DISPERSION OF DETONATION NANODIAMONDS IN A LIQUID MEDIUM

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Abstract

Nanodiamonds can be synthesized by detonation using high explosive mixtures of trinitrotoluene/hexogen. In order to recover the nanodiamond from the detonation by-products, detonation soot is purified by an acidic treatment followed by a thermal oxidation. Transmission Electron Microscopy images revealed that nanodiamonds are essentially agglomerated. Most applications require nanodiamond individual particles. Therefore the agglomerates must be broken in order to separate elementary particles. The oxidation treatment performed during the purification process allows obtaining nanodiamonds which can be dispersed in an aqueous medium. Such suspensions remain stable during months, but a sedimentation phase made of agglomerates is still observed. The nanodiamonds dispersed in the stable supernatant represent around 30-40 wt% of the total nanodiamond weight.

Ball milling of different durations were performed on nanodiamonds. This process tends to increase the agglomeration of nanodiamonds, but an additional short sonication allows breaking weakened bonds between nanodiamonds and obtaining better results. Ultrasonic stirring with a sonotrode is the most efficient treatment because it allows reaching an amount of nanodiamonds dispersed in the stable supernatant of 85 wt% of the total nanodiamond weight. The dispersion of nanodiamonds in different media at miscellaneous pH values shows that ionic strength is an important factor to take in care so as to obtain good suspensions.

Introduction

A few years ago, nanodiamonds had known a renewal of interest and much research are presently undertaken about the potential applications for this material. Dolmatov proposes a review of properties and applications of detonation ultra dispersed diamonds [Dolmatov 2001]. Hence nanodiamonds can be used for biological applications such as the separation and the purification of proteins [Bondar 2004a, 2004b], as well as in magnetic recording system technologies [Kurmashev], electroplating [Burkat] or ultrafine polishing [Artemov].

Nanodiamonds can be synthesized via detonation wave at pressures around 20-30 GPa and temperatures ranging from 3000 to 4000 K during a few microseconds. Much research has been performed on the diamond synthesis by detonation and particularly on the composition of the explosive charges and on the environment in which the charges are fired [Fousson, Titov, Kuznetsov, Mal'kov, Donnet, Dolmatov 2004]. In the detonation soot, metallic impurities and carbon phases distinct from diamond (amorphous carbon and graphite) can be found.

Several treatments can be used to remove this impurities, usually an acidic treatment followed by an oxidation treatment are performed [Fousson, Pichot, Danilenko, Chiganov, Osswald]. Most of the time after the purification process, the nanodiamonds are highly agglomerated. It is then essential to separate the nanodiamonds to obtain individual particles in order to be able to study their properties and to use them for applications.

To achieve this goal, two ways can be investigated, either chemical or mechanical treatments. Therefore, several parameters are studied, the nature of the dispersive medium, the functionalization of the nanodiamonds, the type of mechanical stress, ball milling or ultrasonic waves. According to Zhu et al. [Zhu], the role of the different factors should be examined together to obtain stable suspension of nanodiamonds. For instance, nanodiamonds treated with a chemical/mechanical treatment are stable in the pH range 3-5 and the use of anionic surfactants allows obtaining stable nanodiamond suspension in the pH range between 8-11. In references [Eidelman] and [Krüger], ball milling was performed, by using micron-sized ZrO_2 or ceramic beads respectively, on the nanodiamonds aggregates and stable suspensions of individual nanodiamond particles could be obtained. Ultrasonic stirring is often used to obtain suspensions of nanodiamonds.

The oxidation treatment performed at ISL during the purification process allows obtaining aqueous suspensions which remain stable during months, the purpose of this study is to increase the rate of nanodiamonds present in the supernatant.

Experimental

Detonation soot was obtained by firing an explosive charge composed of TNT /RDX (70/30) inside a steel tank. The resulting detonation soot was treated using a 25 / 75 wt% mixture of hydrofluoric (HF, 40 wt%) and nitric (fuming HNO_3) acids to remove metallic particles. To eliminate sp^2 carbon species such as graphite and amorphous carbon, an oxidation treatment was carried out under air at 420°C in a muffle furnace. The powder became grey with a continuous evolution towards a lighter colour as long as the thermal treatment was continued. Transmission Electronic Microscopy, Raman spectroscopy, X-ray diffraction and Thermo-Gravimetric Analysis showed that this purification process is very efficient [Pichot]. Aqueous suspensions stable during months can already be obtained, but a sedimentation phase made of agglomerates is still observed.

To increase the rate of dispersed nanodiamonds, different treatments were tried:

- *Ball milling:*

Nanodiamond powder roughly suspended in ethanol was placed in a 50 mL grinding jar, ball milling was performed at 300 rpm during 10, 20, 60, 180 and 900 minutes. Metallic beads were used. After ball milling, the suspensions were analysed with a particle size analyzer using light scattering technique, and Scanning Electron Microscopy (SEM) was performed on the dried product.

- *Ultrasonic treatment:*

Dispersions containing 100 mg of nanodiamonds powder in ethanol were prepared. The dispersions were sonicated during 10, 20, 60 and 360 minutes with a sonotrode which supplies a power of 400W at a frequency of 24 kHz. The resulting suspensions were characterized by particle size analysis.

- *Dispersion in different aqueous media:*

100 mg of nanodiamonds powder were added to solutions with different pH. Four solutions at 1 $mol.L^{-1}$ were prepared: hydrochloric acid at a pH of 0, potassium chloride at a pH of 5, a $NaHCO_3$ / Na_2CO_3 buffer at a pH of 10.5 and KOH at a pH of 14.

Particle size distribution measurements were performed at ISL on a Beckman Coulter N5 Submicron Particle Size Analyzer and a Beckman Coulter Micron Particle Size Analyser LS320. The SEM micrographs were taken using a DSM 982 Gemini SEM from Zeiss.

Results and Discussion

Ball milling

Suspensions obtained after ball milling were kept in flasks during one day. Sedimentation occurs during this time and leads to different turbidities depending on the milling history of each sample (figure 1). From the samples treated during 10 to 180 minutes, it can be clearly seen that the colour of the supernatant becomes less cloudy, and is totally transparent for 180 minutes. The sample corresponding to 900 minutes shows a slight grey coloration of the supernatant. At the bottom of all the flasks, sedimentation sludge is observed. The amount of this deposit becomes more important with the increase of the time of treatment.

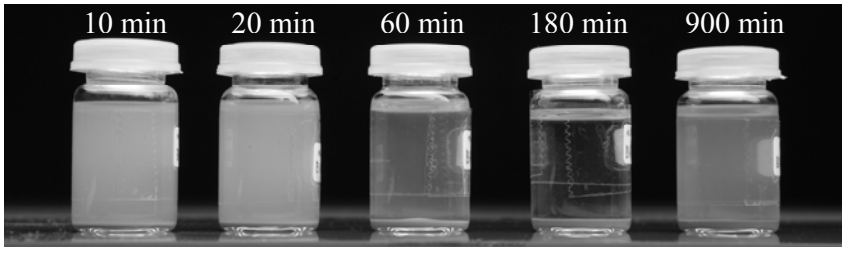

Figure 1. Photography of nanodiamonds suspensions obtained for different times of ball milling treatment after one day decantation.

The colour of the supernatant is linked to the quantity of nanodiamonds in suspension. In other words, the less the supernatant is transparent, the more the particles are in suspension. This result shows that the ball milling process applied here tends to agglomerate nanodiamonds.

A cloudy phase is still observed for a prolonged milling time of 900 minutes. It is probably due to metallic nanoparticles which come from beads used to mill. Indeed, a 0.025% decrease in beads weight was noticed

during the process which might signify that nanodiamonds have eroded the beads. This nano-erosion process could be an interesting way to elaborate nanosized metallic particles.

The suspensions were evaporated at 95°C and then dried under reduced pressure (60 mbar) during 30 minutes. SEM images (figure 2a) showed that the powder is macroscopically organized in crescent. But when imaging at a lower scale, nano-sized aggregates (about 20 nm) are observed (figure 2b). These aggregates which are composed of elementary nanodiamond particles self assemble to give macroscopic crescents.

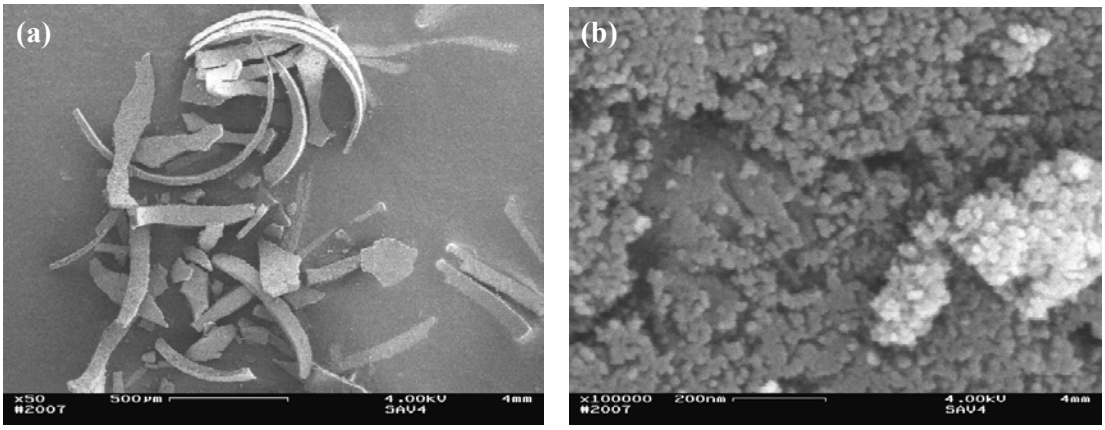

Figure 2. SEM images of the dried powder obtained after 60 minutes of ball milling treatment.

The dried powder was dispersed in ethanol in order to evaluate if the particles could be put again in suspension. The mixture was then stirred during 1 minute with an ultrasonic bath. An interesting result occurred showing that after the ultrasonic stirring, the sedimentation of the particles was really far slower, indicating that the crescents shaped macro-particles may have been broken by the ultrasonic stirring. Particle sizes distribution was determined for: the raw nanodiamonds, the sample mechanically milled during 60 minutes and the sample obtained by dispersing this last powder after having dried it (figure 3).

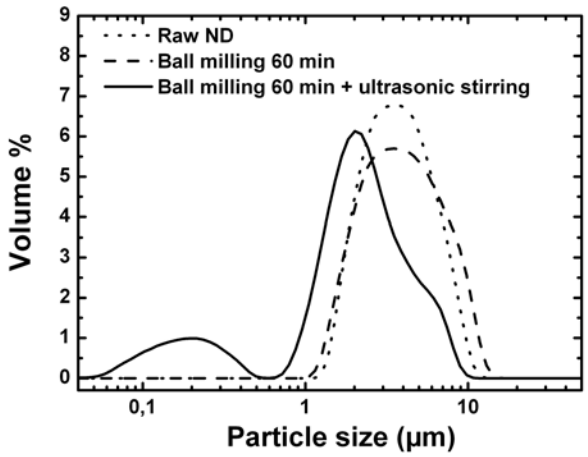

Figure 3. Particle size distribution of miscellaneous suspensions: raw nanodiamonds and suspensions treated during 60 minutes by ball milling without and with ultrasonic treatment.

Figure 3 shows that the only ball milling treatment does not decrease the size of the particles in suspension, but further ultrasonic treatment applied to ball milled suspension provides smaller particles. According to Osawa [Osawa], ball milling weakens some bonds, but also contributes to create new ones. Globally, ball milling leads to particles agglomeration in micron sized clusters which are broken by ultrasonic stirring. Particle size analysis quantitatively confirms the qualitative observation relative to the time of sedimentation of the different suspensions.

However, the use of ball milling technique is limited by the contamination coming from the erosion of the beads. Given the high hardness of diamonds it seems impossible to avoid the phenomenon. So, the use of ball

milling to efficiently disperse nanodiamonds would require an additional chemical treatment to eliminate metallic impurities.

Ultrasonic treatment

The results obtained from the particle size analysis on the suspensions treated by strong ultrasonic stirring are shown in figure 4.

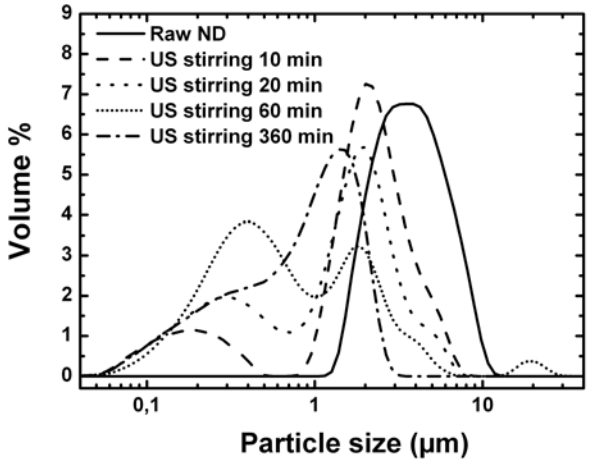

Figure 4. Particle size distribution of the suspensions treated by strong ultrasonic stirring.

The effect of ultrasonic stirring on the size of particles in suspension appears clearly. The size of nanodiamonds aggregates is reduced when the time of sonication increases. After 60 minutes of treatment, it decreases considerably below 1µm. This result is confirmed by the observation of the sedimentation of the suspensions (figure 5). The sediment phase of nanodiamonds at the bottom of the flasks (dark circles) is less important when the time of treatment increases. A prolonged sonication (360 minutes) activates chemical reactions between surface functional groups and induces the particles agglomeration (figure 4).

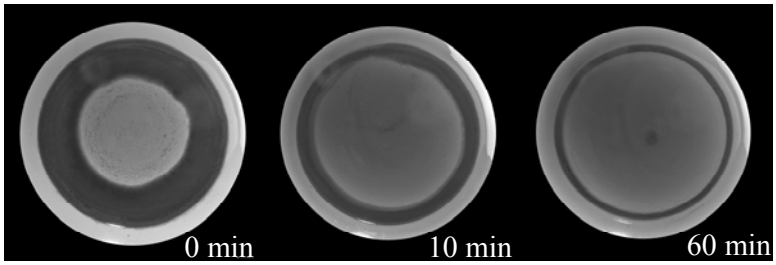

Figure 5. Photography of the sediments at the bottom of the flasks for 0, 10 and 60 minutes of ultrasonic stirring.

The most stable suspension in which the particles sizes were the smallest was obtained for 60 minutes of ultrasonic treatment. Then, to evaluate the amount of particles dispersed in the supernatant, the following experiment was performed: 100 mg of nanodiamonds were dispersed into ethanol in two 100 mL flasks. An ultrasonic strong stirring of 60 minutes was performed on one of the suspension. After different times of sedimentation, 10 mL of the suspensions were taken off the flasks and placed in a round bottom flask. The liquid phase was then evaporated at 95°C and dried under reduced pressure (60 mbar). The resulting solid was weighed on a precision balance. The results of this experiment are shown in figure 6. After one month of sedimentation, the amount of nanodiamonds in suspension in the non sonicated suspension was found to be around 33 wt% of the nanodiamonds initial weight. This ratio reached 85 wt% in the sonicated suspension. For both flasks, the suspension becomes stable after around 100 hours. Indeed, impurities coming from nanodiamonds elaboration process (SiO_2, TiO_2) are bigger than the nanodiamonds themselves and partly contribute to the sediment at the bottom of the flask. This could be a way to ultimately purify the nanodiamonds by taking off the sediment and keeping only the supernatant where only nanodiamonds are present.

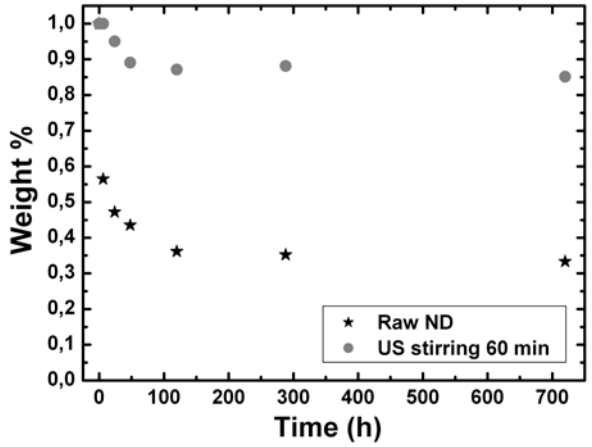

Figure 6. Evolution of the weight ratio of nanodiamonds in suspension as a function of the sedimentation times.

Nanosize analyser was used to determine the particle size in supernatant in the different suspensions treated with ultrasonic stirring. Reliable results were found for only two samples (figure 7), because for the others particles polydispersity was too important. Figure 7 clearly shows that the sizes of the aggregated particles become smaller when the sonication time increases.

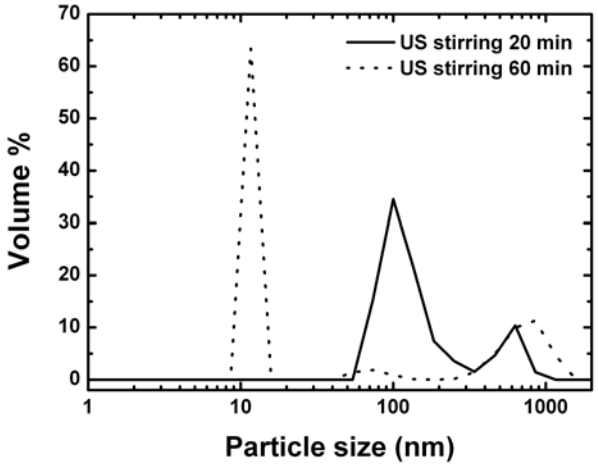

Figure 7. Particle size distribution of two suspensions sonicated with an ultrasonic horn during different times.

Dispersion in different aqueous media

Nanodiamonds were dispersed into miscellaneous solutions having a pH value ranging from 0 to 14 (figure 8). After 60 hours of decantation, the supernatants are transparent in all the flasks containing an ionic concentration of 1 $mol.L^{-1}$. For comparison, a reference suspension containing nanodiamonds dispersed into deionised water was prepared. Figure 8 shows these flasks after 60 hours of sedimentation. All the nanodiamonds suspensions have set down except for the flask of deionised water.

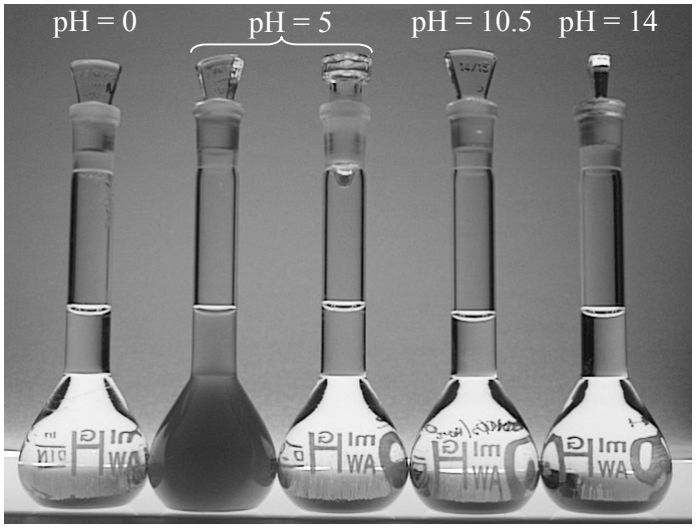

Figure 8. Photography of nanodiamonds suspensions prepared at different pH values after 60 hours of sedimentation, from left to right: hydrochloric acid at a pH of 0, deionised water, potassium chloride (1 $mol.L^{-1}$) at a pH of 5, $NaHCO_3$ / Na_2CO_3 buffer (1 $mol.L^{-1}$) at a pH of 10.5 and KOH at a pH of 14.

A video sequence performed on these five flasks showed that the speed of sedimentation of the different suspensions is the following: from the faster to the slower are potassium chloride, hydrochloric acid, $NaHCO_3$ / Na_2CO_3 buffer and KOH suspensions. These qualitative results clearly show that pH and ionic strength play a major role in the nanodiamonds sedimentation process. Further investigations are necessary to fully understand the chemical mechanisms governing nanodiamonds sedimentation.

Conclusion

Many factors have to be considered for the dispersion of nanodiamonds in a liquid medium: the applied mechanical stress (milling, ultrasounds), the liquid dispersing medium, the concentration of nanodiamonds, the pH and the ionic strength of the suspension are important parameters.

Ball milling tends to agglomerate nanodiamonds, but additional sonication allows breaking weakened bonds between nanodiamonds and dispersing them better. The best results are obtained for ultrasonic stirring with a sonotrode: it was possible, by using this treatment, to reach an amount of nanodiamonds dispersed in the stable supernatant of 85 wt% of the total nanodiamond weight. Nanodiamonds dispersion in different media at different pH are to be studied more carefully but the first results reported herein show that ionic strength of the suspension as well as its pH are important factors to care about for obtaining good dispersions. Further studies will be undertaken by coupling all these methods of dispersion.

Moreover, the dispersion of nanodiamonds could lead to the ultimate purification stage by separating the supernatant from the impurities rich sediment phase.

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