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Re-dispersion of NanoAmando® Hydrogel

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Abstract. Hydrogel is recognized to be a convenient form of weakly bound aggregates of single-nano diamond particles (NanoAmando®) suitable for transportation. Re-dispersion into primary particles can be achieved with ease by dissolving the gel into water and subjecting to powerful sonication. An ultrasonic set-up for the on-site preparation of large amounts of well-dispersed NanoAmando colloidal solution is mentioned.

Like all other low-nano particles, our NanoAmando, diamond crystallites in single-nano size, have high tendency to aggregate [1]. Even if NanoAmando is one of the smallest known nanocarbons, primary particles contain about 5000 carbon atoms [2], and does not vaporize, dissolve, melt, nor sublime. Fortunately it give stable, clear and relatively high concentrated colloidal solution in water and a few other organic solvents like ethanol and DMSO [3], hence NanoAmando is usually applied in dilute *colloidal solutions*. Colloids are, however, inconvenient to transport or store, hence we usually ship our NanoAmando as *flakes* or *gel*. These forms are naturally aggregates and the aggregates must be re-dispersed to monodisperse state before use. This remark may not be necessary to most of the readers, but we are much concerned about using NanoAmando in well-dispersed state because their behavior depends critically upon the state of particle surface, which in turn is affected most sensitively and adversely by even the slight aggregation.

Which is easier to disintegrate in common laboratories, flake or gel? The answer is gel. Flakes can be re-dispersed by pulverization in agate mortar followed by extraction with solvent and sonication, but this process is not as easy. We find that long pulverization in mortar leads to back-aggregation and also may cause inhalation. Coase particles tend to result in incomplete extraction. In contrast, gel can be dissolved simply by dilution with the solvent used to prepare gel. Still there are a few points to observe due to the peculiar behavior of single-nano particles. Here we describe a detailed procedure to turn NanoAmando gel into well-dispersed aqueous colloid from hydrogel.

General Procedure

Hydrogels of NanoAmando supplied from NCRI are in concentrations of 10-15% and well soluble in water. Simply adding deionized water to gel while swirling the gel container by hands instantly gives clear solution, which might appear highly dispersed colloidal solution. However, visual judgment on the disperse state of invisible nanoparticles is unreliable. Reality is that dispersion to single-nano particles is achieved only after intense sonication including careful monitoring of particle-size distribution, and that even if good dispersion were obtained, giving such a slight shock as further dilution quickly leads to re-aggregation. For these reasons we recommend to perform dissolution/dilution of gel only once to reach the desired particle size. The purpose of this technical note is to present a handy set-up to recover well-dispersed colloidal solution from gel. For this operation, one needs to have a powerful sonication system, and a particle-size analyzer by dynamic light scattering (DLS) method [4].

Examples

Peparation of Gel.

One hundred mL was taken out of a stock solution of aqueous colloid using a measuring flask, and transferred to a 200 mL round-bottom flask, and water was evaporated in a rotary evaporator under 40 Pa at 60℃. The content of flask became thick and acquired intense black color as water was removed. When about two-thirds of the water was evaporated and the remaining content lost mobility to adhere to the inner wall of flask, evaporation was stopped and the pasty hydrogel was scraped out quickly into a wide-mouthed bottle. The flask was rinsed with 15 ml of water, the washings combined with the gel, the mixture swirled in warm water bath to give 42 ml of homogeneous dark gel.

Separately, 5 ml of colloid was pipetted out from the stock solution into a 10 ml round bottom flask and completely evaporated beyond the gel point to dryness. Tan-colored, smooth and fine needle-like residual solid weighed 0.31385g, hence the nanodiamond concentration of the stock solution was determined to be 6.277% (wt/vol). After correcting for a loss by abrupt boiling, the concentration of gel prepared above was determined to be 13.5 wt%.

A small piece of hydrogel was taken out by using a small spatula and dissolved in 2 mL of water, sonicated in a desktop supersonic washer (110W, 24-31 kHz, ‘Bakusen’ W-113MK-II from Honda Electronic Co.), and submitted to DLS analysis on a particle analyzer from Otsuka Electronic Company (FPAR-1000 model equipped with a 660 nm laser). The measurement revealed that gel formation caused more than half of the particles aggregating to as large as 32 nm in average diameter (Table 1, the second entry). The aggregation is considerable, compared to the high dispersion of the starting stock colloidal solution which

consisted of an average diameter of 4.7±0.6 nm in 99% abundance (Table 1, the first entry). This size range is statistically equal to the value of 4.5±0.5 nm reported by Vul' *et al* for the size of primary crystallites in the agglutinates of detonation nanodiamond based on the intensities of powder X-ray diffraction [5]. However, the inter-particle forces in the hydrogel are expected to be weak, and our purpose here is to see how quickly the aggregates can be disintegrated to its primary particles by judicious irradiation with ultrasonic wave.

Table 1. Time change in particle-size distributions[a] analyzed by Marquardt method in the course of sonication.

Sonication time, *m*	1st peak		2nd peak	
	av.size± stad.dev., *nm*	abundance, *wt%*	av.size± stad.dev., *nm*	abundance, *wt%*
-[b]	4.7±0.6	98.6	50.7±8.8	1.4
0	9.3±1.2	38.8	31.9±24.0	61.2
30	8.2±1.5	96.6	47.0±14.4	3.4
60	6.4±1.0	97.2	42.6±11.3	2.8
90	6.8±1.1	95.0	37.6±16.1	5.0
120	6.5±0.8	94.4	38.4±15.2	5.6
150	6.4±0.9	97.6	46.7±11.6	2.4
-[c]	5.7±0.9	95.2	36.1±15.1	4.8

[a]Each line of particle-size distributions represents an average of a large number of measurements. Each 'measurement series' takes 150 seconds, during which 80-90 distribution determinations were repeated over a selected size-range (max. 3 nm to 5 μm) and an average distribution within each series is calculated. The series is repeated five times, thus giving five sets of average size-distributions. Among these, one set showing a median value for the most abundant distribution is entered in the Table. [b]Before gel formation. [c]After leaving for 20 days at room temperature in a closed brown-glass bottle.

Re-dispersion of Gel into Colloid under Intense Sonication.

A colloidal solution obtained by diluting a gel with large amounts of water was sonicated with an intense supersonic generator. In order to process large volume of colloidal solution, a flow set-up was used (Fig. 1 and Photo 1 and 2).

Seventy nine mL of the same stock solution as used in the previous section was concentrated to *ca* 30 mL of dark-colored gel containing 14.03 wt% of nanodiamond, and diluted with deionized water to give 995 mL of 0.5 wt% colloidal solution. The heart of our

re-dispersion system is an ultrasonic processor from Dr. Hielscher GmbH (type UP400S, 400 W, 24kHz) equipped with a titanium horn H22D having a diameter of 22 mm and giving an acoustic power density of 85 W/cm^2. The horn was immersed in an all-glass flow cell GD22K, through which the colloidal solution was circulated by pumping with a Verderlab peristaltic tube pump (Series VL from Verder Co.) at a rate of 0.5 L/min. Cooling of the flow cell by running water is essential to remove heat generated by the ultrasonication. UP400S was operated at the maximum amplitude of 100 μm with power discharge pulse length of 0.6 s and pause 0.4 s.

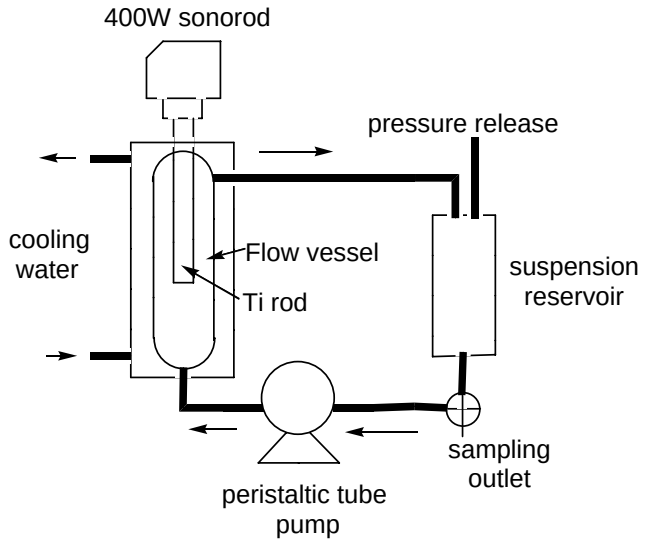

Fig. 1. Schematic illustration of an ultrasonication set-up. A 300 mL separatory funnel was used as the reservoir of circulating suspension (see also Photos 1 and 2).

As expected, disintegration of the van der Waals aggregates are quite fast in this set-up, and complete in 60 min (Table 1). The final size was somewhat larger than expected, but the difference is statistically not highly significant. Optimization of disintegration conditions including concentration, structure of reservoir and flow rate will be attempted later. It would also be worthwhile to study the rate of re-aggregation during storage of the dilute colloids thus dispersed. In the present case, re-measurement of particle-size distribution indicated no significant re-aggregation after storing the colloid in a brown bottle at room temperature without purging the dead space in the bottle with inert gas for 20 days (the last line in Table 1) [6].

Conclusions

1. Gel of NanoAmando provides a good alternative form to transport NanoAmando

over long distances.

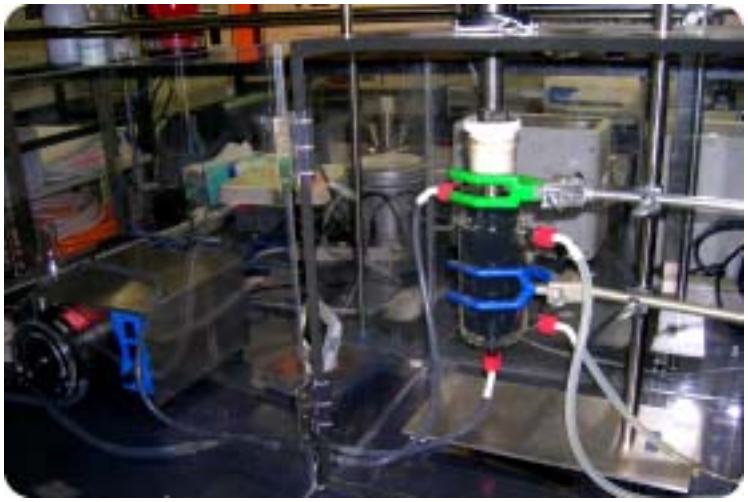

Photo 1. Peristaltic tube pump (left) and sonorod in flow vessel. The latters are contained in a plastic box for suppressing excessive noise.

Photo 2. Reservoir for suspension-colloid is placed below the flow vessel to prevent overflowing through the loose contact between sonorod and PFTE joint.

2. Re-dispersion of hydrogel can be readily accomplished by a setup consisting of ultrasonic processor with circulation flow cell, and peristaltic tube pump to prepare large volumes of aqueous colloidal solutions of single-nano diamond particles in short time.

3. Operating conditions of the setup need to be improved.

Acknowledgment. We owe to Dr. Houjin Huang and Professor Dean Ho for arousing our attention to hydrogel.

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