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The mechanism of growth and decay of carbon nano-onions formed by ordering of amorphous particles

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A B S T R A C T

The phenomena occurring during electron–beam irradiation of amorphous carbon nanoparticles have been studied. 300 keV electrons cause first ordering of amorphous particles leading to an imperfect shell structure which can be followed by either growth or decay. Growth occurs by a process, similar to Frank–van der Merwe growth of crystals, through forming and coalescence of two-dimensional islands into graphene layers. Decay occurs by two mechanisms: void formation and opening to the surface, and a layer-by-layer detaching of graphene shells. These two mechanisms occur often simultaneously. Void formation is due to densification and ordering. Detachment of layers is due to defect-induced local curving of the outmost layers resulting in an increase in the spacing between outer shells to 0.35–0.50 nm. Growth and decay are competing processes and exact conditions for their stimulation or suppression could not be established so far.

1. Introduction

A common feature of different layered materials is the ability to transform into spherical shells [1–3]. However, according to ref. [4], a thorough investigation of their irradiation-induced phenomena has not so far been made except for carbon structures. The curling of graphene layers under the influence of a high-energy electron beam has been first recognized by Ugarte [5] and confirmed for many different structures [4,6,7]. The driving forces for curving and closure of the graphitic layers were realized in the tendency towards saturation of the high-energetic dangling bonds at the edge of these graphene-like elements [5]. High-temperature irradiation experiments lead to more perfect curved structures [7] through annealing out defects, while defect configurations are created at lower temperatures.

The formation mechanism of multi-shell fullerenes from amorphous carbon particles is based on irradiation-induced ordering [5]. Hiraki et al. [8] observed similar transformation resulting in multi-shell structures originating from diamond-like nanoparticles. Ozawa et al. [9] suggested a 3D spiral-growth mechanism (snow-accreting growth model) carrying out irradiation experiments with various types of soot and other different carbon samples.

Banhart et al. [7] discussed the electron-irradiation effect on nanotubes and nano-onions in a wide temperature range (50–800 °C). In the formation of spherical onions they suggested irradiation-enhanced surface tension as the main driving force.

Although carbon materials and their changes under irradiation are well-studied [4,10,11], because of the great variety of the different phases and morphologies there are still uncharted areas on this subject.

The ordering, growth and decomposition of onion-like carbon structures from amorphous nanoparticles were the focus of our present investigations.

2. Experimental procedures

The studied samples were prepared by DC arc evaporation in a nitrogen atmosphere at room temperature. The pressure was 1 mbar during the evaporation process. The arc-voltage was 20 V, the current was 5–10 A, the effective duration of the evaporation was 30–60 s, as the duration of one individual arc was a few seconds, and we obtained 10–20 arcs for one sample. We used graphite electrodes as carbon sources, and freshly cleaved NaCl as the substrate. The substrate–electrode distance was approximately 50 mm. For TEM studies we removed the carbon deposit from the substrate by floating off in distilled water and placing it on a copper micro-grid. Besides using self-supporting deposits, in other sets of experiments we also used films deposited on continuous and holey carbon foils.

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Electron-irradiation experiments were carried out in a high resolution transmission electron microscope (HREM) using a JEOL 3010 instrument operating at 300 kV accelerating voltage. The time scale of the transformations varied between 10 min and 1 h at beam current density of $\sim 10^{-2}$ pA/nm^2 ($=10^4$ A/m^2), about ten times longer than the usual practice.

3. Results and discussion

At 1 mbar pressure the mean free path of the C-atoms is in the order of 0.1 mm. Because of this small distance, primary collisions took place near the electrodes. As a result, aggregates of small amorphous carbon granules were obtained in which the boundaries of individual particles are not easily appreciable. The diameter of the particles is about 5–20 nm [12] (Fig. 1). As the evaporation took place in nitrogen, N atoms may be incorporated into the carbon network. EDS measurements showed that the nitrogen content is $\approx$5–10 at%.

We monitored the changes of such amorphous particles during one-hour irradiation. The first observed change an alteration in shape which approached an ellipsoid form by rounding of the corners (Fig. 2(a) and (b) black arrows).

Following the initial changes the process had two main stages: ordering and growing.

After 5–10 min of irradiation, graphene fragments of around 1 nm in size appeared at the surface and inside the particles. The alignment of fragments did not correlate with each other, their orientation was rather random. The effect of $\sim$10 min irradiation from the beginning of the observation resulted in partial correlation between them. This correlation manifested itself in parallel-ordered graphene fragments, especially near to the particle surface. The ordering of graphene fragments into parallel shells and the transformation into onion-like nanoparticles (Fig. 2(b) and (c), white arrows) were accompanied with rounding of the shape. Some growth of the particles could be detected already at this stage.

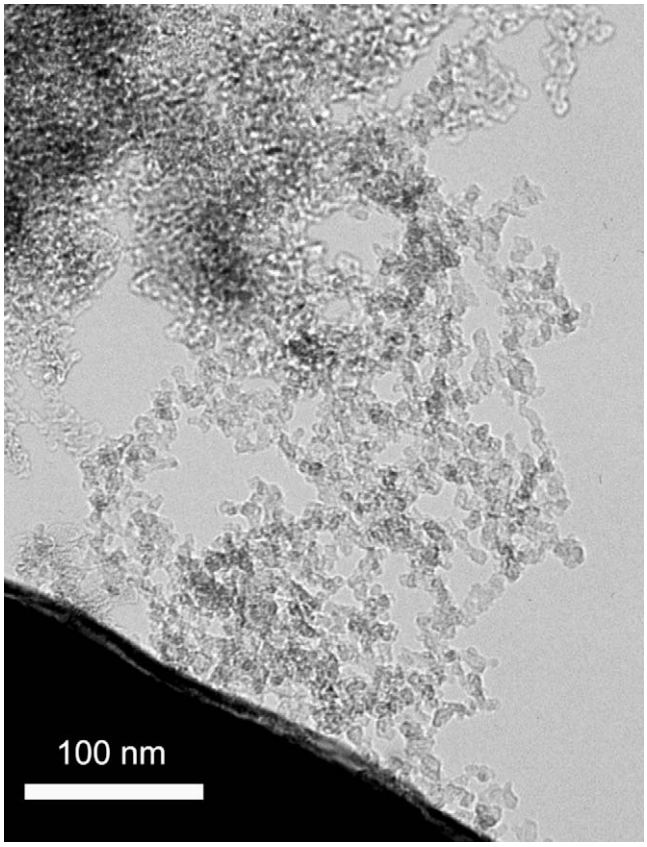

Fig. 1. As-deposited amorphous particles forming a loose agglomerate seen at a bent edge of the supporting foil.

The above-mentioned rounding and arrangement into a layered onion structure of furnace black were observed in ref. [9]. The phenomenon was attributed to the revealing of the hidden ordered structures under disordered and defective surface layers. Internal ordering of these structures under irradiation was also anticipated [9]. A similar behaviour was described as atomic rearrangements in ref. [7] for graphite platelets, onions and tubes. In our case even the bulk of the particles is amorphous, they can contain random graphene fragments arising from the growth mechanism of arc-evaporated carbon [13]. So, the appearance of graphene-like surface layer(s) is the result of an ordering process due to irradiation as also observed in refs. [5,7].

The growth of the onion-like nanoparticles started after the first surface layers had formed (Fig. 2(d)). With the beginning of growth, ordering and growth took place simultaneously.

The appearance of a new graphene layer on the surface started with the formation of two-dimensional (2D) concave (arrow in Fig. 3(c)) graphene islands resulting in an apparently rough surface (Fig. 2(d), black arrow). This step is schematically shown in Fig. 3(b) and (c). The islands grew and coalesced into convex fragments of a new graphene layer, displaying dangling or backfolding edges (Fig. 3(c) and (d)). Finally they formed a smooth surface layer (Fig. 3(d)), resulting in the growth of the particle by one, not necessarily complete layer (Fig. 2(e) and (f), black arrows). This mechanism strongly resembles the Frank–van der Merwe growth mechanism of crystals [14], when two-dimensional islands form, grow and build up a layer (Fig. 3(a)).

The observed growth process is repeated by the formation of the concave 2D islands on the already completed layer, creating further surface layers leading to a multi-shell structure. In Fig. 2(a)–(f) the formation of 10–12 subsequent layers has been observed.

It is assumed, that the material required for the growth was transported by surface diffusion from the irradiated parts of the sample to the observed places. The other feasible source is from organic matter of the ambient atmosphere cracked by the beam.

The above observations can be interpreted with the help of accumulated experience in observation of changes of layered carbon structures under high-energy electron-irradiation. Electron-irradiation causes the formation of five- and sevenfold-rings in a sixfold-ring network [11]. We suppose that the 2D fragments contain such defects either due to their formation mechanism [13], or, to the irradiation effect [11,15]. The graphene-fragments containing non-sixfold-rings become curved. As long as the curvature of the fragment is higher than the curvature of the underlying layer, the 2D fragments tend to attach to the surface mostly as concave pellets (Fig. 3(c)). We suppose they grow by an atom-by-atom process via diffusion, activated by irradiation. As the size of the 2D fragments increases, the accumulating strain and stress flatten them. This can result in coalescence and a (collective) flip of coalesced fragments into convex shape by the movement of defects. Once the shape of the particle is adopted and the fragments are as large as their average nucleation distance, new fragments on their top occur (Fig. 3(c) and (d)), and the process repeats itself as long as material is supplied. The forming onions are far from perfect; incomplete layers can easily be observed in them. As the size of the particles increases their structure improves (Fig. 2(f)), which may be due to the self-compression caused by the outer layers [7,16] and/or the heating effect [7] of the beam, which is more pronounced for larger particles.