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Consequences of strong and diverse electrostatic potential fields on the surface of detonation nanodiamond particles

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ABSTRACT

Discovery of strong electrostatic fields on the surface of primary particles of detonation nanodiamond by Barnard and Sternberg not only provided a highly likely explanation on the long pending origin of agglutination in the crude detonation product, but also marked the first recognition of a new type of interfacial interaction that can be as strong as C–C covalent bonding. The sign and potential distribution of the electrostatic field are specific to the crystallographic indices of facets and size of particles, thus the new electrostatic feature could well be unique to nanocrystals. This article interprets various enigmatic behaviors of nanodiamond particles that we have so far been unable to understand in terms of surface electrostatics. A mechanism of self polarization in the energy-minimized nanodiamond crystals in terms of orbital interactions through space and bond is presented.

1. Introduction

Recent discovery by Barnard and Sternberg [1,2] of strong electrostatic fields on the surface of the single-digit nanodiamond particles gave fresh insight on the origin of agglutination among the primary particles in *as-produced* detonation nanodiamond [3]. They performed systematic energy-minimization of octahedral, truncated octahedral (TO), cuboctahedral and cubic models of nanodiamond particles sized between C_{142} and C_{1798} by using DFT/TB level of theory with self-consistent Mulliken charge distribution. Their major results and conclusions are as follows:

1 Common to all four kinds of polyhedra examined, carbon atoms on {111} facets and several layers of carbon atoms below were transformed into graphitic carbons during the energy-minimization. Those on the reconstructed {100} facets and below, as well as central core region of the model maintained sp^3-hybridization. Finally there were formed, between sp^2- and sp^3-domains, layers of sp^{2+x}-hybridized carbon atoms, thus giving a sort of triple core-shell structure.
2 Prominent electrostatic potential fields developed on the surface of the energy-minimized polyhedral models, which varied depending upon the type of polyhedra, crystallographic indices of facets and size of models. Remarkably, sign and potential distribution pattern remain characteristic to the facet type. In a TO model (Fig. 1), all six {100} facets carry strong positive electrostatic field, whereas {111} facets display more complicated distribution with central negative field surrounded by positive fields in two distinct patterns designated as $\{111\}_a$ and $\{111\}_b$.
3 Suppose a pair of TO primary particles approach towards each other, with the two closest facets either $\{111\}_a/\{111\}_b$ or $\{100\}/\{111\}_b$, sharing the same inter-facet normal vector. In these cases, if relative rotation around this axis as well as facet-facet normal distance reach coherence, prominent attractive force develops between the particles. Coherent inter-facial interactions are predicted to produce coulombic binding energies comparable to those of C–C covalent bonding. They called such interactions as *coherent interfacial Coulombic interactions* and suggested the interactions as the cause of agglutination.

We surmise that strong and diverse electrostatic potential fields developed on the facets of primary particles of detonation nanodiamond not only cause their self-assembly but also are responsible for other surface interactions like solvation and adsorbent substitution reactions. We review in this paper our attempts to explain several enigmatic behaviors of the primary particles that we observed in the past but could not understand, in terms of electrostatics of the crystal facets. We also present a mechanism of self-polarization, observed for the first time in the all carbon system, using qualitative orbital interaction theory. In view of the increased role of graphitic shell in

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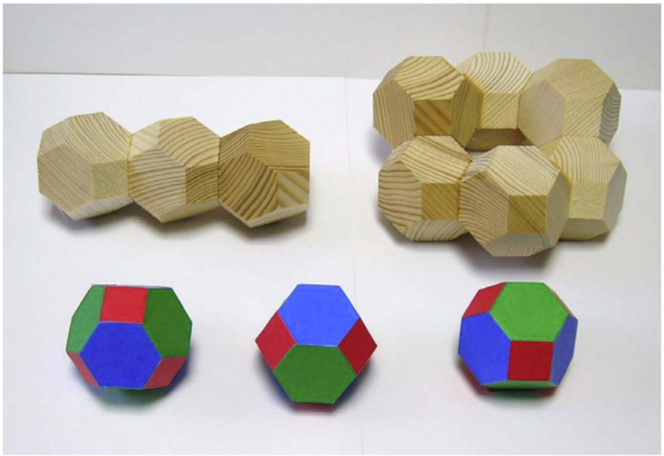

Fig. 1. *Front raw*: Three different views of wood-craft models of truncated octahedron (TO), the most likely crystal structure of primary particles in detonation nanodiamond or single-nano buckydiamond (SNBD) particles. According to DFT/TB calculations of Barnard-Sternberg, its square facets {100}, colored red, carry strongly positive electrostatic potential, whereas half of hexagonal {111} facets, designated $\{111\}_a$, blue, display mostly negative potential distribution, and the other half $\{111\}_b$, green, intermediate potential pattern. *Back raw*: Strong electrostatic attractive interaction develops when SNBD particles approach forming parallel and coherent pairing of facets, $\{111\}_a$–$\{111\}_b$ and $\{100\}$–$\{111\}_b$. Two oligomeric configurations formed by the former type of facet pairs are shown. Coherent interfacial interactions like these are proposed to be the origin of agglutination seen among SNBD particles in the crude detonation nanodiamond.

the primary particles of detonation nanodiamond, we name these particles as single-nano buckydiamond (SNBD) throughout this paper.

2. Hydration

2.1. Highly oriented layer of water on SNBD surface

We had detected nanophase of water in the hydrogel of SNBD by means of differential scanning calorimetric (DSC) analysis, and presented a hydration model wherein a layer of water molecules tightly surrounding the surface of each SNBD particle. Analysis of DSC data indicated that the inner part of water layer having a thickness of 0.6 nm and weight ratio of 0.24 to that of a SNBD particle does not freeze until −8 °C [4]. We felt that ad the conventional explanation of active surface of nanoparticles in terms of large specific area is insufficient for such a remarkable hydration. With the advent of Barnard's theory, we can infer charge-dipolar interactions between the particle surface and water molecule as responsible. As bipolar water molecule can act as proton donor in the hydrogen bonding with the negative electrostatic field in the center of {111} facets as well as dative partner through oxygen lone-pair electrons in the donor-acceptor interaction with the positively charged {100} facets, the nanophase of water consists of two types of clusters wherein water molecules are oriented in almost opposite directions depending upon the type of facets they cover (Fig. 2). For this reason, inter-cluster interactions in their boundaries should be attractive to each other rather than repulsive, thus strengthening the hydration layer as a whole.

2.2. Differential hydration in the three forms of SNBD; colloidal solution, hydrogel and flakes

Tight-adhering shell of water surrounding the surface of dispersed SNBD particle are supposed to move with the particle [4], hence we should always take its effects into accounts whatever the form of product (Fig. 3). For example, aqueous colloidal dispersion of SNBD seems permanently stable, never showing sign of flocculation, despite the noted tendency of single-nano particles to form large aggregates. The remarkable stability of DNBD colloidal particles can be interpreted as the result of neutralization of surface charges by hydration.

In this regard the SNBD colloid is out of the range of DLVO theory. Unremarkable positive ζ-potential of SNBD was difficult to understand but now it is clear that the observed ζ-potential is the sum of individual potentials over the facets. DLVO theory needs to be revised for polyhedral nanocrystalline colloids. Revised theory should be able to interpret the enigmatic relative stabilities of SNBD colloids in organic solvents as well (DMSO is by far the best solvent, even superior than water, whereas DMF has no affinity at all [5]).

Abnormally strong hydration should be the reason for ready gellation of SNBD into hydrogel, which starts at relatively low concentrations of 8–10%. Initially gel is soft and deforms itself quickly to the shape of container, but continued removal of water leads to harder and harder gel, giving a thick and black film on the inside wall of rotary-evaporation flask, which gradually splits into narrow strips of a few mm wide and several cm long, then into whiskers having sub-mm widths and cm lengths. Whiskers can be pulverized in a mortar into flakes and further into fine powder upon thorough grinding. After drying at 60 °C under a vacuum of 30–40 hPa for 2 h, the resulting crisp powder still contains 2–3% of water. While dried powder is difficult to redisperse, incompletely dried flakes are readily re-dispersible in water (or in good organic solvents like DMSO and ethylene glycol) by intensive sonication to give the same stable colloidal solution of SNBD.

It is difficult to prepare artificial agglutinates. It seems that agglutination takes place only after thorough drying while allowing subtle adjustment for coherency. Despite a number of attempts we have not been able to reproduce agglutinates. All these behaviors of SNBD/water binary system demonstrate strong adherence of water shell onto electrostatic field over the facets of particles. Water in SNBD cannot be removed completely unless heated at 150 °C for 15 h under high vacuum, as judged by *in-situ* IR spectroscopy [5,6]. These observations lead to two conclusions. First, agglutination among SNBD, or self-assembly of freshly grown SNBD particles by coherent interfacial coulombic interaction, is a rare phenomenon that arises only during explosion of Composition B (TNT + RDX) wherein strictly anhydrous condition was probably generated at some point. Second, hydration on dispersed SNBD is a persistent phenomenon caused by strong bi-functional bonding of oriented water molecules with strong electrostatic fields on the facets. Therefore in general it is always necessary to

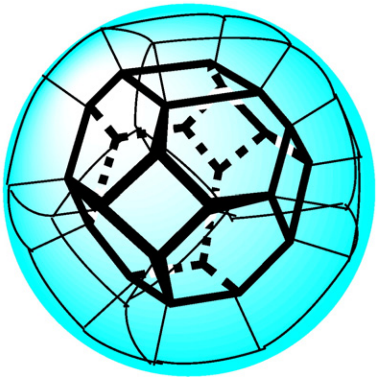

Fig. 2. Strong electrostatic field on the facet of SNBD particles tightly binds with water solvent molecules in its colloidal solution to form nanophase of water over the surface. Due to different electrostatic potential distribution in the three types of crystal facet (Fig. 1), orientation of water molecule in the nanophase is different depending on the facet it covers. Hence the nanophase of water consists of mixed clusters, which interact with neighboring cluster boundaries in general by attractive force generated by opposite alignments of water dipole. Combined with strong charge-dipole attraction at the facet surface, this feature leads to the formation of highly dense, persistent and non-freezing hydration shell of well-oriented water molecules over the surface of a SNBD particle.

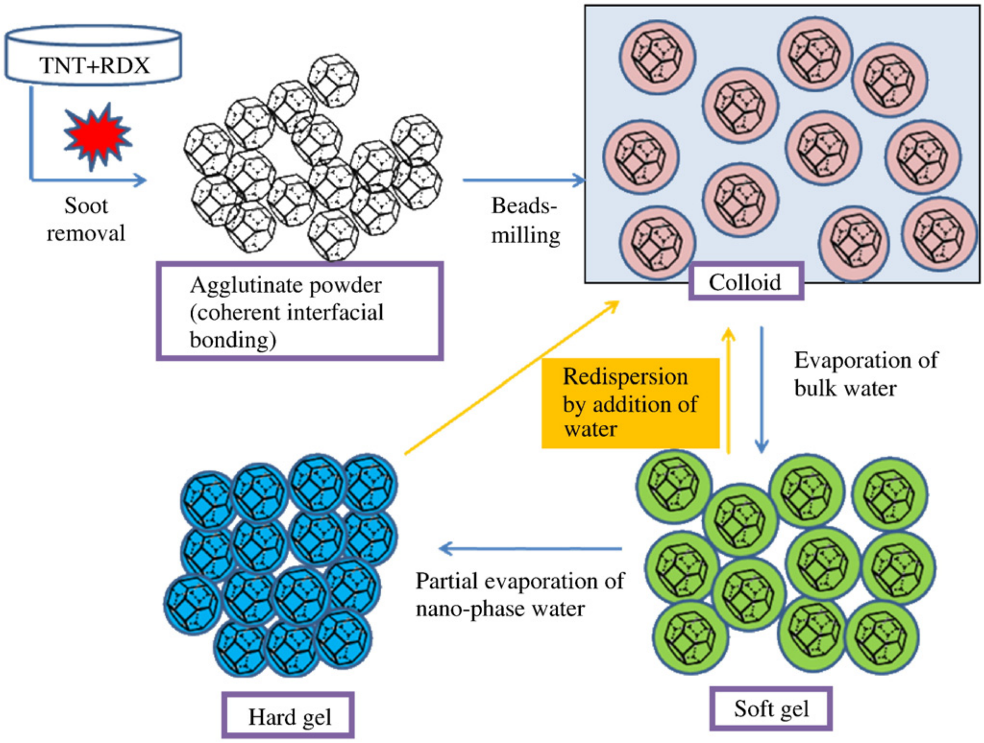

Fig. 3. All three forms of SNBD particles, aqueous colloid, hydrogel and flakes, carry nanophase of water. Colloidal solution is stable up to about 10% concentration and the high dispersity is realized by the shell of strongly oriented water molecules. In gel, particles are still protected from direct contacts by the water nanophase. Weak aggregation does occur in gel but can be disintegrated by dilution and light sonication. Evaporation of water in rotary evaporator leaves a few % of water in the flakes, which can be re-dispersed by intensive sonication. It seems that the persistent water molecules remaining in the flakes prevent coherent interfacial orientation among SNBD particles. We are still unable to reproduce agglutinates from once dispersed SNBD.

consider the effect of hydration shell for all the events of SNBD particles.

2.3. Self-organization of SNBD particles

Huang, Dai and their coworkers had noted one particular consequence of the above statements before the work of Barnard, which led to large-scale self-assembly of SNBD particles in water to give films, fibers and whiskers [7]. Now we qualitatively understand these self-assembling processes as the results of directive facet-facet coulombic interactions weakened by the water shell adhered to the particle surface. They made an interesting remark to use water with pH<4 in order to achieve self-organization. We believe that acidic water loosened the structure of water shell on the facets, thus enabling better control of assembling process. Possibilities of modifying the solvation shell structure are elaborated below.

3. Substitution

3.1. Survey of ion/molecule interactions with SNBD facets

Here we classify perturbations upon the nanophase of water on the SNBD surface by ions and dipolar molecules from bulk water phase as the first step to understand and control the behavior of SNBD particles. A salt X^+Y^- will bind in general more strongly than dipolare molecules with the electrostatic field of facets to replace adhered water:

$$X^+ + (HOH)/F^- \leftrightarrows X^+/F^- + H_2O \tag{1}$$

$$Y^- + (H_2O)/F^+ \leftrightarrows Y^-/F^+ + H_2O \tag{2}$$

where F^- and F^+ are the facets having strong negative or positive electrostatic field, respectively, and '/' signifies the interface between shell and facet. In general, the preferred centers of above substitution reactions will be the atoms at edges or vertices, because here backside attack is possible as in the organic S_N reactions. According to the results of calculation [1], the highest negative charge density is always found in the center of facet while the highest positive charge densities are often located at or near the edges and vertices. Therefore anions Y^- will be the preferred reagents rather than the cations X^+ in the substitution reactions (1 and 2). These reactions are basically reversible but can be shifted towards the right-hand side of equation by adding enough ions because of the inherently stronger charge-charge interactions as compared to the charge-dipole interactions.

Similarly, substitution of bound water molecule by a neutral dipolar molecule N–P (N = negative pole, P = positive pole) can be depicted as follows:

$$N\text{–}P + (HOH)/F^- \leftrightarrows N\text{–}P/F^- + H_2O \tag{3}$$

$$N\text{–}P + (H_2O)/F^+ \leftrightarrows P\text{–}N/F^+ + H_2O. \tag{4}$$

In these cases, it is usually difficult to predict the direction of equilibrium in the absence of specific information of reagents but the above-mentioned preference for electrophilic attack will be maintained.

3.2. A novel drug delivery system based on hydrogel of SNBD

Huang, Ho and their coworkers are developing a new drug delivery system using SNBD as the carrier platform [8,9] without prior knowledge of the work of Barnard/Sternberg [1]. In their first experiments, aqueous solution of doxorubicin hydrochloride (Fig. 4, I) was added to colloidal solution of SNBD to immediately observe doxorubicin·SNBD complex to form gel and precipitate. In the light of

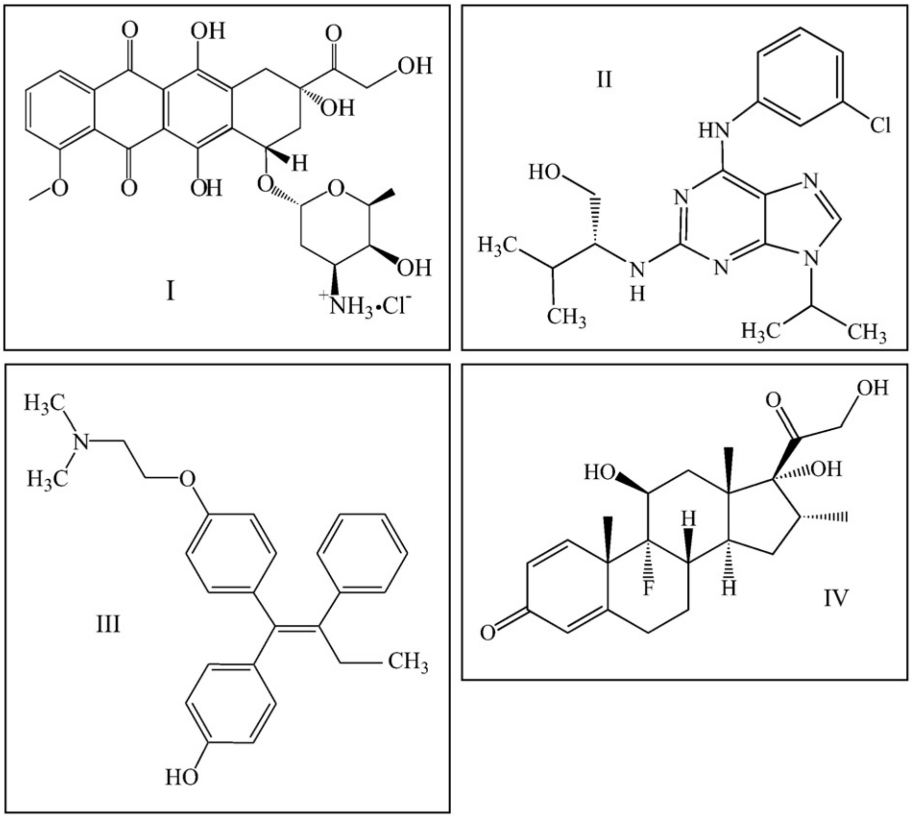

Fig. 4. Drug molecules used by Ho group in the development of a new drug carrier strategy using SNBD particles as the platform for safe delivery and slow release. I = Doxorubicin (Adriamycin), II = Purvalanol A, III = 4-Hydroxytamoxifen, IV = Dexomethasone.

the above arguments on the substitution of adsorbed water by ions, we can formulate the gel formation as follows:

$$\text{A–N}^+ + (\text{HOH})/\text{F}^- \leftrightarrows \text{A–N}^+/\text{F}^- + \text{H}_2\text{O} \tag{5}$$

$$\text{Cl}^- + (\text{H}_2\text{O})/\text{F}^+ \leftrightarrows \text{Cl}^-/\text{F}^+ + \text{H}_2\text{O} \tag{6}$$

where $\text{A–N}^+\text{Cl}^-$ means doxorubicin hydrochloride (I). Strong charge-charge interactions (5)–(6) quickly drove the adhered water molecule out to bind the drug ammonium ion at the highly negative central portion of $\{111\}_a$ and chloride anion at the positively charged edge of SNBD. As the substitution proceeds and the hydration shell loses more and more water, the SNBD·doxorubicin hydrochloride complex suffers from decreased solubility in water and separates as gel.

Huang observed that the loading of doxorubicin salt onto SNBD gel increased up to ten times as much by the addition of NaCl [8]. This observation can be interpreted in terms of ‘salting-out’ effect, well-known in proteins research: increase in the hydrated Cl^- concentration diminishes activity of water medium, as the consequence the solubility of drug hydrochloride in water is decreased and its sedimentation into SNBD promoted. These changes are equivalent to shift the equilibria in Eqs. (5)–(6) more to the right-hand side. Bound drug molecules are temporarily inactivated, hence the notorious side effects of this drug suppressed. After the SNBD·drug complexes reached to the inside of cancer cell, NaCl concentration in the blood is slowly reduced to move back the equilibria in Eqs. (5)–(6) towards left and release drug ions within the sick cell. The process is desirably slow as it involves breaking of the strong charge-charge bonding between facet and drug ion, and also passes through a series of solvent re-organization.

The platform approach mentioned above is versatile and a variety of modifications are in perspective. One important variation is to cloister potent but water-insoluble therapeutics onto SNBD [10]. For example, Purvalanol A (Fig. 4, II), a promising compound for hepatocarcinoma treatment, is insoluble in water but soluble in DMSO. In a 5% DMSO solution in water, Pulvalanol A did not dissolve but gave a turbid dispersion. Addition of SNBD to this suspension led to a clear solution! In this case, we can think of two-step substitution mechanism, wherein a critical step of drug binding to SNBD facet seems to have taken place with the assistance of adsorbed DMSO (Eqs. (7)–(8)):

$$\text{DMSO} + (\text{H}_2\text{O})/\text{F} \leftrightarrows (\text{DMSO})/\text{F} + \text{H}_2\text{O} \tag{7}$$

$$\text{P} - \text{OH} + (\text{DMSO})/\text{F} \leftrightarrows (\text{P–OH} \cdots \text{DMSO})/\text{F} \leftrightarrows (\text{P–OH})/\text{F} + \text{DMSO} \tag{8}$$

where P–OH stands for Pulvalanol A molecule.

Smaller but polar drug molecules like 4-hydroxytamoxifen (Fig. 4, III, an emerging drug for breast cancer) or polyhydroxylated drug molecules like dexamethansone (Fig. 4, IV, a clinically relevant anti-inflammatory) are insoluble in water but give fine suspension in water. Addition of SNBD particles to the suspensions of III and IV gave clear aqueous solutions. In these examples, we can imagine that both collapsing of drug agglomerate D_n into dispersion and binding of dispersed polar drug molecules D with SNBD occur on the charged facet of SNBD (Eqs. (9)–(10)):

$$\text{D}_\text{n} + (\text{H}_2\text{O})/\text{F} \leftrightarrows (\text{D}_\text{n})/\text{F} + \text{H}_2\text{O} \tag{9}$$

$$(\text{D}_\text{n})/\text{F} \leftrightarrows (\text{D})/\text{F} + \text{D}_{\text{n}-1}. \tag{10}$$

In all the variations mentioned above for drugs II–IV, preliminary examinations proved that the drug activities could be recovered upon release of the bound drug molecules [10]. In the case of SNBD·doxorubicin complex, gel may be coated on poly-L-lysine film and compiled by layer-by-layer technique into multi-layer assembly and dried to give versatile biofunctional nanofilms. In these films, SNBD particles are believed to be largely covered by tightly adhered nanophase of water molecules, thus giving essentially the same environment to SNBD·drug complex in water [9]. Finally, cytotoxicity of SNBD particles have gone through elaborate essay against a variety of cells and proved one of the safest of all nanocarbons and nanoparticles ever known [11]. The SNBD platform approach of drug carrier appears highly promising.

4. Mechanism of spontaneous polarization

4.1. Origin of electron mobility

Last but not least, we comment on the origin of electron migration within a SNBD particle that led to such a remarkable and diverse distribution of electrostatic potential to appear on the particle surface. There should be certain path for electron transfer from electropositive diamond core entity to electronegative graphitic surface. We believe that the intermediate sp^{2+x}-domain play a crucial role in the spontaneous polarization of SNBD particle. When the outermost layer of the intermediate domain separates from the core to form a graphitic shell (to be exact patches of curved graphene layer, Fig. 5ab) in the course of energy minimization, it leaves a number of free-spin electrons on the surface of intermediate domain, which will temporally enter into lower antibonding molecular orbitals (AMOs) of core entity localized on its surface (Fig. 5d). These free-spin electrons are likely to migrate by orbital-interaction-through-space (OITS) [12] into lower AMOs of graphene shell, which should be in the bonding energy region as in the giant fullerenes. This scheme does not conflict with high but stable negative Mulliken charge on the graphenic {111} facets of SNBD.

What will happen on the positive holes in the lower AMOs of core entity created by the transfer of free-spin electrons? It is hard for these positive charges to efficiently delocalize into diamond core because of the large band gap in the diamond MOs despite ideal alignments of σ-bonds for hyperconjugation, or orbital-interaction-through-bond (OITB) in diamond BMOs (Fig. 5d). Therefore positive charges must stay within thin sp^{2+x} domains. This picture is also compatible with the high but stable positive Mulliken charge densities on {100} facets.

For further analysis, we need more detailed information on both geometry and density of states in SNBD particle. In view of strong dependence of the surface electrostatic field on the size of the model as observed by Barnard [1], we should wait for the computation on the real-size model of C_{ca6000} hopefully at higher level of theory, which is in progress in a few computational groups.

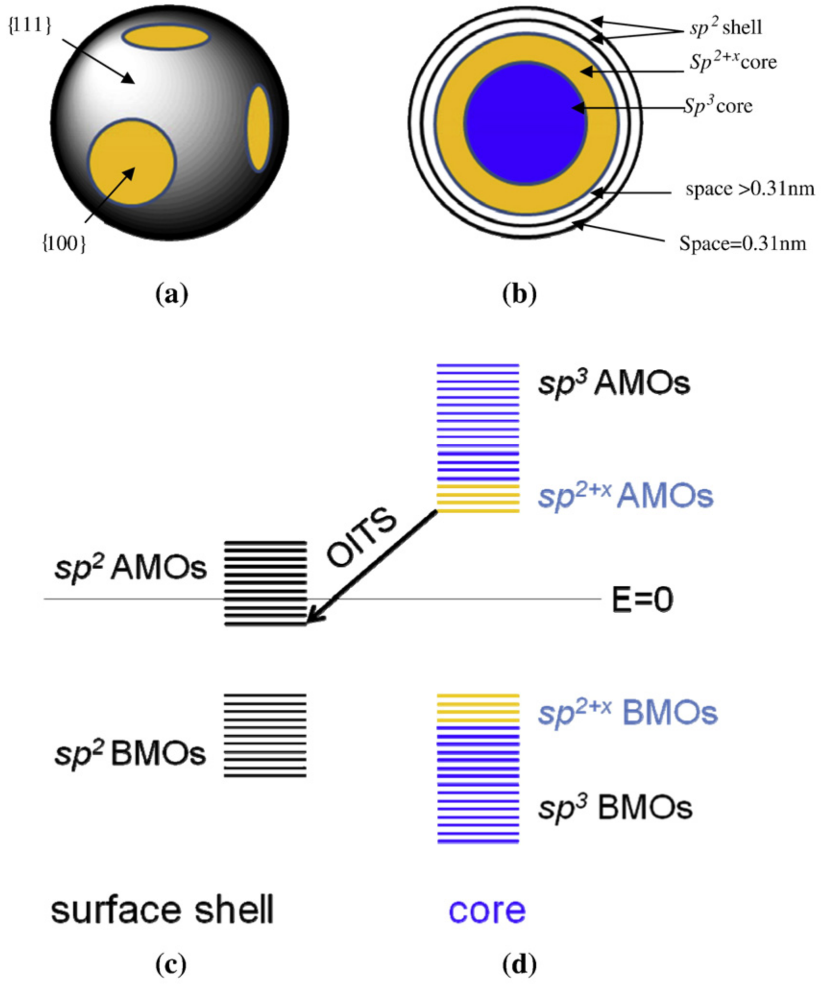

Fig. 5. Illustration of single-nano buckydiamond (SNBD) particle as consisting of sp^3 diamond crystal[blue] + sp^{2+x} intermediate domain[orange] (core entity), covered by holey sp^2 graphitic shell [black] in perspective (a) and in cross sectional view (b). Spontaneous polarization within a SNBD particle may be considered to occur as follows: when the uppermost layer of sp^{2+x} intermediate domain detaches itself from the core entity to form the innermost sp^2 graphene layer in the course of geometry optimization, a number of free-spin electrons are generated and they will temporally enter into the lower antibonding molecular orbitals (AMOs) of core entity (d). Then these high-energy electrons will migrate to the lower AMOs of surface graphitic shell located in the bonding energy region of fullerene-like MO (c) as the result of orbital-interaction-through-space (OITS). The positive holes generated by this electron transfer in AMOs of core entity have to stay within the sp^{2+x} domains due to hindered orbital-interaction-through-bond (OITB) across wide gap in the core diamond MOs. These pictures are compatible with the high and stable Mulliken charges in opposite signs on {111} and {100} facets, respectively. See text for more explanation.

5. Final remarks

We have previously assigned C–C covalent bond formation as the plausible cause of agglutination [3,13]. The C–C bonds are likely to form among primary particles when the growth of diamond crystals is suddenly terminated by the passing of shock wave during the detonation synthesis. At this time, a large number of radical centers remain unreacted on the surface of primary particles and will recombine with the radical centers of neighboring particles to form agglutinates of primary particles. However, such an inter-particle C–C bond formed by recombination of carbon radicals is like a fine thread connecting two giant stones and cannot be strong, but still we cannot totally exclude this possibility. For the C–C covalent bonding hypothesis to be significant, multiple bonding in every bonding pair would be necessary, which will be most likely occur between parallel facets or edges.

On the other hand, the coherent interfacial Coulombic bonding hypothesis has its own weak point: searching coherent rotation angle around the axis of inter-facet normal vector will take considerable time. Unless coherent angle is found, the interaction cannot be strong enough to survive intact during subsequent treatments as we see in the ready re-dispersion of aggregates that exist in flakes.

We are still not in a position to declare the final solution regarding the origin of agglutination.

6. Conclusions

Discovery of diverse electrostatic potential fields on the surface of SNBD by Barnard and Sternberg exerts significant influence not only on the agglutination believed to occur during the detonation synthesis, but also more broadly on the behavior of SNBD particles.

Abnormally persistent hydration known to occur on the surface of SNBD is considered as the first-hand manifestation of the electrostatics and contributes to surprisingly high stability of colloidal solution, gel and even lightly dried flakes.

Mechanism of our new drug delivery system based on drug·SNBD hydrogel complex including inactivated transportation and slow release of drugs are explained in terms of ligand exchange equilibria on the charged facets of SNBD. In the near future, precise control of drug delivery conditions by using rates and equilibria parameters relevant to the ligand exchange reactions on the SNBD platform should become possible.

A crucial step in the novel self-polarization of SNBD particle is the transfer of high energy electrons from the lower AMOs of core diamond to the lower AMOs of buckyonion shell surrounding the surface by orbital interaction through narrow core/shell space of about 0.31 nm. In this way, high negative charge on {111} facets are stored in the AMOs of buckyonion that are in the bonding energy region and high positive charge are confined to the uppermost domains of diamond core including {100} facets.

Acknowledgements

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