

MECHANISM OF CARBON NANOTUBES FORMATION FROM GRAPHITE REVISITED

A new mechanism of fullerene and nanotube formation from graphite under conditions of laser evaporation in an electric arc is proposed. The role of the tightening graphene layer and a catalyst in the process of nanotube synthesis has been analyzed. The catalyst atom is coordinated on the graphite surface and at high temperature starts cutting and sewing graphite lattice that results in nanotube formation. Fullerenes are forming through cutting caps with a part of nanotube. Atomization of graphite is not an obligatory step. The facts proving the mechanism described have been systematized and generalized.

It is no secret that carbon has already six allotropic modifications (Fig. 1). Three of them – diamond, graphite and carbyne – have been known for a long time. Since 1985 they have been supplemented by another allotrope named fullerene. Recently fullerenes as well as nanotubes discovered in 1991 and in nanorings discovered in 1997 have attracted attention of scientists engaged in different fields – chemists, physicists, biologists, mathematicians all over the world.

Until now all discussed mechanisms of graphite to fullerenes transformations [1–8] included graphite desintegration in plasma giving rise to small clusters (C_2 , C_{10} etc.), which then somehow arrange into clusters C_{20} , C_{40} etc., and finally into fullerene itself. Since self-assembling of fullerene is a spontaneous process and centres around which this arrangement could take place are absent, one could suppose that the driving-force of this process is an energetic advantage of the formed cluster and its high symmetry (I_h). Nevertheless, these arguments are bottomless. Thus fullerene C_{80} has the same high symmetry I_h , as C_{60} , but it was not found among products of the high temperature process in the electric arc. At the same time fullerene C_{70} , further after C_{60} in its content in the fullerene soot, has symmetry D_{5h} that is lower than C_{60} , therefore the cause should be quite different.

The reason perhaps consists in the value of binding energy? Our computation (PM3) of energy E_c per one carbon atom for C_{60} and some further clusters showed that E_c value rises monotonously with the number of carbon atom increase (157,6 – 158,7 – 159,3 – 160,6 kcal/mol for C_{60} – C_{70} – C_{80} – C_{100} , correspondingly), i. e. C_{60} does not possess some «stability island».

Then, maybe, the reason is special size of the C_{60} cluster? Really, it is easy to see, that the diameter of the spherical C_{60} equals 0,71 nm. The C_{70} diameter

along its small ellipsoid axis also equals 0,71 nm. The diameter of the spherical C_{80} is equal to 0,82 nm. Compare these values with the cross-section of the abundant single-layer nanotubes (5,5): it equals 0,66 nm. We gradually bring the reader to the idea that we have to compare the mentioned geometry parameters of fullerenes and nanotubes with double inter-layer distance in graphite that equals 0,671 nm.

Our main idea of the mechanism formation of fullerenes and nanotubes from graphite in plasma does not include its full desintegration into very small fragments mentioned above. Fullerenes are the products of cutting fragments from the end of nanotubes named *caps*, and which contain ready five-membered rings while nanotubes are the products of cutting fragments from graphene rims, that we call *troughs*, which may be considered as oblongated caps.

The caps formation is a spontaneous that is energetically advantageous process. Here extrusion of 6 carbon atoms and appearance of 6 five-

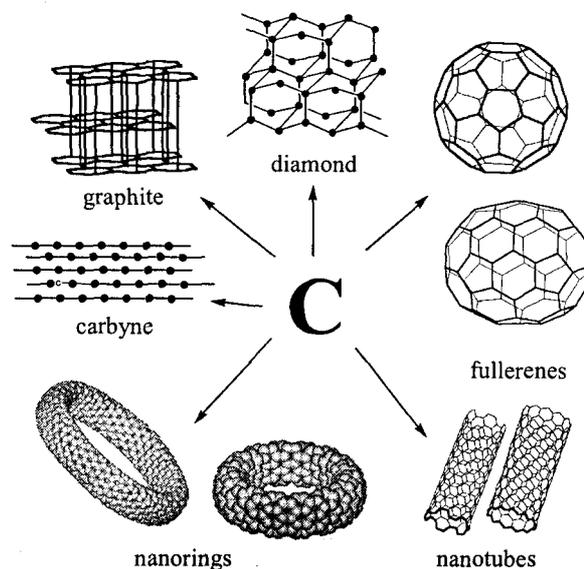


Fig. 1. Carbon allotrope modifications

membered rings separated by six-membered rings take place. As a result coordination-unsaturated three-valence carbon atoms at the nanotube ends disappear and in spite of additional strain of valency angles and bond distances, the resulting capped nanotube appears stable.

The simplest fullerene which may be cut from the end of the (5,5) nanotube is C_{60} . The next fullerene cutting from this nanotube contains an additional band of 10 carbon atoms thus we have fullerene C_{70} , but the probability of this cutting is much less than in the previous case, thus the ratio between fullerenes C_{60} and C_{70} in the soot is 8:1 or more.

This experimental fact is well known. Consequently, the reason of these two mentioned fullerenes C_{60} and C_{70} formation and the C_{80} (I_h) fullerene absence becomes clear, the latter cannot form from A-nanotubes (5,5). It needs Z-nanotubes (10,0), but they are formed less.

In graphite the rims of graphene lattices contain in ideal coordination-unsaturated carbon atoms but in usual storage for a long time graphite they are always covered by oxygen and water molecules and other particles which are present in enough quantity in the atmosphere surrounding graphite. These could also be functional groups like $-OH$, $-CO_2H$, $-CN$, etc.

In plasma the nanotubes rims and graphite layers are decomposing and fresh rims are forming. During this process the possibility of their connection exists. As a result spherical caps of nanotubes and oblongated caps (graphene troughs, GT) of graphene layers are formed.

If nanotube caps may arise spontaneously, then in the same way GT may appear. If the graphene layer rim is straight then it needs no carbon atom extrusion. Similar to nanotubes GT can have A- or Z-structure. A-GT formation goes by electron pairing of three-valency carbon atoms of graphene layer with a zigzag rim. Z-GT is obtained like in diene synthesis with the participation of benzyne or biradical structures of armchair graphene layer rim (Fig. 2).

The question arises: could two *neighbour* graphene layers form GT? Our answer is: it is dubious. In this case the graphene lattice bend would

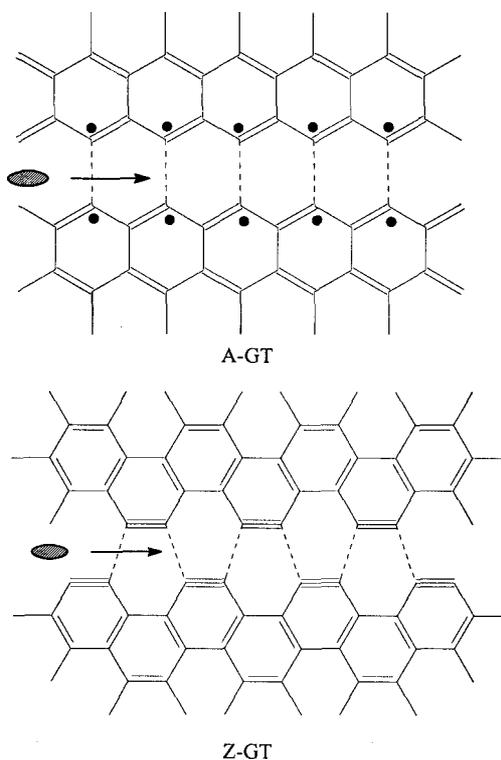


Fig. 2. Connection of graphene lattice rims. The pecked lines show forming bands. The shaded ellipses mean catalyst moving along the rims of graphene monolayers. Actually the layers are situated one above another and GT is forming in the place of their connection

have too large curvature that corresponds to very thin nanotubes of (3,3) or (5,0) type, but it is well known that such nanotubes do not form at all. On the other hand, if the connection appears *next but one layer* that is between layers separated by **intermediate** layer, then the curvature of the forming GT will correspond to the nanotube (5,5) or (10,0), depending on the shape of the GT rim.

There is another reason more causing graphene layers to connect next but one: it is known that in graphite the neighbour layers are shifted by 0,12 nm, but layers next but one are situated exactly one in front of the other. This is the obligatory condition for GT formation (Fig. 3).

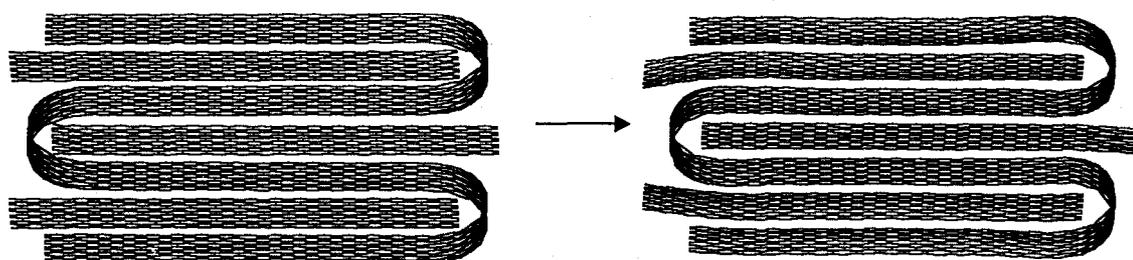


Fig. 3. GT formation when intermediate layer is present

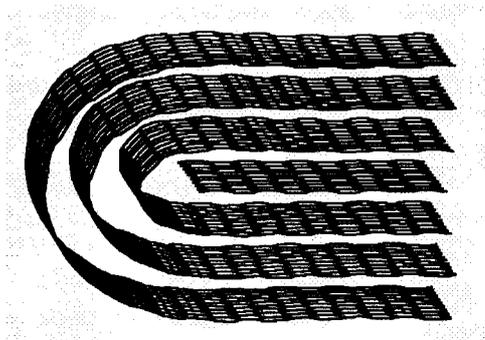


Fig. 4. Multi-layer GT formation

It is known that not only one-, but also two-, three- etc. layered nanotubes may be formed. In each case the interaction takes place next but three, five etc. intermediate layers (Fig. 4). Eventually multi-layer (onion) nanotube may be formed.

We have modelled different conditions of GT formation. Certainly, bending graphene mono-layer tending to become maximum planar is energetically unfavourable. That is why bent once, twice etc. graphene monolayer is gradually drawing up thus GT and nanotube formation from GT is unlikely (Fig. 5).

Optimization of the geometry of connected graphene layers shows that the intermediate layer not participating in the GT formation is needed for tightening bending layers (Fig. 3). If it exists the inter-layer distances remain almost the same as in the case of the stack of non-bonded graphene layers. Removal of the tightening layer leads to the gradual drawing up of the connected by GT graphene layers (Fig. 5), that confirms an importance of the intermediate layer for stabilizing the whole stack.

The next step of the high-temperature process is nanotube formation. Here a catalyst plays the role of a lock of a zip. Moving along the GT rim, it is cutting GT from graphene layer and simultaneously sewing free edges forming a new nanotube and new GT. The number of C-C bonds remains unchanged

thus this process is isothermic. The layer that fulfilled its tightening role is shifting or decomposing after that.

Consequently, formation of fullerenes and nanotubes does not need total graphite atomization and further assembling of spherical or tubular clusters from very small particles. In plasma, bending, connecting and cutting the graphene layer rim take place with the obligatory participation of the intermediate tightening graphene layer.

The confirmation of the described mechanism is the fact of fullerene formation *via* pyrolysis of the ready single-wall nanotubes [9]. As in the case of graphite, C_{60} is formed in larger quantities, then comes C_{70} and other usual higher fullerenes (C_{76} , C_{78} , C_{84}), while, as before, C_{80} does not form at all. Probably, a catalyst inhibits fullerene formation due to blocking NT caps, therefore graphite yields entirely NTs in the catalyzed process.

Conclusions

- At high temperature transformation of graphite into fullerenes and nanotubes the presence of the intermediate tightening layer is obligatory.
- The mechanism of the catalytic synthesis of carbon nanotubes under arc conditions includes adsorption of catalyst atoms upon the graphite surface, downturn of graphene layers and their further connection.
- The synthesis results predominantly in (5,5) nanotubes since they are not only the most stable possible ones, but also because their diameters are as close as possible correspond to the double distance between neighbouring graphene layers that corresponds to the diameter of the C_{60} fullerene molecule.
- High temperature self-assembling of fullerenes and nanotubes from diamond and carbyne unlike graphite is impossible in principle.

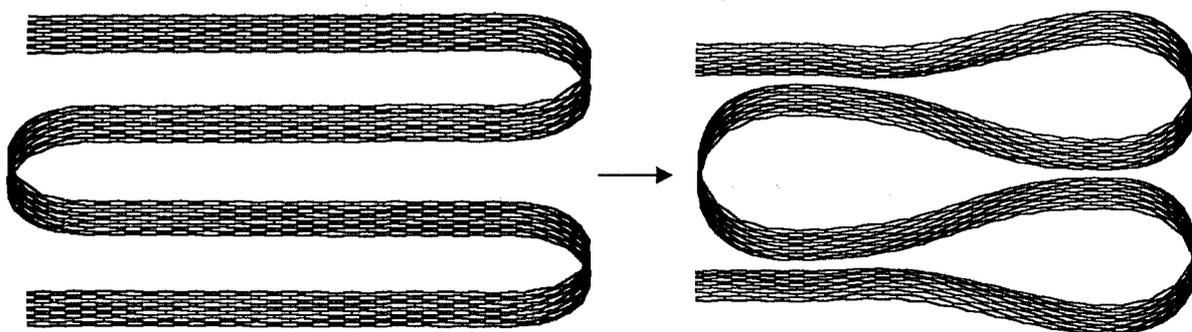


Fig. 5. Optimization of bent graphene mono-layer in the absence of the intermediate tightening layer

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НОВИЙ ПОГЛЯД НА МЕХАНІЗМ УТВОРЕННЯ КАРБОНОВИХ НАНОТРУБОК З ГРАФІТУ

Пропонується новий механізм утворення фулеренів і нанотрубок з графіту за умов лазерного випаровування в електричній дузі. Проаналізовано роль стяжного графенового шару і каталізатора в процесі синтезу нанотрубок. Атом каталізатора координується на поверхні графіту, а при високій температурі починає різати і зшивати графенову сітку, що приводить до утворення безпосередньо нанотрубки. Фулерени утворюються шляхом відриву ковпачків з частиною нанотрубки. Атомізація графіту не є обов'язковою стадією. Систематизовано й узагальнено факти, що підтверджують описаний механізм.