

Remarks on the Handling of Colloidal Solutions of 5-nm Diamond Particles

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Abstract. Stable and transparent colloidal solutions of dispersed 5nm diamond (5nD) particles became available but its handling is by no means straightforward if parallel behavior to microcolloids were presumed. This report presents brief background on the history and manufacturing method, characteristics including colloidal stability, number of particles and black color, and tips on its handling with emphasis on its sensitivity to air, pH and electrolytes, and on storage of 5nD.



INTRODUCTION

Commercial nanoparticles are generally available in the form of powder.¹⁾ Visible powders are composed of conglomerates and must be re-dispersed before use. However, the aggregates of nanoparticles, 1-100 nm in diameters, are in general tight and difficult to re-disperse into primary particles. In the case of our 5nm diamond (5nD) particles, the origin of the abnormally strong interparticle forces acting between primary particles of diamond single crystals was recently proposed to be a novel type of Coulombic interfacial interactions that we have never encountered in chemistry.²⁻⁴⁾ Therefore, we need to carefully monitor the dispersion status while measuring particle-size measurements all the time. Unfortunately particle-size determination of nanoparticles is not a common technique in usual laboratories. Even if one was lucky enough to find, for example a dynamic light scattering equipment, it is not easy to obtain reliable results.⁵⁾ For these reasons, works involving nanoparticles (especially 5nD) are often reported without mentioning the particle size. In our opinion, information on the particle-size is by far the most critical factor and should not be dismissed.

Under such circumstance, we decided to supply our 5nD particles in the form of *colloidal solutions* whenever possible. Only in this form, we can guarantee the highest possible dispersity. Naturally this cannot be a common practice for other nanoparticles as nanocolloids are usually unstable when dispersed down to their primary particles and tend to produce sediments sooner or later upon standing, oftentimes in a matter of a few minutes. *Fortunately, 5nD colloids are exceptionally stable.* The reason for the stability will be mentioned below. Nevertheless, it should be taken for granted that we are talking about kinetic stability. Actually the 5nD colloids are thermodynamically unstable; even the slightest undesirable perturbation like dropping a few crystals of electrolytes, e.g., NaCl, leads to the formation of large amounts of precipitates in an

instant.

BACKGROUND

Brief History

Our dispersed 5nD crystals are the primary particles of detonation nanodiamond, known since 1963, but it is only very recent (2003) that the primary particles were isolated in dispersed form⁶⁾ and became available on macroscopic amounts. Before this breakthrough was made, only their agglutinates were available in powder form.⁷⁾ Agglutinates form only turbid and unstable suspension, although we recently noticed that the commercial agglutinates do contain a small fraction of very small aggregates with 10-20 nm in diameters.⁸⁾ Our colloidal solution of 5nD offers a rare opportunity to explore an entirely new field that we can expect to develop by the entry of the first typical single-nano carbon particles into the scene of science and technology. The situation reminds us of a well-known event that took place when the arc synthesis of C₆₀ from graphite rod was discovered in 1990.⁹⁾

Manufacture

To our knowledge, the only scalable method of disintegrating the crude agglutinates of detonation nanodiamond into its primary particles is the wet beads-milling, in which agglutinate powders are agitated at high speed with large excess of micron-sized ceramic beads¹⁰⁾. Water is the most commonly used medium of milling, offering high affinity towards 5nD particles, good volatility and safe operation. A few organic solvents that have comparable or even superior capabilities for the milling and at the same time form stable colloid of 5nD are known; these are dimethylsulfoxide (better than water), ethylene glycol, N-methylpyrrolidone, and ethanol in the order of decreasing solvent power. In practice it is more convenient to perform beads milling in water and then subject the aqueous colloid to solvent-exchange whenever non-aqueous medium was needed.

The beads-milling technique involves conflicting factors, namely to obtain the highest possible proportion of particles having diameters less than 5 nm and to suppress contamination by beads material (in our case zirconia). We are still unable to overcome the conflict by executing the experimental design technique alone. Hence we chose to suspend the milling before the contamination level by zirconia exceeds 0.2%, leave the milled mixture overnight, then upon irradiate the turbid colloid with intense ultrasonic wave emitted from vertically vibrating 'sonorod' (Fig. 1). We presume that the incompletely decomposed core agglutinates in the final stages of milling process will absorb localized strain during the standing to readily decompose by intense sonication on the next day. Finally, small amounts of non-disintegratable small sediments were precipitated by centrifugation and removed by decantation.

Colloidal solutions of 5nD are prepared throughout under exclusion of air. After preparing suspension of agglutinates, the whole operation until bottling of purified solution (Fig. 1) is run under small positive pressure or direct bubbling of nitrogen. In earlier days of our work

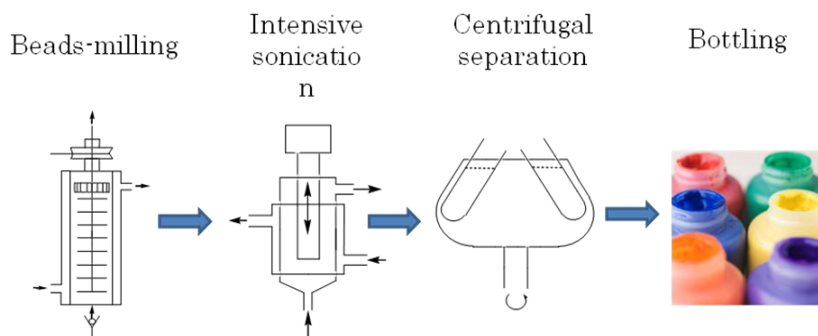


Fig. 1. Preparation of 5nD colloidal solution.

the colloidal solutions were freely allowed to contact with air, we used to observe persistent formation of small amounts of amounts of grey solid powders precipitating slowly at the bottom of containers during storage. We found that the precipitate formation could be suppressed by excluding air during and after the disintegration operation. However, concentration of free spins (8×10^{19} spins/g) that have been detected in 5nD by EPR analysis is not significantly affected by contact with air.¹¹⁾ Hence we cannot assign the precipitates that occurred upon contact of colloidal solution with air to the oxygenation of free radicals. Once the precipitations were formed, the colloidal solution became inactive when used as the seeds in the homoepitaxial CVD diamond growth.¹²⁾ One more desirable precaution would be to exclude dust. Ultimately the manufacture of 5nD should be carried out in a clean room.

CHARACTERISTICS

Stability

The outstanding stability of the colloidal solution of dispersed 5nD particles in a few solvents, notably water and DMSO, is a driving force in our decision to distribute colloidal solutions in preference to other forms like hydrogel. For a long time we could not reach the decision while we could not understand the reason for the stability. When permanent and large

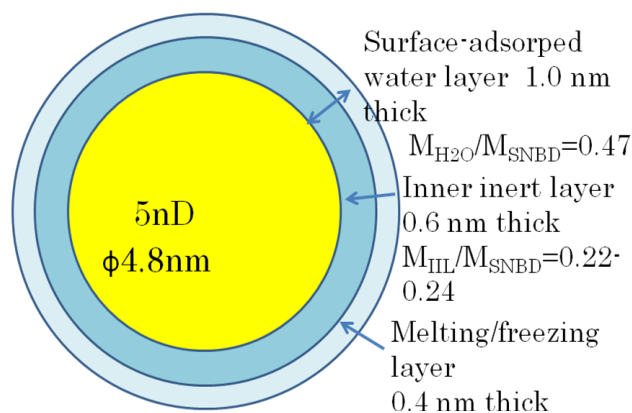


Fig. 2. Hydration shell on the surface of a 5nm diamond particle drawn on a simplified seamless model

electrostatic charges on the surface facets of polyhedral 5nD crystalline primary particle were discovered in 2007 by Barnard using SCC-DFTB calculations,²⁾ it became clear that the reason for the unusual colloidal stability of 5nD was the strong solvation onto the charged surface. Tight solvation shell around the particle (Fig. 2)¹³⁾ prevents direct contacts among particles to cause

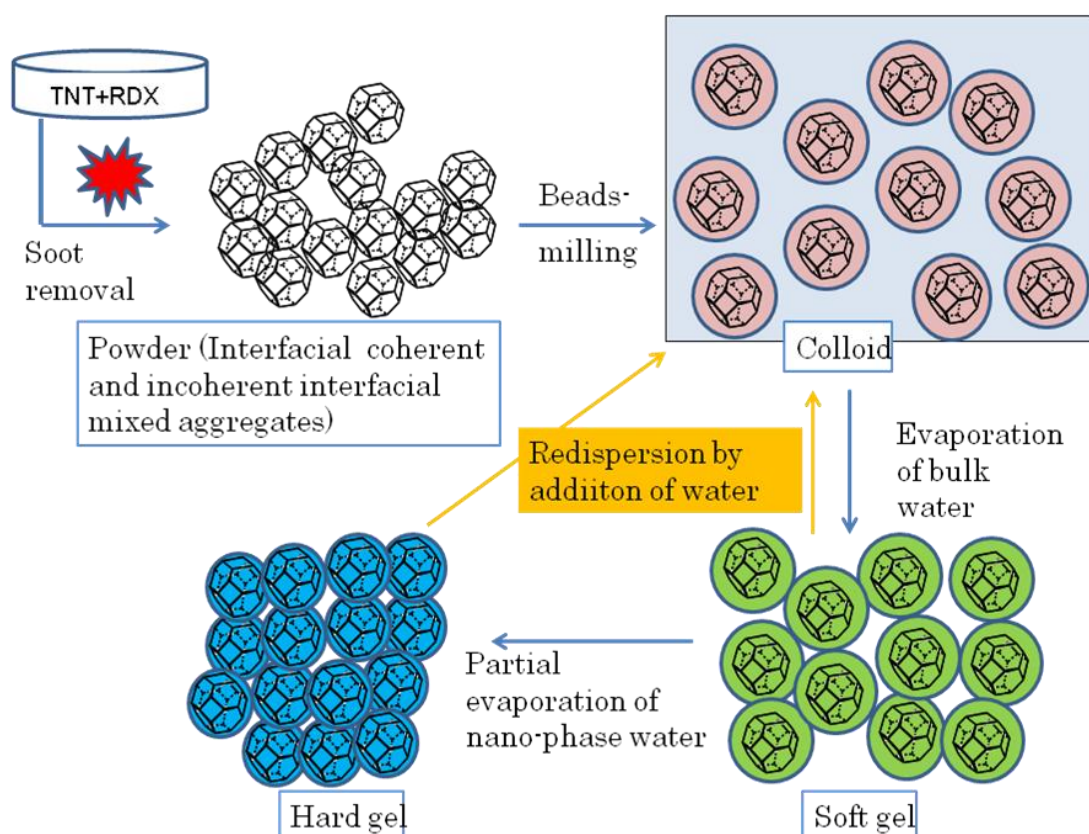


Fig. 3. Illustration on the role of hydration on various forms of dispersed 5nD.

aggregation by electrostatic attraction.⁴⁾ The reason for the generation of surface charge was presented on the basis of orbital interactions within the core-shell structure of 5nD. It appears likely that the solvation shell exerts profound effect not only on the colloidal solution but also on the formation of soft- and hard gel by evaporation of water from the colloidal solution (Fig. 3).⁴⁾

Number of Particles

In the chemistry of relatively smaller molecules, for example adamantane $C_{10}H_{16}$, the model hydrocarbon for the building block structure of diamond crystal, MW 136, the primary particles are so small and numerous that we do not count their numbers but use a weight-based unit called *mol*, which corresponds to the gram amount of molecules in Avogadro Number. As nanoparticles are at least a few digits larger and heavier than conventional molecules, it is sometimes useful to monitor the amount by the number of particles. Basic numerical features of our 5nD are given in Table 1¹⁴⁾. Note that most of the numbers given in this Table are still not determined precisely but estimated based on the DLS diameter and preliminary density measurement.

Table 1. Basic numerics of a 5nD particle and the estimated number of particles in a unit weight

Selected numbers for one 5nD particle	Diameter $D(=2r)$	4.8 nm	100 nm ^d
	Volume $v(=4\pi r^3/3)$	$5.79 \times 10^{-20} \text{ cm}^3$	$5.23 \times 10^{-16} \text{ cm}^3$
	Weight $w(=\rho v)^a$	$1.74 \times 10^{-19} \text{ g}$	$1.64 \times 10^{-15} \text{ g}$
	PW ^b ($=wN$) ^c	104,000	9.88×10^8
	Number of C atoms	8,660	8.23×10^7
Number of particles in 1g of 5nD $n(=1/w)$		5.75×10^{18}	6.10×10^{14}

^a ρ =sp. gr. of 5nD=2.99 (preliminary results), and that of natural bulk diamond=3.52 g/cm³.

^b ‘Particulate weight’, a concept corresponding to ‘molecular weight’.

^c $N= 6.022 \times 10^{23}$ (Avogadro number).

^d A model of agglutinated product of detonation nanodiamond.

The number of carbon atoms in a 5nD particle is close to the MM2-optimized estimate of about 8000.¹⁵⁾ Hence the numbers of 5nD particles in a unit weight (the lowest line of Table 1) may be viewed with some confidence. We note here about the order of this figure, 10^{18} . The largest limits that we can ‘feel’ its magnitude by comparing with some familiar matters are million (10^6 , measure of richness in dollars), billion (10^9 , population of China), and perhaps trillion (10^{12} , national budget of Japan in dollars). When a figure exceeds these limits, usual expression would be ‘beyond imagination’. This number of 10^{18} is really huge: billion (10^9) times billion! For this reason, 1ml of 0.01% 5nD colloid contains 10^{14} , namely hundred times billion particles, which sounds almost unbelievably numerous!¹⁴⁾

It is clear from the above analysis that, if the effect of nanodiamond that one is going to study depends on the number of particles, only small amounts of 5nD may be sufficient. For instance, if we are going to grow very large CVD diamond films, each $30 \times 30 \text{ cm}^2$, on the substrate plates coated with a single-particle layer of 5nD at the highest possible density (4×10^{12} particles/cm²), we can seed as many as 160 plates by 1L of 0.01% colloidal solution (a concentration usually used for immersion seeding).¹⁶⁾

Black color

A sensational surprise regarding our 5nD colloid is its very intense black color that appears for solutions higher than about 0.1% in concentrations. The color is so intense as to preclude any possibility of applications for optical purposes. The reason for this remarkable coloration is still unclear. We are inclined to deny the role of thin graphitic layer considered to cover the surface for the highly concentration dependent coloration, but tend to adopt Rayleigh- or Mie-type dispersion theory intensified by multiple dispersion caused by the extremely large number of particles.

HANDLING

We emphasize here again the importance of keeping the solution well dispersed. Heating, for example up to near-boiling temperature, does not cause much aggregation, as expected from the Coulombic origin.²⁾ Hence concentrating of colloidal solution in a rotary evaporator is a safe way to increase the weight-based concentrations. Remember that dilute solutions are adequate in most cases as the number-based concentrations are surprisingly high.¹⁴⁾ Concentrated colloids are, however, prone to form gel,¹⁷⁾ hence it is easier to handle dilute solutions. Slow freezing should be avoided as partial freezing of solvent causes the colloidal particles to aggregate. Especially noteworthy is the fact that the freezing point of DMSO is considerably high, 18.45°C. On the other hand, rapid freezing will trap the dispersed 5nD particles as they are and probably offers the best way to keep the colloidal solution dispersed for extended period of time.

Colloidal behavior of 5nD particles is more sensitive to the addition of ionic and polar species, which will change the solvation of facets, than heating or cooling. Stable pH region is between 3 and 6 for our present products.¹⁸⁾ Under pH values above or below these limits, flocculation of light grey material occurs quickly and eventually a large amount of soft precipitates fill the whole solution. Colloidal dispersion of 5nD particles is much more sensitive to electrolytes than to protons to cause quick precipitation of soft gel containing the electrolyte ions. According to SCC-DFTB calculations, hydration occurs only with negatively charged surfaces of [111]facets to form HOH•••F⁻ type H-bonding complexes, where F⁻ denotes a negatively charged center on the [111]facets.¹⁹⁾ In contrast, complexation of facets with electrolytes M⁺X⁻ may occur in both ways to give: M⁺•••F⁻ and X⁻•••F⁺ type of charge-charge binding on the facets, where F⁺ denotes a positively charged center on the [100] facets.

Storage

Dead space in the containers of colloidal solution shipped from us is filled with argon gas. Exclusion of air from the dead space is effective to suppress formation of turbidity and in worse cases of grey powdery sediments upon prolonged storage. We recommend to purge air in the opened bottle with argon or nitrogen before recapping. It would be safe to exclude air from the reaction vessels but we have not yet studied the effect of short contact with air upon the performance of colloidal solution in any detail. Nor we know the effect of stray light on the behavior of colloidal solution stored in semi-transparent bottles. It would be safe to store the solutions in cool and dark place when not in use. DMSO colloids should not be kept in refrigerator at any time, and should be stored in a heated container in winter time to avoid freezing.

CONCLUDING REMARKS

The label of bottle contains the following information: (1) date of bottling, (2) weight-based and number-based concentrations, (3) solvent (basically water unless otherwise

noted), (4) particle-size distribution of the primary particles with weight-based population, and (5) a Lot No. In cases of needing inquiries, E-mail address can be found on the label. Please include the Lot No. on the label in the message. We recommend to purchasing colloidal solutions as dilute as possible like 1-2 wt%, when 5nD particles are needed, and use them up within a few months at the longest. Do not leave the bottle with its cap removed for a prolonged period of time.

Biocompatibility of 5nD has been well-studied and concluded to have no cytotoxicity detectable by available assays.²⁰⁾ Nevertheless, genotoxicity as well as the long-term effects of extremely hard nanoparticles like 5nD upon human body are still unknown. It is advised to avoid direct contact with or inhalation of 5nD particles as much as possible.

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