Carbon spheric nanoparticles: possible formation mechanism

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Abstract

Possible mechanisms of carbon spheric nanoparticle formation are discussed. The growth mechanisms of nanoparticles with isospiral structures are not easily compatible with several experimental facts. The model of shell-by-shell growth of nanoparticles is not confirmed by our molecular dynamics simulation. We suppose that nanoparticles with shell structures arise from liquid cluster crystallization. We propose a new explanation for the origin of this liquid cluster: it is a result of melting of graphitic nanocrystals evaporated from electrodes.

1. Introduction

The discovery of spheroid carbon clusters, fullerenes [1], and their macroscopic synthesis [2] has resulted in an increase of the interest in other carbon nanostructures: nanoparticles [3] and nanotubes (see, for example, Refs. [4,5], and references therein). The surprising thing is that such symmetrical crystal nanostructures form on the surface of the graphite electrode under the hot arc plasma conditions. The production and the research of properties of crystals consisting of nanoparticles or nanotubes are very interesting. Particularly, it is important to study the crystals of this type doped by metals, because such crystals may display superconducting properties. However, nanoparticles have not yet been produced in macroscopical amounts.

To elaborate the methods of macroscopical synthesis of nanoparticles and nanotubes, it is essential in particular to know the mechanism of nanoparticle formation. In the present paper we compare the possible mechanisms of spheric carbon nanoparticle formation and present molecular dynamics simulations of one possible mechanism. As a result of our analysis and simulation we conclude that the most probable mechanism of spheric carbon nanoparticle formation is the crystallization of a liquid cluster. We propose a new explanation of the origin of this cluster.

2. Models of formation mechanism

The "curving sheet" model was first proposed as a universal mechanism of nanoparticle and fullerene formation (see, for example, Refs. [6,7]). According to this model, the growing carbon sheet curls itself in a nautilus-like cluster to reduce the number of dangling bonds. In some cases a closed fullerene structure may occur. Other clusters grow as isospiral soot particles. This elegant model has, however, several shortcomings. It does not explain a high yield of fullerene C60 under certain conditions of synthesis (see, for example, Ref. [1]). Moreover, investiga-

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tions of the second ionization potential show that all large carbon clusters, such as C$_{300}$, are fullerenes but are not isospiral particles [8]. It was proposed in Ref. [6] that soot of flame forms according to the "curving sheet" model. But there are serious arguments (see, for example, Ref. [9]) against isospiral structure of soot particles from flames: (1) soot particles contain atoms of O, H and other elements, (2) the chemical properties of soot particles are closer to those of benzene than to those of graphite, (3) NMR study of soot particles shows that they include polycyclic aromatic hydrocarbons, (4) the X-ray scattering spectrum of soot particles is more similar to that of polycyclic aromatic hydrocarbons than to that of graphite. The authors of the "curving sheet" model interpret the structure of nanoparticles shown in images from Ref. [2] as isospiral. However, Iijima in Ref. [2] has drawn the conclusion that the nanoparticles produced have the structure of concentric closed graphitic shells. Such a point of view is confirmed by TEM investigations made with better resolution [10,11].

It is unlikely that carbon clusters consisting of 20-40 atoms may exist in plasma in the form of a curved sheet, as it was proposed in the model discussed. The calculations of the binding energy of carbon clusters C$_n$ [12] show that fullerenes with $n > 25$ and monorings with $n < 20$ have a greater binding energy than curved sheets and cups. According to the molecular dynamics simulation carbon clusters with $n > 30$ have a closed surface shape [13].

As mentioned above, spheric carbon nanoparticles consist of concentric closed graphitic shells. The bonds between atoms inside the shell of such nanoparticles are almost analogous to the ones between atoms in one layer of graphite. A more weak interaction between shells is described by the van der Waals potential, analogously to the interaction between layers of graphite. In contrast to graphite there are 12 pentagons in addition to hexagons in the structure of each shell.

Several formation mechanisms of spherical nanoparticles with such structures are possible. The first possibility is the sticking of carbon atoms and microclusters on the fullerene [6,10,14] (a model of shell-by-shell growth). The second one is the crystallization of a liquid cluster on the cathode in the electric arc [15]. In principle, it is possible to produce nanoparticles with shell structures from amorphous particles by annealing them with the help of laser light [16], an electron beam [17], or in an oven [18]. It was also proposed [17] that only amorphous nanoparticles can be produced in the arc and that the shell structure is the result of annealing amorphous particles during research by the transmitting electron microscope.

3. Simulation of shell-by-shell growth

The molecular dynamics simulation was used for fullerene formation studies in some papers (see, for example, Ref. [13]). However, the very complex potential for the interaction between carbon atoms allows one to follow up the development of the system during 100 ps only. This period of time is not enough for the symmetric fullerene formation, therefore only fullerenes with defects were simulated.

Here we used the molecular dynamics method to simulate the shell-by-shell growth of spheric nanoparticles. Our aim was to obtain the highest temperature $T^{\text{max}}_e$ when physically adsorbed carbon atoms and microclusters still held on the nanoparticle surface. For $T > T^{\text{max}}_e$ the adsorption of atoms and microclusters is impossible, therefore, the formation of the next shell is impossible too.

We used fullerene C$_{60}$ as the possible first inner shell of the nanoparticles. Iijima has obtained TEM images of nanoparticles that confirm this possibility [19]. We have simulated a system consisting of fullerene C$_{60}$ and a carbon atom or a microcluster C$_6$. The interaction between carbon atoms and microclusters with the surface of fullerene is described by a van der Waals potential as the interaction between layers of graphite. The complete potential including the repulsion at small distances can be approximated by the Lennard-Jones potential $U=4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} + \left( \frac{\sigma}{r} \right)^6 \right]$. The parameters of this potential for carbon atoms are $\epsilon = 28$ K and $\sigma = 3.4$ Å. These parameters were derived from the graphite compressibility (and used for the solid C$_{60}$ simulation [20]). The interaction between atoms inside C$_{60}$ and inside C$_6$ was described by the Born potential,
$$U = \frac{1}{2} \left( \alpha_k - \beta_k \right) \sum_{i,j=1}^{60} \left[ \left( u_i - u_j \right) \cdot r_{ij} \right] \frac{1}{|r_{ij}|^2}$$

$$+ \frac{1}{2} \beta \sum_{i,j=1}^{60} (u_i - u_j)^2,$$

where $k = 1$ for a single bond and $k = 2$ for a double bond in the case of $C_{60}$. $u_i$, $u_j$ are displacements of atoms from their equilibrium positions, $r_{ij}$ are distances between atoms, $\alpha$ and $\beta$ are force constants. We take $\alpha_1 = \alpha_2 = 1.14 \times 10^6$ dyne/cm and $\beta_1 = \beta_2 = 1.24 \times 10^5$ dyne/cm. The Born potential with these values of the force constants was used for the calculation of the internal vibrational spectrum of $C_{60}$ [21]. The single and double bond lengths of $C_{60}$ used were 1.391 Å and 1.455 Å [22]. For the microcluster $C_6$, we assumed force constants of benzene $\alpha_6 = 7.62 \times 10^5$ dyne/cm $\beta_6 = 0.667 \times 10^5$ dyne/cm [23]. Bond lengths for $C_6$ are 1.316 Å and the angles between them are 90.4° (see Ref. [24]). We simulated our system at temperatures at least ten times less than the temperature of fullerene melting, therefore the Born potential is adequate for our simulation.

The equations of motion were integrated using a first order algorithm [25]. The integration step used was $\tau = 2.5 \times 10^{-15}$ s. The total energy of the system was conserved to within 0.5%.

According to the calculations, the ring is the ground state of the microcluster $C_6$, but chains were also found by various methods (see, for example, review [7], and references therein). In the case of a chain less atoms can be located close to the nanoparticle surface than in the case of a ring. Therefore, the chain escapes from the nanoparticle at a lower temperature than the ring.

Initially a carbon atom or microcluster $C_6$ locates at a random place on the fullerene $C_{60}$ surface. Then the system consisting of fullerene $C_{60}$ and the carbon atom on the surface of fullerene comes into equilibrium at the temperature 40 K during $10^4$ steps (equal to 60 oscillations of the atom about the surface). We heated this system with a rate of $3 \times 10^{-3}$ K/step until an atom or a microcluster escaped. We carried out 25 numerical experiments for an atom and a microcluster $C_6$. We have calculated the average and maximum escape temperatures for a carbon atom: $T_r \sim 120$ K and $T_{esc}^\text{max} \sim 182$ K. The microcluster $C_6$ escapes from the fullerene surface (with temperature 30 K) before the system reaches equilibrium.

As was experimentally shown, the transitions between isomers of polycyclic aromatic hydrocarbons take place only at a temperature higher than 1300 K [26]. Nanotubes with shell structure grow only at temperatures higher than 1200 K [27]. Adsorption of atoms and microclusters on a nanoparticle is possible only at a temperature $T < T_a$. Therefore, the calculated escape temperature is insufficient for the growth of the next graphitic shell of a nanoparticle.

Here we consider only the physical adsorption of carbon atoms and microclusters on the surface of fullerene. The process of chemical adsorption is studied in detail in Ref. [28]. In the latter case the microcluster inserts the cage, that is, the size of the outer shell increases only but the next shell does not arise.

Therefore, we draw the conclusion that our simulation demonstrates the impossibility of shell-by-shell growth of a nanoparticle.

4. Discussion

Saito et al. proposed that the liquid carbon cluster originates on the surface of a cathode [15]. Such a cluster steps forward over the surface of the cathode, therefore, the arc field is greater near it. So ions, cluster ions, and atoms and microclusters (because they have become induced dipoles) are attracted by the arc field on the growing cluster. Then this cluster crystallizes (see also Ref. [16]). But the existence of the liquid cluster on the surface of a cathode essentially means that graphite is not wettable by liquid carbon, which is very doubtful.

We propose another mechanism of the origin of a spheric nanoparticle on the surface of the cathode. The arc between graphitic electrodes operates when graphite evaporates in the form of nanocrystals [29]. The temperature in the core of the arc is about 10000 K. Notice that the melting temperature of the nanocrystal is less than that of the bulk crystal [30].

$$\frac{T_\infty - T_r}{T_\infty} = \frac{2\gamma}{Lr} \left( \frac{1}{\rho_1} - \frac{1}{\rho_2} \right),$$

where $T_r$ is the melting temperature of the nanocrystal with size $r$, $T_\infty$ is the melting temperature of the bulk crystal, $\gamma$ is the surface tension of liquid carbon, $L$ is the heat of melting, $\rho_1$ is the density of graphite, $\rho_2$ is the density of liquid carbon. These nanocrystals
can melt easily in the arc. The produced liquid clusters have an ionization potential [29] close to the work function of the bulk that is noticeably lower than the ionization potential of atoms and microclusters,

$$\phi_n = \phi + \left( \frac{e^2}{2r} \right) \left( 2n - \frac{1}{2} \right),$$

where $\phi_n$ is the ionization potential of the $n$th electron from the cluster, $\phi$ is the work function of the bulk, $e$ is the charge of an electron. Such clusters can be the majority positive charge carriers in an arc [29]. Therefore, these clusters are moved by the electric field of the arc to a cathode. It is probable that crystallization of a liquid cluster into a nanoparticle with a shell structure begins before its arrival at a cathode. Therefore, the crystallizing nanoparticle conserves its spheric shape even for the case when graphite is wettable by liquid carbon. Note that such a crystallization to a shell structure is a universal phenomenon, which does not depend on the type of interaction between particles constituting the liquid cluster (see, for example, Ref. [31] and references therein, for Coulomb clusters).

Thus we have discussed various models of spheric carbon nanoparticle formation. As we have shown, the "curving sheet" model poorly agrees with some experimental facts. The model of shell-by-shell growth is not confirmed by our molecular simulation.

We suppose that the most probable formation mechanism for the spheric nanoparticle with shell structure is crystallization of a liquid carbon cluster, first proposed in Ref. [15]. But we propose a different explanation for the origin of such a cluster. Namely, nanocrystals of graphite are evaporated from electrodes and melt. Charged liquid carbon clusters move to the cathode and crystallize near it forming spheric nanoparticles with shell structure. There is a possibility of formation of such nanoparticles by annealing of the amorphous particles by an electron beam during the TEM study.

Two possible formation mechanisms were proposed for carbon nanotubes with shell structure. First is the model of shell-by-shell growth of a nanotube [10,11,32]. The surface of nanotubes is analogous to that of graphite like that of a nanoparticle. Therefore, we suppose that such growth is very doubtful as in the case of a nanoparticle. Thus we consider that according to the second model shells of nanotubes grow altogether [4,27]. The nanotube formation will be described elsewhere.

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References