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Synthesis of Carbon Onions by Gold Nanoparticles and Electron Irradiation

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Carbon nanostructures have shown unexpected ordering under irradiation with electrons or ion beams. One of the most fascinating phenomena is the formation of perfectly spherical graphitic onion structures. These structures were discovered by Ijima in 1980[1] but were left unnoticed until the discovery of the fullerenes. Ugarte[2] reported a technique to produce remarkable rounded onions using electron beams. A number of techniques have been reported to produce bucky onions such as annealing of diamond particles at high temperature,[3] implantation of carbon atoms on silver,[4] arcing graphite rods in distilled water,[5] and chemical plasma enhanced vapor deposition on $CoSiO_2$ catalysis.[6] It is known that when the initial carbon targets are polyhedral carbon particles produced by arc discharge, the fullerene onions can be produced by electron irradiation of ~150 A/cm (at 200 keV) quite rapidly.[7] However, in the case of direct irradiation of holey carbon films targets, higher dose (~180 A/cm^2), higher voltage (400 keV), and larger irradiation times are required.[8] In this case the observed onion structures were only produced in the edges of holes in the carbon film. Xu and Tanaka[9,10] reported the transformation of an amorphous carbon film into carbon onions by electron irradiation in the presence of Pt and Al nanoparticles. The effect was attributed to the catalytic effect of the nanoparticles.

In the present work we found a condition in which fullerene onions are produced by nanoparticles at an explosive rate and use less extreme irradiation conditions than the ones used in the absence of nanoparticles. This phenomena is correlated with a thorough reconstruction of the particle surface in which steps and stacking faults are produced on the surface. This structure is continuously changing because of the electron irradiation. Since in this condition the fullerene production is 10 times faster than in the case of Xu and Tanaka, it may be used to generate a large amount of fullerene onions.

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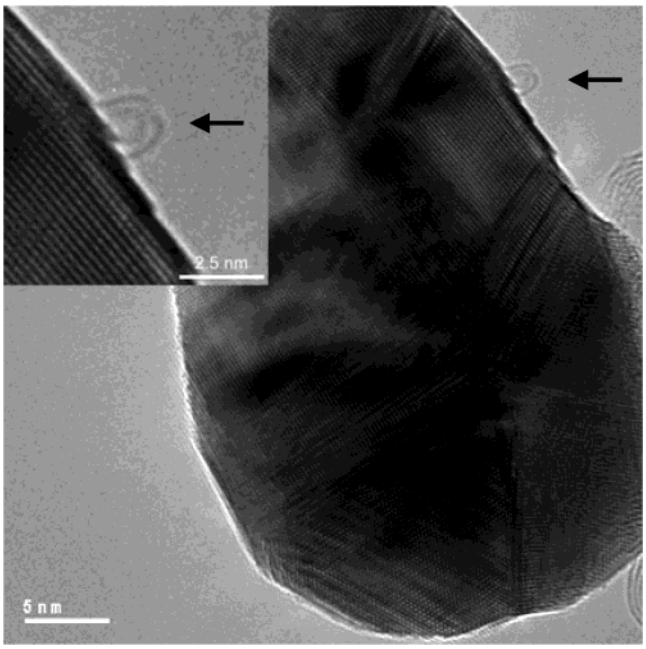

Figure 1. The particle after strong irradiation at 180 A /cm^2 for several minutes. The shape has been altered significantly. The inset shows the details of the $C_{60}@C_{240}$ structure formed on the steps (indicated by an arrows).

Nanoparticles were prepared by the bioreduction method reported before.[11] Samples of Au and Au/Pd were used for the present experiment. A drop of solution was put on a TEM grid coated with ultrathin evaporated carbon. The samples were studied in the JEOL 2010 F fitted with a field emission gun. The beam energy was 200 keV. Samples were observed at a current density of 50 A/cm^2 and then irradiated at currents between 100 and 180 A/cm^2 during periods lasting from a few seconds to 2 min. The beam current was reduced for image recording and then the irradiation was continued. The first intense irradiation produced a hole at the side of the particle and changes dramatically its structure. Subsequent irradiation during short periods induced fullerene formation.

The experiment started with the irradiation of a gold nanoparticle with the electron beam. We started with a decahedral gold nanoparticle. Figure 1 shows the initial state of the fullerene formation on the particle surface. Around monatomic surface steps a nested fullerene onion consisting of two shells is formed. According to the standard notation, this corresponds to a nested polyhedron $C_{60}@C_{240}$. However, this is only a rough approximation since the particle is not spherical and therefore not a perfect polyhedron. It should be noticed that catalytic activity of nanoparticles in fullerene formation has been assumed in the literature. However, Figure 1 is the first direct evidence of the role of surface defects on fullerene formation. A closer examination of this figure indicates that the fullerenes originated on the kinks along the steps. The interlayer distance in the polyhedra will be defined by the separation of the step edges. However, as the onion grows, the interlayer distance will approach that of graphite. We observed

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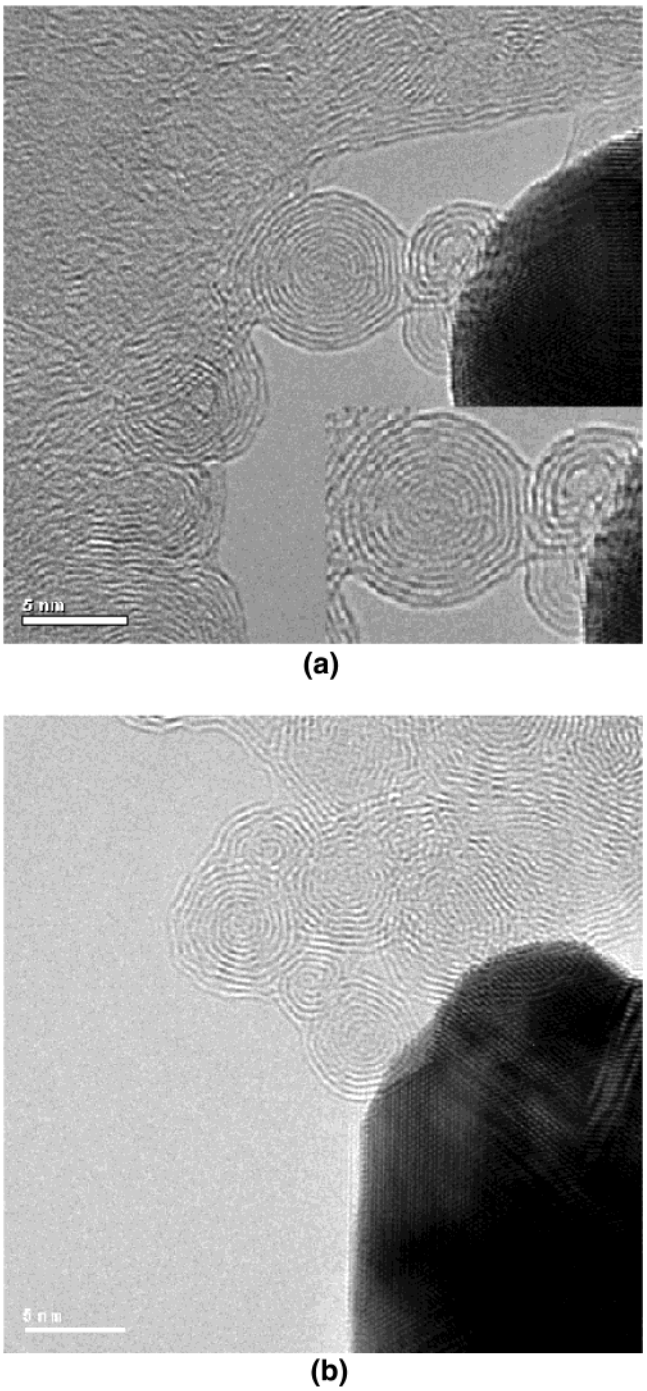

Figure 2. Formation of fullerene onions on a gold nanoparticle. In (a) the inset shows the details of the interface between two fullerenes and between a fullerene and the particle. (b) shows an image corresponding to the final state where a large number of fullerenes have been produced.

that as the irradiation proceeds for a few seconds, the formation of new onions begins to accelerate. At this stage a dramatic increase in the rate of formation is observed. Figure 2 shows a sequence of the formation of a larger fullerene on the surface of a nanoparticle. All of the sequence is completed in only a few seconds. The carbon planes are first deformed (Figure 2a), and as soon as the onion leaves the surface, it acquires its final rounded shape. This is in contrast with the case of Xu and Tanaka[9,10] in which fullerenes encapsulate the nanoparticles. This process goes on indefinitely as long as the nanoparticle maintains contact with the

carbon film. The average final size of the onions is of the order of 3.5 nm, which corresponds to 9−10 shells. The intershell distance is variable but close to the graphitic distance of 0.34 nm. It can also be observed that there is a compression of the layers next to the surface and that the onion shape relaxes to a more spherical shape as it becomes further apart from the surface. The merging of two onions can be observed in Figure 2a and even a suggestion of the formation of two Archimedean spirals which finally became two separated fullerenes can also be noticed. The stage observed after several seconds of irradiation is shown in Figure 2b. A large number of fullerene onions have been formed.

For this rapid nucleation of fullerenes to take place, the gold nanoparticle surface should be in a structure fluctuation state. The shape of the particle has been dramatically altered after electron irradiation. This phenomenon is well-documented in the literature.[12−15] Particle fluctuations are induced by the electron beam and are the result of energy transfer to the particle from inelastic interactions of the electrons traveling through it. The fluctuations are a complex phenomena and imply a surface which is constantly undergoing modifications. This however seems to produce an increase in the catalytic activity.

A growth mechanism can be summarized as follows: a knock on collisions between electrons and carbon atoms leads to diffusion of atoms on the carbon film. As shown by Banhart,[8] a knock on displacements is the dominant mechanism in radiation damage in carbon films. A further displacement effect is the radiation-induced diffusion in which electron impacts can lead to diffusion of atoms, even at energies below the threshold displacement as shown by Urban and Seeger.[16] Carbon atoms reach the particle and surface diffusion takes place until an embryo is formed, which subsequently grows. Figure 1, in which the formation of a $C_{60}@C_{240}$ ring in a surface step is shown, suggests an important reduction in activation energy for the formation of polyene chains around the kinks. As the irradiation continues, a threshold for particle fluctuation occurs and the surface has rapid reordering in which many kinks appear and disappear. This seems to trigger a dramatic growth of irregularly shaped fullerenes, which eventually become onions.

The diameter of rounded fullerenes was measured and within the experimental error a sequence $C_{60}@C_{240}@C_{540}@C_{940}@C_{1500}$... was obtained. This corresponds to the quasi-icosahedral concentric shells suggested by Kroto and McKay.[17] A close observation of smaller onion structures being formed in the surface of the particle indicates that their shape is irregular. This strongly suggests the growth mechanism suggested by Kroto and McKay in which an initial corannule molecule is formed and spiral growth of the structure adds new layers which are not closed and subsequent growth is produced. The spherical shape will be achieved after the onion has left the nanoparticle surface. This has been proved recently by Ozawa et al.[18] who observed that in the initial states of formation the fullerene shape corresponds to an Archimedean spiral. We have also observed similar effects in our materials. The spiral structure in the larger fullerene can be seen in Figure 2a.

For the catalytic effect to be observed fluctuations in the particle structure are a necessary condition. Our experimental data show evidence of the concept of a flexible surface introduced by Somorjai and Rupprecher[19] according to which surface structures adapt to a specific function.

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