon 'vibration' is also observed at the surface of the onions. The shell structure is not perfect and has some defects. The same onion after 30 s of electron-beam irradiation is shown in Fig. 2(b) and changes of the vertices of the onion are observed. The lattice plane with smeared contrast is a disordered region, which moved to the left as indicated by double asterisks in Fig. 2(b).

One of the onion structures in Fig. 1(d) is enlarged in Fig. 3 and structural change due to Pd intercalation is observed in the lattice image. The Pd clusters show dark contrast which is due to the higher atomic number of Pd, and {111} lattice fringes with a separation of 0.23 nm are observed around the onion. Inside the onion, the graphite sheets show larger lattice distances (0.38, 0.39 and 0.44 nm) compared to that of ordinary graphitic carbon (0.34 nm). An enlarged HREM image of graphite {002} planes with a distance of 0.39 nm in Fig. 3(a) is shown in Fig. 3(b). Dark lines corresponding to graphite {002} planes are indicated by the white bars marked G. Dark contrast is observed at several positions between the graphite sheets as indicated by arrows. The distance between these dark dots is in the range 0.32–0.44 nm.

4 Discussion

4.1 Graphitization of carbon with Pd clusters

Graphitization of amorphous carbon and crystal growth of Pd clusters was observed by electron-beam irradiation, as observed in Fig. 1. Various transition metals accelerate the graphitization of carbon[33,34] by the solution–precipitation mechanism, which results in rupture of carbon–carbon bonds by the catalytic particles. The carbon atoms dissolve in the metal particles, and diffuse and precipitate as graphite at the particle surfaces. Encapsulation of small Pd particles in the graphite structure has been reported, and the Pd-catalyzed graphitization of amorphous carbon occurred after annealing at temperatures above 600 °C.[34] In the present work, the temperature of the samples was estimated to be below 100 °C,[15] *i.e.* low compared to the usual graphitization mechanism. The graphitization of amorphous carbon in the present work is attributed to both the energy transfer from the electron beam and the catalytic effect of Pd clusters, which results in the rupture of carbon–carbon bonds and subsequent graphitization. Pd clusters of size 2.5 nm have a large surface area compared to the bulk structure, which results in effective catalysis for transformation of amorphous carbon into graphite at the surface of Pd clusters. The driving force of this graphitization would be the free energy difference between the initial and final form of carbon.[35]

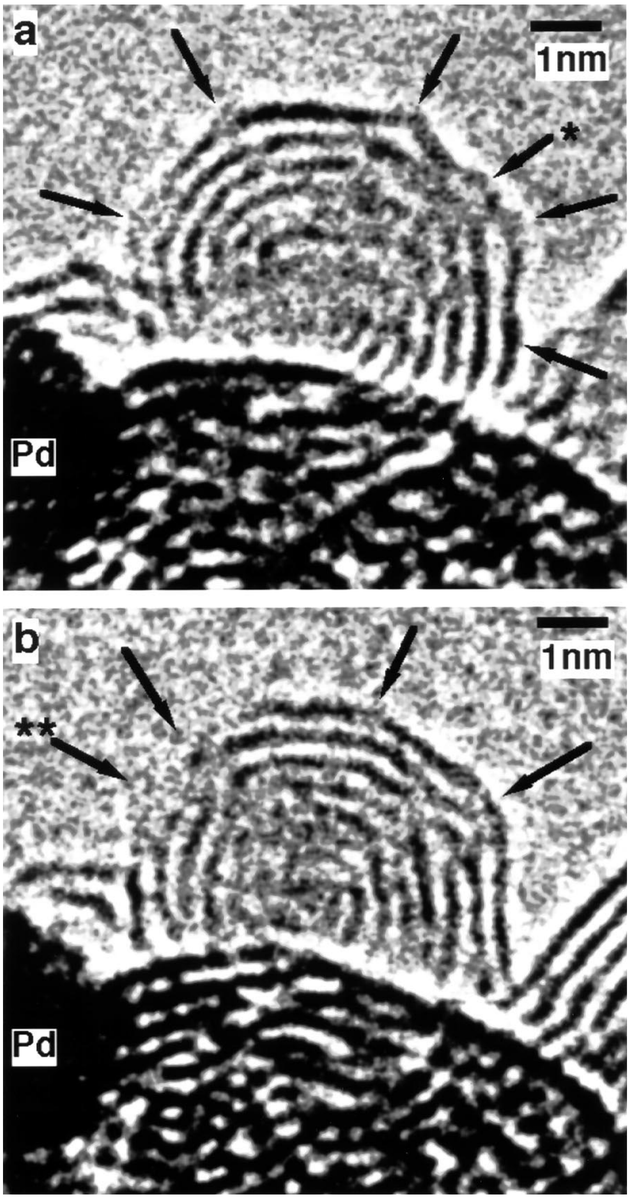

Fig. 2 (a) Enlarged HREM image of onion structure; (b) same onion after 30 s

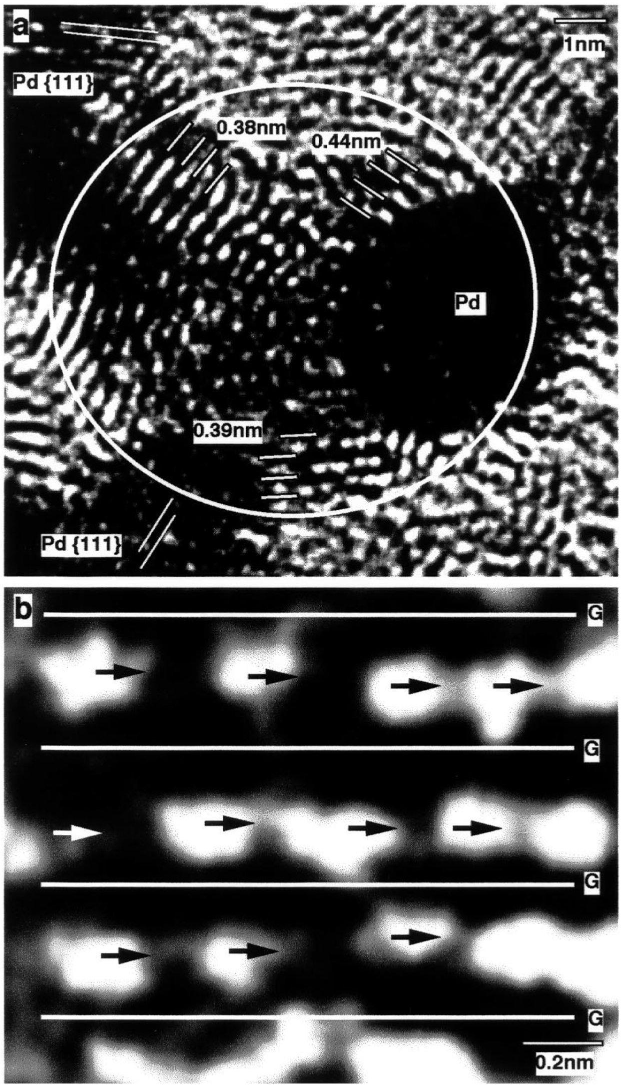

Fig. 3 (a) HREM image of onion structure with Pd; (b) enlarged HREM image of graphite {002} planes with distance of 0.39 nm in (a); the graphite {002} planes are indicated by white lines with G

4.2 Changes of onion structure

The formation of onion structures has been reported and discussed intensively.[3,12–20,36–40] Ugarte reported that the onions had a spherical shape[3] while Ru *et al.* reported that the onions had some vertices and ten-fold (icosahedral) symmetry.[14] From the theoretical calculation of giant fullerenes (onion structures), icosahedral symmetry with five-fold axes is stable,[40] while the icosahedral symmetry leads also to three-fold axes (with a shape showing six-fold symmetry). In the present work, eight-fold symmetry was observed, as also observed by Iijima.[36] It is believed that the present onion would be observed along the three-fold axis, and that these onions have some defect structures. Electron-beam irradiation causes C—C bond rupture which results in structural rearrangement and the formation of a spherical structure by surface relaxation. The replacement of hexagons by heptagon/pentagon pairs, which increases sphericity at the expense of faceting, will stabilize the onion structure.[40]

In the present work, atom clouds and the vibration of facets were also observed at the surface of the onion as shown in Fig. 2, which is a result of the electron-beam irradiation. The presence of 'atom clouds' which show indistinct contrast at the onion vertices indicates the hopping of carbon atoms on the onion surface. It is believed that pentagonal bonding is weaker compared to hexagonal bonding, which leads to hopping of carbon atoms at the onion vertices. Carbon 'vibration' was also observed at the surface of the onions. These atom clouds form carbon vacancies at the onion surface, which indicates that carbon diffusion in the onion can be described by a vacancy mechanism.

4.3 Intercalation of Pd atoms in graphite structure

Graphite sheets with large lattice separations are directly connected to Pd clusters, and show darker contrast compared to ordinary graphite, as observed in Fig. 3(a). These results indicate the Pd atoms are intercalated in the graphite structure. Diffusion of carbon and Pd atoms, which was observed in the graphitization of amorphous carbon and particle growth of Pd clusters, also suggests intercalation of Pd. In addition, dark dots are observed at several positions between the graphite {002} planes as indicated by the arrows in Fig. 3(b), which are believed to be Pd atoms. The distances between these dark dots are in the range 0.32–0.44 nm, which roughly corresponds to 0.35 nm ($=a_0\sqrt{2}$, $a_0=0.246$ nm). This indicates that the direction of the incident beam is aligned to the [100] direction of the graphite when the Pd atoms are assumed to be just above the center of hexagonal carbon bonding. Based on the experimental result in Fig. 3(b), a structural model for Pd intercalation in graphite is constructed as shown in Fig. 4. The lattice parameters are $a_0 = 0.246$ nm and $c_0 = 0.39$ nm, and the atomic ratio of Pd to C is 1 : 8. Atomic arrangements of carbon and Pd are shown along the [100] and [001] directions of graphite in Fig. 4(a) and (b), respectively. The graphite {002} planes are indicated by G in Fig. 4(a). Although normal graphite shows the stacking sequence ABAB …, the first stage intercalation shows the stacking sequence AAAA …,[41] as shown in Fig. 4(a). Several types of structural model can be considered, which depends on the atomic ratio of Pd and C.

Atomic intercalation in graphite sheets has been studied for various elements such as Cs, Rb and K.[41] For ordinary intercalation, the *d*-value between graphite {002} planes is in the range 0.4–0.6 nm, which is larger compared to the present Pd intercalation (0.38–0.44 nm). This indicates that the Pd intercalation in the graphite layer, in the present work, is incomplete *i.e.* the occupancy of Pd in the graphite sheets is less than unity.

The formation of onion structures with diamond and W has been reported,[42,43] and with carbon nanocapsule structures being observed. Various types of carbon nanocapsules with clusters (Co, Fe, Ni, Cu, CrC_x, MoC_x, MoO_3, WC_x, WO_3, TiC, SiC, *etc.*) have also been reported.[4,7–11,21–27] In the present work, no nanocapsule with Pd was observed, which would be due to the difference of formation method and conditions used.

However, Pd intercalation in the graphite layers was instead observed in the present work. Atomic intercalation of Al in carbon onions has been reported,[15] which leads to spherical structures whereas Pd intercalation results in the disordering of the onion structure which would be due to the larger size Pd *cf.* Al. For both metals onions formed in the graphite matrix, although onions generally form on the surface of a carbon matrix. This also suggests that distortions in the atomic-intercalated onions are relaxed in the carbon matrix. The formation of atomic-intercalated onions with low strain is interesting in terms of scientific research and applications, and can be readily synthesized by electron-beam irradiation.

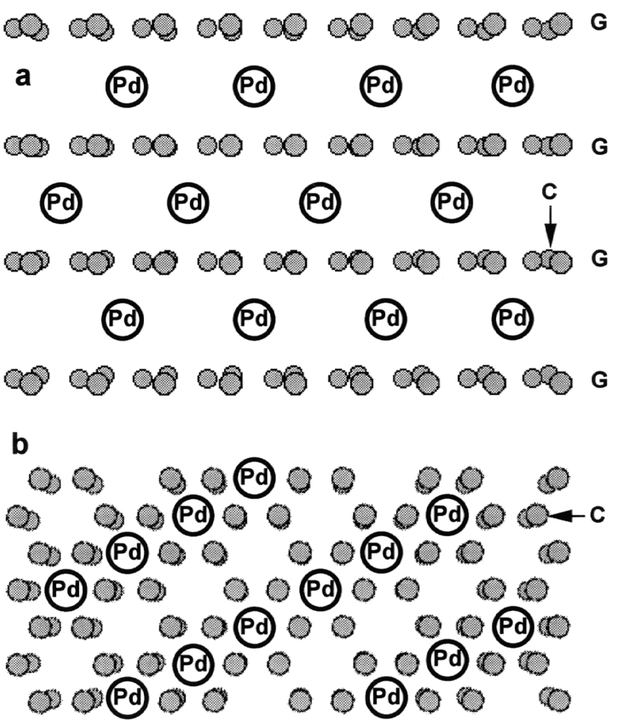

Fig. 4 Structural model for Pd intercalation in graphite along (a) [100] and (b) [001] directions of graphite; the graphite {002} planes are indicated by G

5 Summary

Carbon onions have been produced in a high-resolution electron microscope by electron irradiation of amorphous carbon in the presence of Pd clusters. During electron-beam irradiation, the growth of Pd clusters and the graphitization of amorphous carbon were observed. It is believed that the graphitization mechanism is due to electron-beam irradiation and the catalytic effect of the Pd clusters. The formation of hollow carbon onions was observed after electron irradiation for 20 min. The vertices consist of pentagonal carbon bonds showing as 'atom clouds'. Change of positions of the atom clouds was observed due to carbon diffusion at the onion surface by the vacancy mechanism. In addition, Pd atoms were intercalated in the graphite onion structure, which resulted in an increase of the lattice distance of graphite {002} planes. From high-resolution observations, a structural model for Pd intercalation has been proposed. The present work indicates that electron irradiation on amorphous carbon with catalytic clusters such as Pd can be an effective method for the formation of carbon onions and intercalated structures.

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