

## **Re-dispersion of NanoAmando<sup>®</sup> Hard Gel**

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**Abstract.** Two of the distribution forms of NanoAmando, soft gel and flakes were replaced by a special hard gel retaining 20% water as of spring 2009. Despite the high water content, the hard gel behaves like dry powder, thus offering a convenient form for transportation and storage. The most remarkable advantage of hard gel is its ready re-dispersibility in water or a few organic solvents. The original particle size in the starting colloid can be reproduced by using a conventional supersonic washing bath. By re-dispersing this gel in pure ethanol, transparent and stable colloidal solutions of 5 nm diamond in 99.5% ethanol was prepared for the first time.



### **1. Introduction**

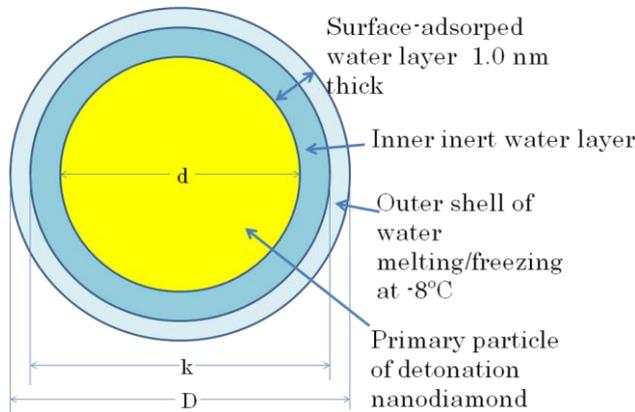
We used to distribute *NanoAmando*<sup>®</sup>, primary particles of detonation nanodiamond [1], in three forms: colloidal solution, soft gel and flakes. The latter two are the re-aggregates of once dispersed primary particles; hence they have to be re-dispersed before use in most cases. Flakes (a wrong word and should have been named ‘powder’) are well-dried powder and were the most popular form because of convenient transportation and storage. However, the aggregation in flakes is tight. Hence we recommended to applying powerful sonication by using a special sonorod in a circulating system under careful monitoring of particle-size [2]. It seems likely that most people who have obtained our flakes neglected the recommendation for inconvenience [3]. We now believe that the well-dried re-aggregates of our NanoAmando involve non-coherent Coulombic interfacial interaction of sizable energy [4,5]. Clearly the dry flakes involve large interparticle interactions which render them difficult to redisperse. In contrast, soft gels are easy to re-disperse to primary particles upon addition of water followed by brief agitation or light sonication, but they are only slightly more concentrated (12-15%) than colloid (2-5%), hence

almost as voluminous as the colloidal solutions. In addition they are not suited for transportation.

As the importance of dispersity of nanoparticles is recognized among the researchers, the need for a more readily re-dispersible forms of NanoAmando surfaced. After some efforts, we found a hard gel retaining much larger amount of water than our previous flake fits our purpose. This paper reports our latest progress along this line. Our first task was to determine how much water we should remove from a colloidal solution.

## 2. Critical Water Content

According to our differential scanning calorimetric study on NanoAmando gel [6], strongly absorbed shell of water surrounds the surface of every primary particle in 1 nm thickness. We have further suggested in that paper that the hydration shell consists of two parts, the outer shell freezing at  $-8^{\circ}\text{C}$ , while the inner shell not freezing at all (Fig. 1). We thought that the hard hydrogel we are going to pursue should retain the inner hydration shell but may be devoid of the outer shell. Assuming uniform density throughout the hydration shells, and using the known values,  $k=6.5$ ,  $D=7.2$  and  $d=5.2$  nm [6], we can estimate the mass ratio of  $k$ -shell  $M_{k, \text{nm}}$  to the



**Fig. 1.** Illustration of hydrated primary particle of NanoAmando.

whole hydration shell  $M_{\text{H20, nm}}$  as follows:

$$M_{k, \text{nm}} / M_{\text{H20, nm}} = (k^3 - d^3) / (D^3 - d^3) = 0.576.$$

Once again using the known ratio of

$$M_{\text{H20, nm}} / M_c = 0.47$$

where  $M_c$  is the mass of naked primary particle of NanoAmando [6], we obtain a first measure of critical water content  $M_{k, \text{nm}} / M_c$  in the hydrogel:

$$M_{k, \text{nm}} / M_c = 0.27$$

In other words, our first goal of water content in the hydrogel is 21

(=0.27/1.27) %. In view of the assumed uniform water density in the hydration shell, we may accept critical water contents of  $21 \pm 2\%$ .

## 3. Preparation of Hard Hydrogel

### 3.1 By concentration of colloidal solution

Procedure of making hard gel is mentioned here starting with the standard 5% aqueous colloidal solution. As in all the other operations of NanoAmando production, we adhere to operate under nitrogen atmosphere in order to avoid the formation and precipitation of

oxygenated by-products.

One liter of 5% aqueous colloid is measured out using a graduated cylinder. Water is removed from the solution using a rotary evaporator equipped with a 1L single-necked eggplant-bottom flask under a vacuum of 50 hPa immersed in a water-bath heated at 60°C. For convenience of collecting gel out of the flask (see below), the evaporation flask is equipped with a wide female ground glass joint (45/50 mm recommended) at its mouth. As the solution is concentrated, black pasty sediments appear and accumulate on the inside wall of flask. Then the sediments begin to lose wet appearance and gradually the whole mass will begin appearing grey instead of pitch black. If evaporation of water is continued under the same condition beyond this point, the sediments will detach from the inner wall to form a ball-shaped mass within the flask. This is an undesirable situation because water will evaporate only from the small surface of ball, and the inside of ball remains wet, leading to uneven distribution of water content. It is advised that, before the ball is formed, evaporation is slowed down by increasing the pressure to 60-70 hPa and lowering the bath temperature to 50°C so that water is removed evenly while keeping the solid mass attached over the inner wall of flask.

The brown powdery solid, still considerably wet, is taken out of the flask by using a long spatula through the wide mouth of flask, and spread in a large Petri dish or watch glass. The harvesting operation is carried out in a nitrogen box. Then the powder is placed in a desiccator containing molecular sieve. The desiccator is evacuated to about 500 hPa (one half atmospheric pressure), and the weight of the powder is measured once every day until it reaches in a few days to



**Photo 1.** Hard gel containing 20% of water looks like dried powder.

a value expected for a water content near 20%, as calculated from the starting volume of colloidal solution and its concentration. Then the coarse lumps are crushed and pulverized in a mortar in a nitrogen box into light brown colored, dense and fine powder (**Photo 1**), and weighed into small bottles, usually in 10 g batches. The void space in the bottle is purged by Argon and the cap closed tightly for shipment.

Water contents of such hard gel can be conveniently determined by weighing about 20 mg of sample into a 2.2 ml vial of known empty weight (including plastic cap), heated up to 150°C under a vacuum in a vacuum dryer overnight, quickly capped tightly after cooling to ambient temperature under vacuum, and weighing the completely dried sample.

### **3.1 By spraying water over the over-dried re-aggregates**

It often happens that the gel is over-dried to water contents significantly lower than the critical value of  $21\pm 2\%$ . In such a case, water contents can be readily re-adjusted by spraying calculated amount of water over the gel surface and mixing well with inside by spatula. At first we anticipated that such hasty misting would only lead to hydration over the surface of aggregates, and not reach to their inside. However, we confirmed that the hard gel remedied in this way could be easily re-dispersed in water by sonication alone. We may conclude that the direct interfacial contacts among primary particles, that will occur in the absence or dearth of water, leads to only weak and greatly incoherent Coulombic attractions between interacting facets. In other words, the notable coherent Coulombic interfacial interactions that are supposed to have taken place within the shock wave of detonation are exceptionally strong inter-particle interaction.

### **4. Re-dispersion of Hard Hydrogel**

The hard hydrogel powder of detonation nanodiamond prepared as above behaves almost exactly as we wished in the beginning of this report: the dense and fine powder can be efficiently packed and conveniently transported. Below we see how well it can be re-dispersed.

An example is given here to prepare 100 ml of 2% aqueous colloidal solution from hard gel containing 20% of water. Into a 100 ml Erlenmeyer flask is placed 2.5 g of hard gel and ca 80 ml of water and the content stirred vigorously with magnetic stirrer for 30 min under bubbling of nitrogen. The Erlenmeyer flask containing suspension, which usually still contains a few pieces of undissolved solids, is transferred to a conventional supersonic washing bath under slow bubbling of nitrogen gas. We used a dual-ultrasound washer, 110W, 24+31kHz, 'Bakusen', Model W-113MK-II from Honda Electronic Co., Toyohashi.

The sonication under nitrogen bubbling is continued at least for 10 hours until the transparent and black colloid is obtained and showed satisfactory dispersity, as determined by dynamic light scattering measurements on a FPAR-1000 equipped with a 660 nm laser from Otsuka Electronic Co. Usually the same dispersity as that of the original colloid solution used for the preparation of hard gel is recovered. For reliable and reproducible DLS analysis of NanoAmando primary particles, we removed the dependence of the size-distribution upon concentration by repeating measurements within the most reliable concentration range of 2.3-1.6 % and extracting meaningful values using our reliability index (R.I.) method [7]. Typical particle-size distribution of the re-dispersed detonation nanodiamond is:  $5.4\pm 0.4$  nm (98.6 wt%),  $65.9\pm 14.0$  nm (1.3 wt%),  $1052\pm 135$  nm (0.1 wt%). If DLS did not give stable results, or  $R.I.<4/5$  [7], after prolonged sonication, it oftentimes helps to subject the colloidal solution to centrifugal purification to completely remove undissolved large particles. Final

concentration of nanodiamond were determined by weighing the dried residue: 1 ml of colloidal solution was pipetted out from the re-dispersed mother liquor into a 2.2 ml vial of known weight (including cap), and water was completely evaporated in a vacuum oven by heating the vial at 150°C under a vacuum of 30 hPa overnight. After the oven was cooled down to room temperature and vacuum was broken, the vial was taken out, quickly capped and weighed to obtain the weight of dry diamond.

In addition to water, a few organic solvents can be used as a medium of transparent colloidal solution of NanoAmando: these are dimethylsulfoxide (DMSO), ethylene glycol (EG), N-methylpyrrolidone (NMP), and ethanol (EtOH) in the order of decreasing solubility. We have several times prepared 5% solution successfully in water and DMSO. For EG, NMP and EtOH, somewhat lower concentrations of 3, 1 and 0.2 wt% were recorded as the highest attainable colloidal concentration by the present re-dispersion method. For NMP, 1% concentration is guaranteed, and for EtOH 0.2%. Note that these colloidal solutions contain up to 0.5% of water carried over from hydration water.

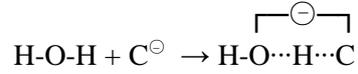
Special note is due here about ethanolic colloid. We had repeatedly attempted to disintegrate agglutinates of detonation nanodiamond in ethanolic suspension by means of beads-milling at 5-8% concentration levels, but never been successful to obtain clear and transparent colloid in ethanol. For this reason we had suspended to ship ethanolic colloid of NanoAmando. Ethanol is the poorest solvent for NanoAmando among the solvents cited above. However, we succeeded for the first time to prepare transparent ethanolic colloid containing 0.5% of water. In this case hard hydrogel was dissolved in pure ethanol. The colloid seems as stable as those in other solvents. However, as water is present in this colloid in 2.5 times the weight of diamond, it seems that colloidal particles are essentially the hydrated nanodiamond crystals and the particles are stabilized by water-ethanol interactions.

## **5. Discussion**

### ***Experimental confirmation of non-freezing hydration shell***

Our strategy of retaining the whole inner hydration shell proved correct. We think that the shell of inert water over the surface of nanodiamond crystals prevents direct interfacial Coulombic interactions among the primary particles in our hard gel, thus excluding the formation of tight aggregates. The weak aggregates in the hard gel should be understood as van der Waals complexes among the hydrated diamond particles. Contrariwise, work presented above supports Korobov's original proposal [6] of inert hydration layer on the surface of the primary particles of detonation nanodiamond. Then it may be worthwhile to discuss the nature of bonding between water layer and the particle surface in the inert and non-freezing hydration layer. It is likely that the bonding is due to a stronger version of hydrogen bonding, wherein

water molecules interact with strong negative charge on the [111] graphitic facets in the diamond crystal [4] and proton of water is moved to near the middle point between O and C:



Theoretical calculations are in progress by A. Barnard on the details of the water-  $\text{C}^{\ominus}$  interactions over the [111] surface of nanodiamond models.

### *Survey of nanodiamond powders*

At the moment three powder forms are known for detonation nanodiamond. They are compared in **Table 1**. Each of these forms represents a stationary point in the time sequence of purification steps. The reason for the best performance of hard gel in re-dispersion clearly arose from the inert hydration shell present only in this form.

**Table 1.** Powder forms of detonation nanodiamond

processing time step		primary product of detonation, pre-disintegration,	partial removal of water from milled colloidal solution of primary particles	complete removal of water from the colloidal solution
name		<i>agglutinate</i>	<i>hard gel</i>	<i>dry aggregate</i>
structure	shell	n.a.	$\text{H}_2\text{O}^*/0.6$ nm thick	trace $\text{H}_2\text{O}^*$
	size	60~200 nm	order of $\mu\text{m}$	order of $\mu\text{m}$
	packing	random, porous	densest	dense
bond- ing	mode	optimal, coherent <sup>¶</sup>	dynamic, van der Waals	equil. <sup>‡</sup> , incoherent <sup>¶</sup>
	energy, <sup>#</sup> keV	-3.3 (facet-facet) <sup>#</sup>	shell-shell	-1.2 (facet-facet) <sup>#</sup>
out- look	shape/touch	fluffy	heavy	usual
	color	grey	dark brown	brown
Water content, wt%		hygroscopic	21±2	2~3
Re-dispersibility		difficult <sup>§</sup>	highest	low

\*Non-freezing, non-melting (inert) water.

¶Coherent or incoherent Coulombic interfacial interaction among primary particles.

‡Equilibrium.

#Interaction energy calculated by SCC-DFTB method, ref. 4.

§Only two unconventional ways are known to disintegrate agglutinates of detonation nanodiamond into its primary particles: beads-milling [1b] and electric polarization [7a].

## 6. Concluding Remarks

As shown above, hard hydrogel of NanoAmando is a quite new but immensely interesting material. While we are still continuing the purification of hard gel, hence have not undertaken systematic determination of its physical properties, several interesting properties and behaviors have already been revealed while exploring applications [6, 8]. Among these, studies on the new type of drug carrier are the most unique and well-advanced [9-13]. Hard hydrogel is not cytotoxic [14].

## References

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