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NOVEL FEATURES OF NANOSCIENCE COMPARED TO PHYSICS AND CHEMISTRY

A few novel observations that we encountered while practicing nanoscience are analyzed and interpreted. Topics taken up here include the invalidation of purity supremacy; concentration dispersion, dilution aggregation; importance of modeling; quantization; and number density effect. Contrary to the general belief that nanoscience has its own advantages and disadvantages, we find that all of the peculiarities picked up in this essay can be interpreted, by basing on traditional concepts, except for the number density effect.

K e y w o r d s: purification, quantization, colloid crystals, quantum-chemical molecular-dynamics simulation, number density effect.

1. Introduction

Already fifteen years have passed since the formal birth of nanoscience and nanotechnology [1–3]. Proliferation and popularity of "nano" during this period are evidently seen in the rapidly increasing number of nano-papers and nano-journals (Fig. 1). We often wonder why this interesting field of research was left unexplored for such a long time. It seems that there existed a few barriers between nanoscience and the classic disciplines like chemistry and physics that have prevented scientists educated in these traditional disciplines from crossing. In this short essay, we will try to present a few such examples and analyze its origin to find out if nanoscience is especially difficult and special.

2. Invalidation of Purity Supremacy

Chemists are trained to start experiments with 100% pure chemicals to be sure not to fail. No paper will be accepted for publication unless all of the new compounds studied have shown correct elementary analyses. Purity has been one of the most strictly enforced principles in chemistry. We were really embarrassed to find out that it is theoretically impossible to purify nanoparticles! They are generally heterogeneous, namely have distribution in size and shape (Fig. 2).

Then we suddenly recognize that chemistry is a very rare branch of natural science wherein the

molecules, the primary particles of matter, are completely identical among the same molecular species. Logically, the smallest constituent of a material must be made of atoms. If the type and number of constituent atoms as well as their bonding orders and schemes are identical, there is no possibility of isomerizm. In nanotechnology, we must deal with a terrible mixture of sizes with unknown purity. This situation seems to be one of the reasons why chemists including ourselves did not dare to work on nanoparticles in the past.

What can chemists (and physicists) do for nanotechnology? We cannot lose the purity supremacy, as this is one of the bases of rigorous science. Hence, we will try to decrease the polydispersity of the nanoparticles at hand. It would be useful to calculate the polydispersity ($=M_w/M_n$) indices for each nanoparticles being handled as a sort of criteria on the uniformity of nanoparticles [4].

3. Concentration Leads to Dispersion and Dilution to Aggregation

A few years ago, we encountered an enigmatic phenomenon, which contradicts the commonsense in science. When Shimadzu Corporation began marketing their new IG series nanoparticle analyzer [5], they found our primary particle of detonation nanodiamond (our present major concern, to be abbreviated to PPDND) to have an average diameter of 11 nm, much larger than our own value of 3 nm measured on
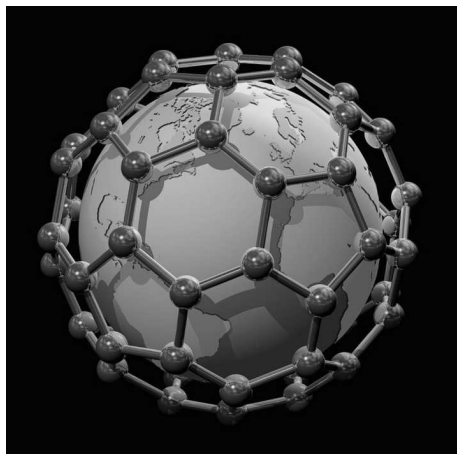
Fig. 1. Discovery of C_{60} fullerene by Kroto, Curl, and Smalley in 1985 [*The Fullerenes; New Horizons for the Chemistry, Physics and Astrophysics of Carbon*, edited by H. Kroto and D.R.M. Walton (Cambridge Univ. Press, Cambridge, 1993)] was one of the driving forces to promote nanotechnology over the world. The picture was downloaded from Internet

Fig. 2. Example of the size-distribution in an aqueous dispersion of the primary particles of detonation nanodiamond (PPDND) determined by dynamic light scattering method measured on a Particle Analyzer FPAR-1000 from Ohtsuka Electronics Co., Tokyo. Average diameter was 5.5nm when conditions in the attrition millng was optimized by quanlity control technique (*a*, in 2002). Re-optimization by the same technique significantly reduced the average diameter of 4.8 nm (*b*, in 2004). Introducing Taguchi's method of quality engineering produced a sharpened distribution centered at 3.8 nm (*c*, in 2012). Finally the latest optimization by Taguchi' method gave a remarkable average of 3.0 nm (*d*, in 2014). The figure was prepared by Mr. S. Sasaki

Fig. 3. Typical example of the dependence of PPDND aggregation in an aqueous colloidal solution upon dilution from 5 to 0.1 wt%, with three different particle analyzer from Ohtsuka Electronics (FPAR1000), Malvern (Zetasizer-nano), and Shimadzu Corporation (IG-1000 Plus). All three analyzers gave similar and reproducible values, if averaged over at least 100 determinations. It is clearly shown that our PPDND colloidal solution is stable in concentrations above 2.5 wt%, but shows the definite tendency to aggregate quickly upon dilution starting from 1 wt%

a traditional DLS analyzer from Ohtsuka Electronics (Fig. 3). As we have long insisted on the importance of dispersed primary particles in nanoscience, this discrepancy aroused a great anxiety in us [6].

The cause of discrepancy was soon found out: different concentrations were used for the two determinations. We had long determined that consistent results on the particle size of PPDND can be obtained when measured in a 2 to 3 wt% solution on Ohtsuka's particle analyzer. However, the recommended concentration for Shimadzu IG was 0.1 wt%. We and Shimadzu engineers repeated measurements using the solutions from the same source, but the discrepancy persisted. PPDND has been believed to give stable colloidal solutions because of its high zeta-potential of about +50 mV, but we concluded that such a large difference in the particle-size must have been caused by aggregation, even though the direction of change was unexpected and contradicts our commonsense. How could the 50-times dilution produce aggregation? Independently, Mchedlov-Petrossyan and his coworkers in Europe reproduced the "concentration dispersion, dilution aggregation" phenomenon [7].

The first hint to this mystery came from Mchedlov-Petrossyan who recalled an old paper of periodic colloids, wherein highly stable colloidal solutions often behave as if colloidal particles form a periodic distribution in the solution similar to the lattice points in solid crystals [8]. The idea of colloid crystal has been well-developed thereafter and even used for the purification of nanoparticles [9]. PPDNDs are actually
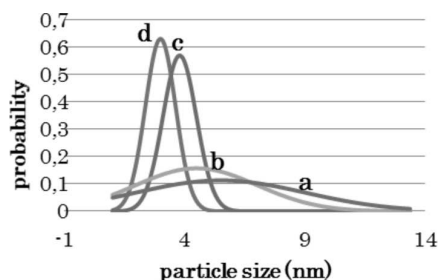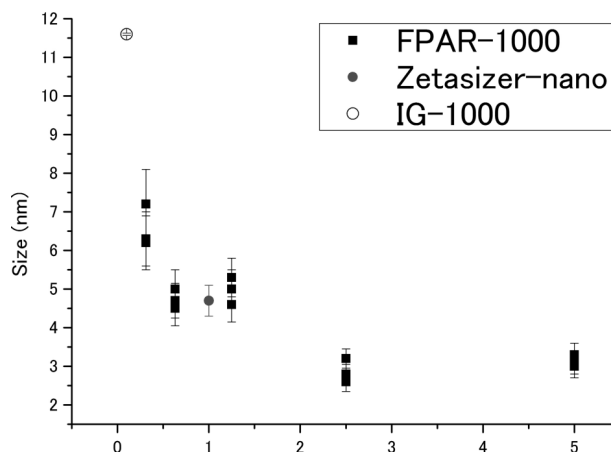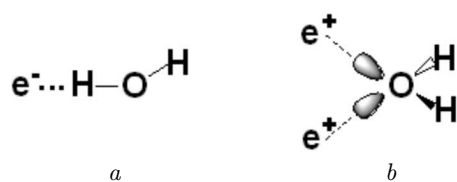
Fig. 4. Interactions of water with surface charges of PPDND. Usual H-bond to the center of negative charge typically on {111} facets (*a*). Possible interaction scheme between the double-footed lone-pair in an oxygen atom of water and the center of positive charge typically on {100} facet first suggested by T. Petit *et al.*, J. Phys. Chem. Lett. **6**, 2909 (2015) (*b*). This type of interaction is likely limited to only a very strong case of hydration
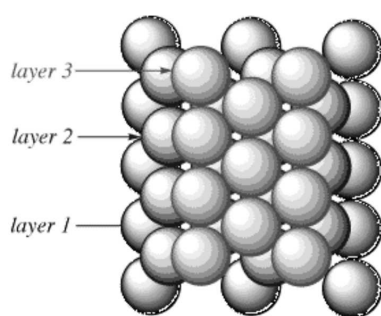

Fig. 5. Illustration of a colloid crystal in the hexagonal closest packing. Each sphere at the crystal lattice represents a hydrated nanoparticle. The picture was down loaded from Internet

an ideal material for a colloid crystal: they are tightly hydrated in water due to their high electrostatic potential, both positive and negative in sign and localized on the crystal facets [1]. The interactions are so strong that a rare phenomenon of PPDND dissolving perfectly well in water occurred (Fig. 4). Hydration shell could be multi-layered, surrounding a PPDND in the center.

Now we think the origin of the "concentration dispersion, dilution aggregation" phenomenon as follows. When the PPDND concentration is increased, and each particle receives enough number of hydration water, free water at some point will be exhausted for hydration. Then one can expect that the spherically hydrated PPDND will start to pack themselves tightly to produce a periodic distribution of PPDND nuclei in a solution, very likely in hexagonal or face-centered cubic closest packing in order to achieve the lowest-energy configuration (Fig. 5). The well-packed hydrated balls cannot move around, thereby producing a very stable dispersion with high viscosity.

If the static solution is diluted, bulk water will penetrate into closely packed structure to destroy the periodicity of a core distribution, promote the exchange of shell water with bulk water, and eventually allow the direct contact of PPDND with bulk water to start the self-aggregation. The phenomenon of "concentration dispersion, dilution aggregation" must be limited to highly and multiply polarized nanoparticles like PPDND, but can be utilized advantageously by conscious scientists.

4. Importance of Modeling

The novel multipolar electrostatic surface structure in PPDND mentioned above was first discovered by Barnard and Sternberg in 2007 using SCC-DFTB calculations, and provided the basis of our understanding on PPDND [1]. While the merits of performing quantum-mechanical calculations are now well-recognized among chemists, the theoretical modeling is scarce in nanotechnology primarily because of a too large number of atoms involved. However, the modeling is more important in nano than in chemistry, because of the lack of experimental means to study nanoparticles at the moment. Thanks to the progress in computer hardware and systems, it is now possible to directly perform calculations of PPDND in real size, namely 3nm in diameter with the total number of carbon atoms of about 2000 at the practical level of theory including SCC- and NCC-DFTB (Fig. 6) [11].

5. Quantization

Bohr's correspondence principle attempts to rationalize the transition from the discontinuous quantum world to the continuous world of bulk materials in terms of the size of objects, but actually considered only the two extreme cases of microscopic and macroscopic matters and did not mention the borderline cases.

In molecules, the quantization is believed to occur, as constituent atoms interact strongly enough with one another by means of molecular orbitals over distances smaller than 0.2 nm or in ions (and plasma) by the electrostatic interactions between ions across distances less than 0.5 nm. For molecules, this definition is clear, but the distance of the ionic interaction is usually longer than covalent bonds, and it is hard to find examples. Here, we wish to mention one in-

teresting case of ionic interaction that satisfies the definition of quantization without forming molecular orbitals found by Barnard in the course of modeling dimers of PPDND [12].

As shown in Fig. 6, *a*, PPDND has a core-shell structure with its holey graphitic shell covering large parts of the surface. Hence, the particle consists of two independently quantized parts: graphene and diamond. The most interesting to our present concern is the multipolar surface charge distribution in PPDND (Fig. 6, *b*). Soon after the diamond growth processes are terminated as a shock wave passed the epi-center but, the reaction zone is still hot enough, PPDNDs are supposed to agglomerate extensively by the parallel binding between facets with opposite charges. Interparticle interactions in the agglomerates have been analyzed using somewhat smaller (total carbon atoms, 837 to 1639) and simpler models than real, but it was found that some of the Coulombic interfacial bonding modes like $(111)^+ - (111)^-$ and $(100)^+ - (111)$ are as strong as the C–C covalent bonding with an extremely small interfacial separation distance of 0.18–0.19 nm [12]. These results satisfy the electrostatic interaction criteria for the quantization mentioned above. Barnard found that the some of the interfacial binding energies in the dimers of PPDND are as strong as C–C covalent bonds [12].

We can think of at least two reasons for the occurrence of such a strong Coulombic bonding. First, each facet in PPDND generally contain 50–100 atoms, all fully ionized. Hence, we are dealing here with multiple pair interactions. In addition, these facets engaged in the interaction immediate after being formed by the nanodiamond-nanographite transition without intervention of solvents or other molecules, when the crystal growth process ended. Hence, the facets must be smooth to the atomistic level to allow the close interfacial approach. Final adjustments of the relative orientation between two facets between two 3 nm particles to the maximum interaction must have been done quickly at high temperatures to complete the unprecedentedly strong coherent interfacial Coulombic interaction (CICI) [12].

The new interpretation of the nature of agglomeration among PPDNDs is likely related to the great difficulty in destroying the crude agglutinates of a detonation nanodiamond in the past. Still now, people try to break up the agglutinates by irradiating intense ul-
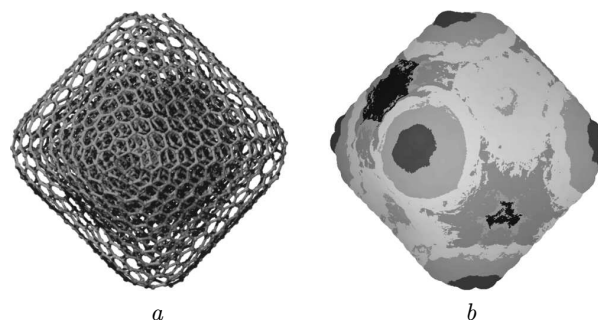

a   *b*

Fig. 6. Example of model calculations and illustrations: the geometry-optimized structure of PPDND in one of the likely candidates for the structure, a doubly truncated octahedron. Total carbon atoms = 2,613, composed of 57.47% of sp^3, 24.26% of sp^2, and 18.45% of sp^{2+x} hybridizations. Stick expression, core diamond in grey, and shell graphitic carbons in green. Shell is systematically distorted as a result of the enlarged area due to the diamond-graphite transition. Openings of a shell are visible at the truncated apices (*a*). Distribution of Mulliken electrostatic fields on the surface. Positive areas = red (highest density), orange (medium). Negative areas = blue (highest), green (medium), and yellow (neutral) (*b*). The computation and drawing done by Dr. Amanda Barnard

trasonic waves. However, if CICI could be broken by a shock wave from the supersonic cavitation of a water solvent, water molecules must have been broken first. CICI is actually stronger than chemical bonds.

A key factor for the first example of a new type of quantization is a very close disposition of the most electronegative graphene shell and the most electropositive diamond core in PPDND. The possible mechanism of novel electron migration within the core-shell structure in PPDND has been mentioned elsewhere [13].

6. Number Density Effect

One of the most remarkable advantages of nanotechnology compared to chemical technology is that, generally, only very tiny amounts of nanoparticles display great effects in composites. For example, the addition of only 30 ppm of 3-nm nanodiamond is enough to cause drastic improvements in the toughness-related behaviors like breaking strengths in poly(ethylene terephthalate) if the nanoparticles are well dispersed in the solid matrix [14]. The tiny proportion of nanoadditives to the major component makes a great contrast to generally comparable proportions practiced in chemistry like polymer blends. The effect has been rationalized by invoking the ideal manifesta-

Number density effect in the hypothetical
bare and spherical detonation nanodiamond particles of various sizes

	3.2	3.0	2.8
Diameter $D = 2r$, nm	3.2	3.0	2.8
Volume $v(=4\pi r^3/3)$, cm^3	1.716×10^{-20}	1.414×10^{-20}	1.150×10^{-20}
Weight $w(=\rho v)^a$, g	5.440×10^{-20}	4.482×10^{-20}	3.646×10^{-20}
Particle weight[b] $(=wN)^c$	32,765	26,995	21,960
Number of C-atoms per article	2,730	2,250	1,830
Number of particles in unit weight ($=1/w$, or per g)	1.838×10^{19}	2.231×10^{19}	2.743×10^{19}
Number density of 0.01 wt% colloid (particles/cm^3)	1.84×10^{13}	2.23×10^{13}	2.74×10^{13}
2D number density of 0.01 wt% colloid[d] (particles/cm^2)	7.0×10^8	7.9×10^8	9.1×10^8

[a]$\rho = 3.17$ (Obs), 3.52 (Lit, natural bulk diamond) g/cm^3. [b]Equivalent to molecular weight. [c]$N =$ Avogadro number 6.023×10^{23}. [d]Estimated from 3D density by taking a radicand of 2/3.

tion of nanopinning actions by small and hard nanodiamond particles, which prevent a transposition of the crystal structure due to the sliding of crystal planes. Thus, the Hall–Petch effect [15–16], as it has been called, should be proportional to the number of particles dispersed.

At this point, we note that the design of composites in chemistry based on the weight composition was unreasonable. Properties of polymer composites should be evaluated in terms of the number of molecule-molecule interactions, but we used to measure the effect in terms of the mixing ratio in weights. Why did such a simple mistake happen? This is because molecules are too numerous in number. For example, 18 g of water contain 10^{23} molecules, simply too large to use in daily life. In this case, the number is so large that even no conventional nomenclature is given. When chemistry started in the 18th century, our wise fathers invented a handy concept called mole, which converts the number of molecules into Mol, which is the unit of weight, not number nor volume, and much more convenient to measure for conventional small molecules.

In the case of nanoparticles, however, primary particles are large. For example, detonation nanodiamond is, in average, 3 nm in size and the molecular weight (particle weight, to be precise) is about 24,000 g, too large to weigh. Hence, we want to go

back to count the number of particles to evaluate the effect. Unfortunately, this is not easy either. For example, 1 μg of detonation nanodiamond contains $2.2 \times 10^{13} = 22$ billion primary particles, according to a simple arithmetic based on the spherical approximation (Table). Weight is too small but particles are too numerous. We will continue, for the moment, to weigh small amounts by a micro balance to gauge the effect of nanoparticles. However, for practice, we should be careful not to mix too many nanoparticles, because they have extremely high tendency to aggregate among themselves and greatly reduce the effect of nanoparticles (Table).

7. Concluding Remarks

Nanotechnology began only recently, when US President B. Clinton declared its start in his 2001 Inaugural Speech. Popularity was at first high but soon faded away, and the feverish research activities of new types of nanocarbons decreased. Public disappointments are the consequence of their neglect of the fact that a particular section of science like nanotechnology takes a long time to develop by building up the fundamental principles one by one like milestones. The polydispersity problem mentioned in this essay is just one example of such milestones. The purity supremacy may be temporarily abandoned for

the lack of means of purification, but we will come back. The rediscovery of a colloid crystal mentioned above is a direction of such progress.

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Е. Озава

НОВІ РИСИ НАНОНАУКИ
У ПОРІВНЯННІ З ФІЗИКОЮ І ХІМІЄЮ

Р е з ю м е

Проаналізовано і інтерпретовано кілька нових фактів, знайдених нами при дослідженні нанооб'єктів. Розглянуті теми включають неістотність чистоти, дисперсію концентрації і агрегацію при розбавленні, значення моделювання, квантування і ефект щільності числа частинок. Всупереч загальному переконанню, що нанонаука має свої успіхи і недоліки, ми показали, що всі розглянуті факти можуть бути інтерпретовані на основі традиційних понять, за винятком ефекту густини числа частинок.