

# Structure of detonation nanodiamond

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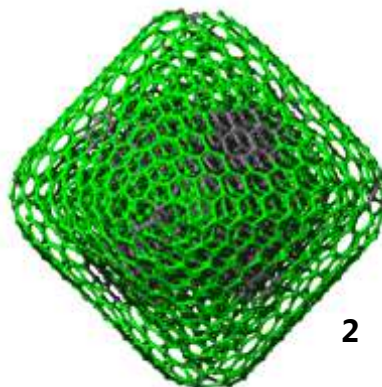
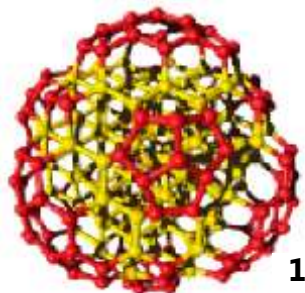
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Detonation nanodiamond (DND) was discovered by Danilenko and his coworkers in 1963 [1], but its primary particle (PP) defied isolation for long time due to unusually strong agglomeration among them. Now that PPDND with  $3.2 \pm 0.5$  nm in diameter are finally recovered from DND, we are ready to explore their applications, which will be rich in variation. No less surprising is the complexity of PPDND in a number of aspects, which, at first, many thought simply as smaller pieces of bulk diamond. In this talk we will review the STRUCTURE of PPDND as revealed recently.



1. **Outer surface.** It is long been shown that  $\{111\}$  facets are graphitized by the back process during the cooling stage after detonation. This local phase transition on a single-nano diamond crystal is different from

the transition in bulk octahedral diamond: this transition occurs surrounded by other types of facets,  $\{100\}$  and  $\{110\}$ , so nanographene facets suffer from mechanical strain, shrinking along the basal plane and lifting outward in radial directions as clearly shown by Raty-Galli in **1** [2]. This is less pronounced in a larger model **2** [3]. However, note that the central portions of graphitized  $\{111\}$  facets in **2** are visibly rippled, where the graphitized shell is collapsed. Such strained portions will be the sites of oxidative attack in the later purification process. A few other surprising consequences will be disclosed.

2. **Surface charges.** Extensive calculations led us to conclude that high electrostatic charge distribution over different facets, both positive and negative, are re-neutralized by the introduction of  $\{110\}$  facets, and almost disappear as the particle diameter increases beyond about 3.5 nm. Interestingly the recently found diameter of primary particles corresponds

exactly to the borderline between charged and neutralized particles. We believe this agreement is not a coincidence but has a reason, which will be discussed in the presentation.

- 3. Second and deeper surface layers.** When the computable size of model was smaller, e.g., less than 1700 atoms in 2007 [4], one or two layers of graphene were followed by thick layer of  $sp^{2+x}$  ( $0 < x < 1$ ) carbon atoms, or *amorphous diamond*. It is now possible to geometry-optimize well beyond 2400 atoms, the size of a real primary particle. Then we see little perturbations in diamond core even near the surface. Clearly the critical structure borderline of 3.5 nm has a few more implications.
- 4. Loose density near the surface.** Figure 2 demonstrates visibly large empty space below the surface graphene layer, which might be corresponding to the nano-pore found by Korobov's nitrogen absorption experiments [5]. This empty void can be spontaneously expanded by incorporating solvent molecules to produce clathrates like we see in the thin-layer graphenes [6]. This possibility has some relevance to the new DDS involving PPDND as drug carrier [7].
- 5. Shape of particle.** We are still unable to define the shape of PPDND primarily due to lack of contrast in their TEM images. At the moment our best guess by systematic optimization of all possible candidate structures of PPDND is doubly truncated octahedron (2 but extensively oxidized and more rounded) [8].

Thus, PPDND turned out to be a distinct hybrid nanocarbon with core-shell structure. The surface is dominated by holey graphene, giving the most unusual diamond ever known. Applications inspired by the unique structure are being unveiled and a few of them will be introduced in the lecture.

## References

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