

The Formation of Morphological Structures of Carbon and Oxide Silicon Nanoparticles

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Abstract

The concept morphostructure formations nanosized individuals on the basis of carbon and quartz is offered. Under offered circuit in “the first stage” substances are generated by atoms – “elementary individuals”. They - form “simple morphostructures”, for example, fullerenes, film and a one-wall carbon tube. They have, at the best the two-dimensional structural order.

The second stage of growth morphostructures is connected to formation of more complex of “elementary particles” on the basis of the approximated rounded molecules. They - form “simple morphostructures”, for example, fullerenes, film and carbon tube also.

The third stage - clusters. Clusters, similarly to atoms and molecules, can form cyclic formations (oligomer/polymers), crystals and can enter structure of the mixed constructions of a layer. They can form also simple morphostructures, for example, fullerenes, film and carbon tube.

The fourth stage - compact formations of polymer and so on.

Introduction

The knowledge about mechanism of crystal formation is very important for understanding of crystal growth characteristics. As shown by many researchers in nanosized scale the certain stages of processing formation which leads to formation of stable phase of mater are the same [1, 2]. A large number of papers are devoted to the revelation of substance of atomic interactions in nucleation process [3].

The structural transformation “disorder-order” at transition from liquid to solid phase (from dynamic short-range order to long-range order -3D) can't happen instantly, in one stage, but occurs in several consecutive steps. Besides, there are works [4], showing that the effect of normalization of “rigid” atomic groups $[\text{SiO}_4]^{2-}$, $[\text{SiO}_4]^{4-}$ is similar to the same way as the atoms. According to the interpretation of authors the objective standard of effect of center normalization of these atomic

groups is serve the calculation of relative density of filling by these centers the families of crystal planes.

As the stable “protonucleus” of substance formed in this environment which contains chemical spirit, the stable forms of nanomatters which have its own crystal-chemical characteristics are formed.

Previously we have published the materials about morphological structures which were found experimentally as well as individual carbon particles, the classification of these nanoindividuals was made [5]. The reason for selection of seven most common formed types of nanoparticles was the investigation of materials synthesized by the most common methods. For carbon formations this is synthesis in arc, in flames, at carbonization in mechanochemical and plasmachemical processes and etc. The formation of particles on the base of silicon oxide was investigated in precipitation process [6].

The purpose of this work is the conceptual basis of possibility of stagewise nature of crystallogenesis, consideration of transformation pictures of subnucleus in these stages. This article

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was made on the base of results report, which was made by us during the International Conference “Carbon” which was held in Shanghai city, 2011 year [7].

The peculiarities of the structure and morphology particles were made with the help of (TEM, JEM 100CX, U – 100 kV). In addition, the materials which obtained with the help of X-ray phase method and electron-probe microanalyzer were analyzed.

Results and discussion

Nanosized individual particles of carbon formed in the process of carbonization, during combustion of flames, plasmochemical and mechanochemical synthesis and particles silicon oxides formed when depositing them from solutions were studied. To exclude possible manifestation of “the law of form inheritance”, we carried out “pure” experiments

on nucleation of siliceous particles chemically when dehydrating weak silicic acid obtained from rice husk.

Despite a great difference in the origin, composition, properties of the two types of initial raw material (of vegetable and mineral origin) and technologies of production, there were no radical differences in the morphology and structure of carbon containing nanoparticles formed. One may suppose a common character of nucleation and growth of carbonaceous nanoparticles (Fig. 1).

At “the first stage” of substance formations “elementary” particles (single spheroids) are atoms of the same type (Fig. 1a). They form simple morphostructures (simple forms), for example, fullerenes, film and tubular formations (Fig. 1b). Evidently, particles of this level can not have a volume periodical structural arrangement (registered by X-rays or electrons), at the best, they have a two-dimensional structural ordering.

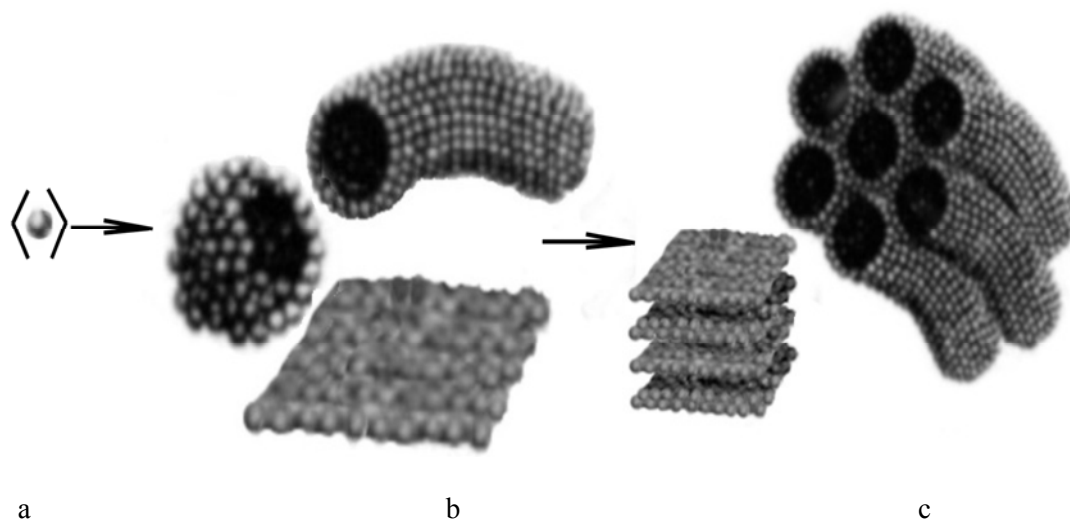


Fig. 1. The scheme of formation of different structural packings: “elementary” particles (single spheroids) – a; spheroids films, tubes and other “simple” formations composed by “elementary” particles - b; “complex one-wall” structures consisting of “simple” formations – c

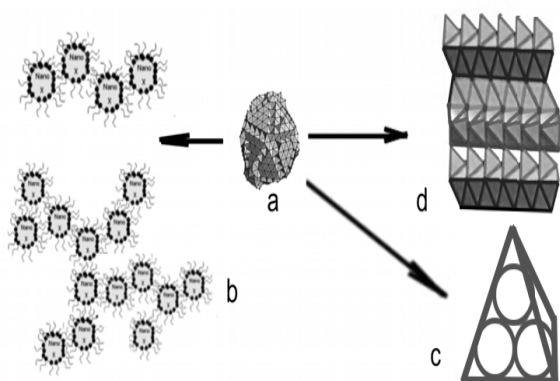
For diffraction patterns of electrons this state is characterized by predominance of quite intensive plane reflexes of the first orders. Particles of this kind (simple forms) can further from different combinations, for example, layer systems (graphite), aggregations and braids and other morphological structures formed on the basis of atoms (ions) (Fig. 1c). There appears a three-dimensional ordering, graphite-like and graphite structures. Probably, multilayer tubes and mixed layer morphological types of particles the walls of which are built from one atomic layer appear at the first stage of particle development, too.

The second stage of the growth of morphostructures is related to formation of more complex “elementary” particles on the basis of rounded molecules, the third stage – of clusters, the fourth stage – of compact polymer formations.

In all cases, complex morphostructures of nanoindividuals can be explained by constructions from “elementary” particles composed with formation of a cyclic structure of “an oligomer”, cluster particles and crystals.

Clusters (Fig. 2a), like atoms and molecules, can form cyclic formations (oligomer/polymers)

(Fig. 2b), crystals (Fig. 2c) and can enter the structure of mixed layer constructions (Fig. 2d).



The initial clusters – a: cyclic linear and volume formations – b; crystals formed by clusters – c; mixed layers with participation of clusters – d
 Fig. 2. The scheme of formation of morphological structures of carbon nanoindividuals on the basis of three kinds of initial structures (“bricks”).

That is crystalline structures also can be formed by stable groups of atomic clusters. The presence of molecules, their fragments or clusters in the lattice nodes and in the interstitial sites of molecules must result in complexation of the form of diffraction reflexes.

A similar pattern is characteristic for formation of particles of silicon oxides. In work [4], the stable structures such as $[\text{SiO}_4]^{2-}$, $[\text{SiO}_4]^{4-}$ could be clustered formations.

On the basis of the available data we have proposed a scheme of hierarchical architectural arrangement (Fig. 2) which, probably, accounts for formation of individuals on the basis of three kinds of initial structural formations which are stable under this thermodynamic condition. The starting point of every “stage” of development of morphostructural arrangement is “an elementary brick” - $\langle A \rangle$.

Initial building “bricks” (A): - atoms (at the first stage); molecules (at the second stage); clusters (at the third stage); compact polymer formations (the fourth stage): functional compounds...

The kinds of particles of the formed building “bricks” (A): “simple” kinds (1), their supercrystalline (2, 3), mixed layer (4) and crystalline (5) structures. Crystals are formed correspondingly: by single atoms at the first stage, by molecules - at the second stage, by clusters - at the third stage, and so on.

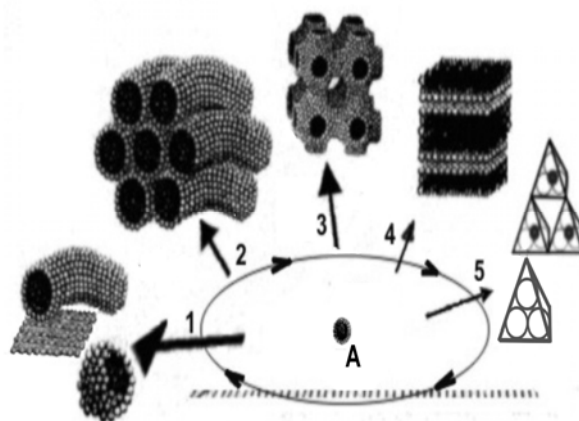


Fig. 3. The scheme, hierarchy of formation of different structural packings.

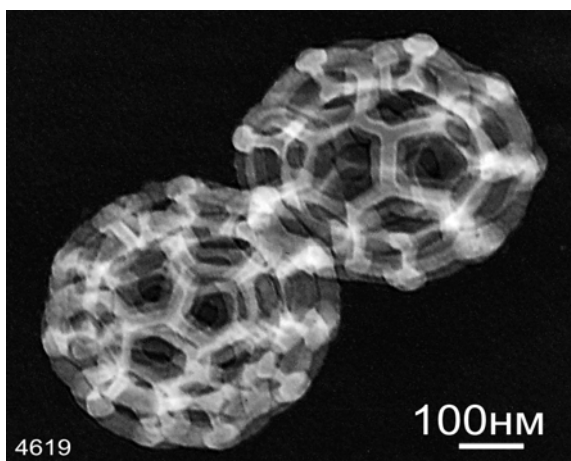
At the first stage of the substance formation “individual” atoms (single spheroids) - $\langle A \rangle$ form is simple forms definite in classification of morphological structures of individual nanoparticles, for example – plane systems. Monoatomic layers of carbon (graphene) are known. Rolled sheets of graphene can form both one- and multilayer nanotubes (Fig. 3, arrow 1). These morphostructural elements formed on the basis of atoms can form other systems. A graphene sheet formed by atoms, for example, can form a graphite-like substance, turbostratum graphite or graphite formed by a strictly oriented graphene layers (probably it is a variety of crystals). Tubes form aggregations or braids of tubes (Fig. 3, arrow 2). Rounded particles (fullerenes) can be grouped into different superstructural packings. On the basis of atoms different clatrate (Fig. 3, arrow 3), mixed layer structures (Fig. 3, arrow 4) and crystals (Fig. 3, arrow 5) are formed.

At “the second stage” growth of morphostructures is related to formation of more complex “elementary” particles $\langle A \rangle$. They are composed of detached (rounded) molecules. Rounded particles, for example fullerenes, can form tubular, film, clouded formations (Fig. 3, arrow 1), superstructures: braids (Fig. 3, arrow 2), clatrates (Fig. 3, arrow 3), mixed layer structures (Fig. 3, arrow 4) and crystals (Fig. 3, arrow 5).

So, a cluster/molecule of fullerene can form individual fullerene particles of a rounded form (a visible diameter up to $0.5\mu\text{m}$ is registered [3]). For some known reasons such nanoindividual inheriting the morphology of fullerene has no diffraction from the beam of electrons and X-rays. The particles can also from greater packings similar to opal structures

(corresponding to Figure 3, arrow 5) and, probably can have photon properties.

At the second stages silicon oxide are of great importance. All diversity of products obtained when dehydrating silicon dioxides is related to appearance of different initial structure forming elements Si_kO_m . These may be detached molecules able to get polymerized where k , m can have different values, and rigid cluster structures where

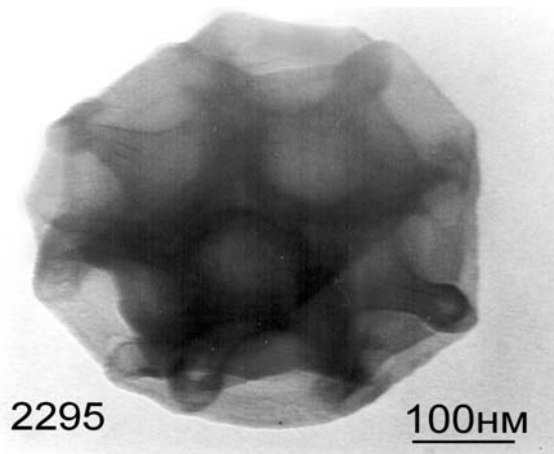


a

Fig.4. Fullerite particles in the samples of: mineral – a, vegetable origin – b

m , n must have strictly definite values. These are known arrangements from opal-like globules (Figure 3, arrows 1 and 2), complex formations (Figure 3, arrows 3 and 4) and crystals (Figure 3, arrow 5).

Thus, the cluster/fullerene molecule may form individual fullerite particles with round shape (Fig. 4) (visual particle diameter about 500 nm was fixed) [8, 9].



b

For obvious reasons such nanoindividuum which is inheriting the morphology of fullerene, doesn't have any diffraction from electron beam and X-rays. These particles may form bigger packages, similar to the opal structures (corresponding to the Fig. 3, arrow of 5 scheme), and probably may have photonic properties. As noted by many authors, with the participation of fullerenes the "glassy" or clathrate (Fig. 5) materials may form [10].

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(registered by X-rays or electrons), at the best, they have a two-dimensional structural ordering. In practice, it would be well-known constructions from opalo-similar globule (Fig. 3, arrows 1 and 2), complex formations (Fig.3, arrows 3 and 4) and crystals (Fig. 3, arrow 5).

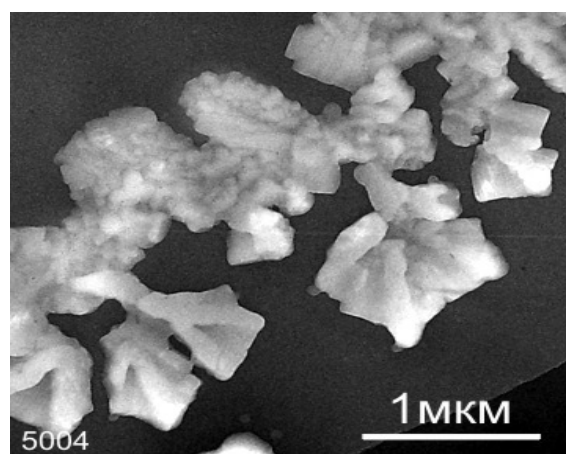


Fig.5. Fullerite formation, which not exhibiting the crystalline structural order (in X-ray and electrons)

In the third phase the cluster act as "elementary" building block according to the scheme of particle

formation. It is also possible to consider the formation of morphostructures of nanoindividuals on the base of compact by different methods of cyclic (oligomeric /polymer chains) – “the fourth stage”. That is, as single-layered and multi-layered films, tubes, ribbons, spheres and so on can be formed by different phases of carbon and oxide-silicon formations.

Conclusions

Evidently, morphostructures of nanosized individuals formed on the basis of carbonaceous particles and particles of silicon oxides are identical. One and the same morphostructure can be formed on the basis of atom, molecule, cluster and so on.

We should pay special attention to the individual constructions which have diamond-like structure periodicity. For carbon is a well-known diamond, but as it follows from scheme of matter formation, such package could be form not only by atom. For silica, this package formed by atomic groups is a known fact. But today this structure is not in demand.

The size of an “elementary” brick of the structure is determining. For example, a one-wall (formed by “atomic” sheet with minimum thickness) carbon tube will have a much smaller diameter than an oxide– silicic tube (formed by a “molecular” sheet with minimum thickness).

Several consequence follow from the considered scheme of particles formation. One of them is the possibility to extend some aspects of formation of morphostructures of one series which is at present studied quite well to another one (C_kH_m and Si_kO_m). For example, the proposition on saturation of solutions during formation of siliceous structures which is the most studied and theoretically founded can be approximated to illustrate formation of morphological structures of carbon (C_kH_m) series; to consider the possibility to complete the known morphostructures of stable phases of silicon oxides (Si_kO_m) by analogy with more studied and experimentally stated kinds of carbonaceous morphostructures.

References

1. Kidyarov B.I. Thermodynamics of crystalline nano- nucleus formation from liquid phase // Journal of Structural Chemistry. New York, Springer. Supplement 1. 2004. V.45. P.31-35.
2. P.G. Vekilov. Two-step mechanism for the nucleation of crystals from solution // J. Cryst.Growth. 2005. V.275. № 1-2. P.65 -76.
3. A.Ya. Mitus'. Theory of crystal ordering. Thesis. Novosibirsk, Institute of Semiconductor Physics SB RAS. 1982. P.13.
4. Klevtsova R.F., Magarill S.A., Pervukhina N.V., Borisov S.V., Glinskya L.A., Podberezhskaya N.V. The effect of ordering of submolecular atom groups in crystals of inorganic compounds // Journal of structural chemistry. 2002. V.43. №4. P.664- 670.
5. Z.A. Mansurov, T.A. Shabanova, Maruf Higazi, M.A. Biysenbaev, N.N. Mofa, R.M. Mansurova. Morphostructures of carbon nanoparticles of different chemical processes // Bestnik of KazNU. Chemical edition. 2007. №1 (45). P. 384 – 389.
6. Zhandosov Zh.M., Shabanova T.A., Shamalov M.E., Biysenbaev M.A., Mansurov Z.A. the obtaining of carbon material with high-surface area and study of products of its synthesis. // «Combustion and plasmachemistry» Almaty 2010. T.8. №3. P. 257-261
7. Mansurov Z.A., Shabanova T.A., Mofa N.N., Glagolev V.A. The morphological structure of carbon- and silicon containing nanoparticles. // International Carbon Conferences, Shanghai. July 25-28. Carbon 2011. - ID 703.
8. Mansurov Z.A., Shabanova T.A., Antonuk V.I., Levin V.L., Kotelnikov P.E., Glagolev V.A., Mansurova R.M. Structural order of carbon material according to data from electron microscopy and X-ray structure analysis // Vastnik of KazNU. Chemical edition. - 2004. - № 4 (36). - P. 451- 455.
9. Mansurov Z.A., Zhylybayeva N.K, Ualieva P.S., Mansurova R.M. Synthesis and properties of sorbents on the basis of the vegetative raw material // Chemistry in the interest of steady development. 2002. №10.- P. 339-346
10. A.M. Glezer. Amorphous and nanocrystalline structures: similarities, differences, mutual transitions. // Russian chemical journal (The journal of Russian chemical society named after D.I. Mendeleev). 2002. V. XLVI. №5. P. 57-63.

Received 28 March 2011