NEW CARBON NANOPARTICLE - ICOSAHEDRAL DIAMOND

Vladimir Ya. Shevchenko\textsuperscript{1}, Alexey E. Madison\textsuperscript{1}, Alan L. Mackay\textsuperscript{2}

\textsuperscript{1}Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences, Saint-Petersburg, Russia
\textsuperscript{2}School of Crystallography, Birkbeck College, University of London, London, UK

ABSTRACT. Regular structures need not be crystalline\textsuperscript{1}. The most striking example of such structures is icosahedral packing\textsuperscript{2}. It has a definite structure, which is not that of a crystal, nor that of a molecule; it is not one of the space-groups (or even point groups) listed in the International Tables; it is not a twin (although it could be described in terms of twinning). Describing a great variety of “unusual”, “unprecedented”, “magic” structures and so on any reference to a pre-existing crystal lattice is meaningless\textsuperscript{1}. Structural inhomogeneity and coherence are characteristic of structures of nanosized particles\textsuperscript{3,4}. Spatially inhomogeneous structures, for which a local short-range order slightly differs from a short-range order of one of stable or metastable structural modifications, or one of non-crystallographic packings, whereas different fragments are coherently joined into a whole, should exist in the nanoworld. Here we show that icosahedral carbon nanoparticles in which the local arrangement of atoms is virtually identical to that in diamond can be formed in nanometer range. They can be transformed reversibly into onion-like shell structures without disturbance of their topological integrity. Icosahedral diamond-like core can coexist coherently with onion shells. The general principle that governs the formation of such structures takes as a basis the non-Euclidean geometry.

Although nanodiamonds have long been the subject of the close attention of researchers, the question as to their structure remains open. Diamond nanoparticles are not at all the small-sized diamond crystals. For example, the detonation carbon particles consist most probably of a diamond core coated with shells having an onion (onion-like) structure with graphite inclusions\textsuperscript{5}. Recently, the structural properties of nanodiamond particles synthesized by detonation and the products of their transformation into carbon onions via vacuum annealing have been studied by various experimental techniques\textsuperscript{6}. It has been shown that the detonation nanodiamond particles have a composite core-shell structure comprising an ordered diamond core of \textasciitilde3 nm covered by a partially disordered outer shell of \textasciitilde0.8 nm. The transformation of the nanodiamond into carbon onions proceeds from the amorphous outer shell of the particles inwards towards the particles’ diamond core. A reconstruction of carbon atoms located in the outer shell leads to the bonding similar to those in nanocrystalline graphite. The observed structure was comparable with the structure of the bucky diamond clusters\textsuperscript{7,8}. The ab initio calculations showed that at about 3 nm the reconstructed surfaces become more reasonable, thus providing an atomistic structural model based on the topology of a diamond core surrounded by a fullerene-like carbon network\textsuperscript{7,8}.

Recently, the structural models of icosahedral diamond nanoparticles compatible with onion-like structures were developed\textsuperscript{9-11}. Different structural fragments are coherently joined into a whole. The local arrangement of atoms in these particles is
universally tetrahedral (not only inside the fragments but also at their interfaces) and virtually no different from that in the diamond.

The fivefold symmetry in diamond-like nanoparticles has been experimentally observed by a number of researchers. In particular, particles with an icosahedral morphology were observed among the diamond nanoparticles synthesized in an acetylene flame. The icosahedral morphology was interpreted as a result of multiple twinning of cubic crystals. It was noted that, among several forms of these multiple twins, there exist almost perfect icosahedra. The fivefold symmetry clearly manifests itself in the electron diffraction patterns. Some grate particles had semi-coherent boundaries but the small particles of several nanometers in size had fully coherent interfaces.

Let us demonstrate how an icosahedral diamond-like nanoparticle (icosahedral diamond) can be constructed if it is treated as a nanostructure that has coherent boundaries and is composed of insignificantly distorted fragments of diamond and lonsdaleite (hexagonal diamond). The geometric principles used for assembling such structures are based on the local approach. Within this approach, nanoparticles with coherent boundaries in the general case are assembled from a limited set of building blocks determined by the fundamental manifolds and the principles of assembling are governed by the topological properties of a fiber space. The great diversity of “unusual” structures can be obtained by mapping or projecting fragments of highly symmetrical structures from different non-Euclidean spaces onto the three-dimensional Euclidean space or mapping these fragments onto curved manifolds embedded into the Euclidean space. Their particular cases are substructures of polytopes, i.e., regular tilings of the three-dimensional Riemannian space (of positive curvature).

An icosahedron can be assembled by joining twenty slightly distorted regular tetrahedra. The number of atoms in the icosahedral packing can be increased by performing the geodesic design of tetrahedra or by filling the tetrahedra by corresponding crystalline fragments (by a fragment of diamond packing, for example). Constructed in such way diamond nanoparticles have a shell structure and a nearly spherical shape. Each shell contains 20k^2 atoms (20, 80, 180, 320, 500, ...), and the particle as a whole consists of 20k(k+1)(2k+1)/6 atoms (20, 100, 280, 600, 1100, ...), where k is the number of the shell. Their size varies within several nanometers. Special cases of this “magic” series are provided by endohedral nanodrops of the (H_2O)_{100} water, which were found in cavities of giant oxomolybdate clusters, and the (H_2O)_{280} Dzugutov clusters. These numbers are characteristic of carbon onions, and icosahedral diamond-like particles can easy (layer-by-layer) undergo into onions and vise versa just only by puckering and smoothening consecutive shells without migration of atoms over considerable distances.

Fig. 1 shows the consecutive shells of icosahedral nanoparticles. The core of these particles consists of 20 atoms forming a regular dodecahedron. Fragments in the form of barrels are attached to each of the 20 dodecahedral faces. The gaps are regularly filled with fragments of diamond and lonsdaleite. So, inserting the consecutive shells (Fig. 1, left) each into another one obtains the diamond-like particle. The smoothened shells (Fig. 1, right) form nested fullerene – onion. Both sets of shells are equal topologically, and may be reversibly transformed each into another by smoothing and puckering of atomic nets. It should be emphasized that, in the framework of the mechanism under consideration, the transformation of an icosahedral diamond-like nanoparticle into a shell nanoparticle is not accompanied by breaking of any chemical bonds.
bonds and leads only to a change in their character and direction. In terms of atomic orbitals, the reversible structural transformations in carbon nanoparticles correspond to dehybridization and rehybridization of the bonds. The topological integrity of the network as a whole remains unchanged.

Figure 1 Formation of icosahedral nanoparticles with coherent boundaries. The consequent shells (from top to bottom) consist of 20, 80, 180, 320, and 500 atoms, respectively (view along the two-fold axis of icosahedron). **left**, Shells forming the diamond-like particle. **right**, Shells forming the onion-like particle. Both sets of shells are equal topologically, and may be reversibly transformed each into another by smoothing and puckering of atomic nets. Combining shells from both sets results to the composite icosahedral core-shell particle with diamond core coherently joined with onion shell.
Another possibility is the coherent coexistence of diamond-like core with onion-like shells. Let us suppose that outer shells undergo the smoothening transformation, whereas the inner core remains diamond-like. This case corresponds to the composite icosahedral core-shell particle without any grain boundaries (in the classical sense) between “diamond” and “graphite” fragments.

Thus, the structures of icosahedral diamond-like nanoparticles can simultaneously involve fragments with specific features of diamond, lonsdaleite, graphite, and carbon onions joined coherently. They can serve as a good model accounting for the structure of detonation nanodiamonds, as well as for the structural transformations of nanodiamonds into onion-like carbon structures and vice versa\(^5,8,23-30\).

REFERENCE