❶Characterization of *NanoAmando* has well-progressed !

Just a few words are due about NanoAmando. When we began working on the detonation nanodiamond in 2001, we had only one goal in mind: to isolate and characterize the elementary particles of detonation nanodiamond (EPDND). In order to inspire ourselves facing such a difficult task, we coined a name of NanoAmando to the yet unknown EPDND and registered it as a trade mark.

In spite of our considerate tribute, NanoAmando remained a tough target for a long time, but a series of lucky events that occurred to us within the past three years finally helped us to unveil the difficult secrets of nanodiamond one by one. Now we are ready to proceed toward the next goal: to find applications of grand-scale. Even though we began writing papers with full information, it will take one or two years to get them printed. Hence I decided to contribute **News** in our Home Page to leak our latest results on NanoAmando so that outside people realize the merits of nanodiamond.

Size From the beginning we used average diameter of NanoAmando readily available by using a dynamic laser scattering (DLS) apparatus as a convenient measure for evaluating monodispersity of NanoAmando. Even small amounts of agglutinates, for example dimers, remaining uncrushed by our stirred-media milling will increase the average. In other words we should seek the smallest possible average diameter to reach monodisperse NanoAmando. A breakthrough toward rapid progress of our project came when we adopted Taguchi's Method of quality engineering to optimize the operation conditions of stirred-media milling. We

skip the details in this News, but at present the average hydrodynamic diameter of our NanoAmando has been staying at 2.6±0.5 nm in the past three years. Backed up with additional evidence, we think this is the final value.

Shape All diamond crystals have exactly the same and well-known 'diamond structure', excepting rare species like Lonsdaleite, but the surface pattern keeps changing as they grow larger. Thus, diamond represents a typical metamorphous mineral. In view of high proportion of surface to internal atoms in nanoparticles, it is useful to know its prevailing shape. As there is no reliable experimental clues regarding the shape of NanoAmando, Barnard and her group in CSIRO, Australia, performed extensive calculations of all possible diamond input structures having diameters between 1.7 to 4.0 nm to obtain a highly valuable dataset consisting of 126 energy-minimum structures of nanodiamonds by using SCC-DFTB program. Using these optimized structures they constructed an interconversion pathways map (Fig. 1).

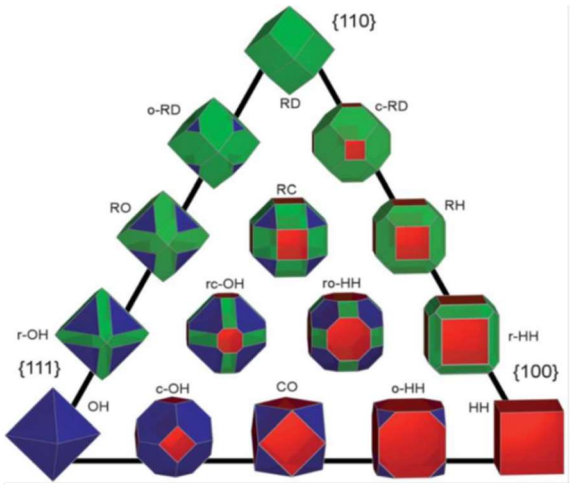

Fig. 1. Metamorphic interconversion pathways map for diamond crystals

We have to omit detailed explanation of this map but one can easily visualize moving from top to bottom or left to right represents abrasion, while the other ways crystal growth. As the detonation nanodiamond synthesis should be a combination of growth processes from the bottom right end towards up and left, but suddenly frozen when shock wave has passed, we may assume that NanoAmando is a mixture of at most 12

intermediates in this map. Which one will be the most abundant? We arbitrarily chose three structures in the center of Fig. 1 (RC, rc-OH and ro-HH) as more likely and adopted the one having a diameter closest to the observed 2.6nm as the most likely candidate: No. 52, ro-HH, diameter of circumscribed sphere 2.628 nm, and total number of carbon atoms 1670 (Fig. 2A). This particular shape is named rhombitruncated cuboctahedron, one of the noble Archimedean semiregular polyhedra, consisting of six octagonal facets, eight hexagons and twelve squares. It has a high sphericity and located in the strategic position in Fig. 1. We will use this shape below as a representative below.

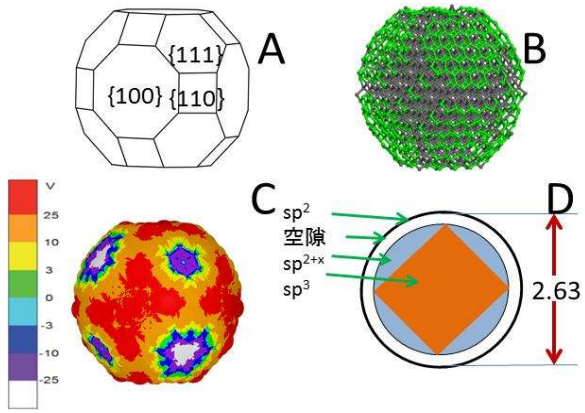

Fig. 2. Optimized geometry of NanoAmando shaped as rhombitruncated cuboctahedron (A-C), and a cross section (D).

Surface structure One of the technical problems persistent in detonation synthesis of nanodiamond will be how to prevent back reaction after the detonation. As the detonation is usually carried out in an explosion chamber made of thick stainless steel or super-hard alloy it is generally difficult to remove the inside heat quickly enough to completely suppress the back reaction. Hence it is not surprising to find the most vulnerable {111} hexagonal facets of EPDND transformed into graphene patches unless special measure has been taken to quench the whole explosion chamber to low-temperature. All the nanodiamond structures in the Barnard dataset have the all the {111} facets completely graphitized as long as the structure has {111} facets (no quenching during geometry optimization).

Although our supplier of crude detonation product has never disclosed any information on their detonation process, our NanoAmando does show clear π-π* absorption in X-ray absorption spectrum. Thus, our supplier does not mind partial back reaction to occur and leave quite a few graphene patches symmetrically distributed and firmly bonded onto the surface (Fig 2B). Such neglect caused a few drawbacks: our NanoAmando is only poorly fluorescent due to internal quenching of luminescence, and its solution develops quite intense black color probably due to effective absorption of visible light by the graphene patches.

However, very close disposition of the most electronegative graphene patches over the most electropositive diamond carbons could have led to strong polarization of mobile free electrons generated upon partial graphitization. The unique polarization of electrons across extremely short graphene-diamond separation seems to have induced many more consequences on NanoAmando:

(1) Distribution of strong electrostatic fields, both positive and negative, over the facets (Fig. 2C).

(2) Attractive interfacial interactions between the closest facets of neighboring particles in opposite charges (agglutination in solids)

(3) Large and positive ζ potential of colloidal solution (stable colloids)

(4) Remarkably high solubility in water (gel formation above 10% concentration) and in DMSO (oxygen hole burning effect).

Internal structure Analysis of the optimized geometry of rhombitruncated cuboctahedron revealed surprising facts: only 1026 carbon atoms or 61.4% of the whole carbon are sp^3-hybridized, the rest consisting of sp^2- (16.5%) and sp^{2+x}- (20.6%, $0<x<1$) hybridized carbon atoms. Compositions of these three

types of hybridized carbon atoms in other intermediate structures are similar to that of rhombitruncated cuboctahedron. At this point we took LDI-TOF-MS of our NanoAmando, which did not show any peak at 20 kDalton expected for a C_{1670} diamond, but showed a rather broad peak at 12 kD corresponding to a C_{1000} species, which agrees to the number of sp^3-carbon atoms in the optimized structure of rhombitruncated cuboctahedron. This surprising observation indicates that sp^2- and sp^{2+x}-hybridized carbon atoms near the surface have been evaporated by irradiation of powerful UV-laser. In fact, a couple of broad fragment peaks, each consisting of sharp peaks separated by C_1 and C_2 masses, are found overlapped in the low-mass region of mass spectrum. The leaned parent peak can be interpreted as decent diamonds crystals, typically the remnant of hexagonal growth nuclei as shown in Fig. 1D. Interestingly enough, the Barnard database does contain a C_{1000} diamond in hexagonal shape dominated by 'diamond structure' and having a diameter of circumscribed sphere of 2.215nm.

Thus, one of the smallest known diamonds, NanoAmando is only 60% true diamond in the center, but the rest 40% occpies the surface portion to make the quasi-spherical single-nano particle a novel hybrid carbon with all known hybridization and unique polarization. I wish to add one more surprise here. The first rigorous identification of nanodiamond was reported by R. S. Lewis (*Nature* 1987) using extracts from presolar Allende meteorite and its MALDI-TOF-MS taken by I. C. Lyon (2005). The results indicate that their nanodiamond is identical with NanoAmando in terms of size and internal structure.

Unique features of NanoAmando Several other sources claim to have isolated EPDND. Although we have never compared their products with NanoAmando in scientific rigor, we have long noticed a number of distinguished

differences between NanoAmando and other products (Tab. 1).

Table 1. Contrasting features between NanoAmando and other claimed EPDNDs.

Features	NanoAmando	Other EPDNDs
Diameter, nm	2.6±0.5 (DLS) 2.8 (Raman) 2.4∼2.8 (TEM)[a]	Many claim 4∼5, but details (method, statistics) usually not given
Shape	Rhombitruncated cuboctahedron (Fig. 2)	?
Color	Light brown (hard gel) Intense and translucent black (conc. aqueous solution)	Mostly grey to tan
Functional groups	No COOH by titration Very weak IR peaks in C=O and C-O regions	COOH always claimed but concentration rarely disclosed
Surface graphene layer	Positive evidence (XAS, computations on real-size models)	Usually claimed but never with evidence
Dispersity	100.00% (on vol. basis in solution)	
ζ-Potential	+40∼50 mV	Large negative values
Solubility	High: water, DMSO Medium to low: EG, PG, NMP etc	Never adequately disclosed. Often give unstable suspension.
Impurity level	Zr: 200ppm, Fe: 100-300 ppm	Usually undisclosed

[a]Meteorite nanodiamonds reported by Lewis, Daulton and Lyon.

Improved milling process Nano-milling in general involves astronomical increase in the number of particles if started from visible particles. Explosive increase in the number of particles is accompanied by the more pronounced increase in the total surface with higher order of magnitudes. In order to accommodate new surface we need more solvent than the starting volume, which may sometimes requires unexpectedly large additional amounts. Therefore it is necessary to estimate the amount of solvent required in the final stage of milling and secure enough amounts (and additional space). If such precaution is omitted, new surface will recombine or viscosity increase to stop the milling. Details of calculation is out of the scope of **News** but will be published elsewhere.