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Unintentional formation of nitrate and nitrite ions during nanodiamonds sonication: a source of radical and electron scavengers

Florent Ducrozet^{a,b}, Hugues A. Girard^{a,*}, Teodor Jianu^a, Sophie Peulon^a, Emilie Brun^b, Cécile Sicard-Roselli^b, and Jean-Charles Arnault^{a,*}

- a. Université Paris-Saclay, CEA, CNRS, NIMBE, CEDEX, 91191 Gif sur Yvette, France
- b. Institut de Chimie Physique, UMR 8000, CNRS, Université Paris-Saclay, 91405 Orsay, France

Ever since studies on diamond nanoparticles (NDs) expanded, their exceptional colloidal stability was investigated as it is a key parameter for their further use in many applications. While a sonication step is required to deaggregate NDs and obtain stable aqueous suspensions, few works focused on the impact of the sonication process on the suspension composition. High-powered sonication induces the formation of a variety of species by radical pathways including nitrite and nitrate ions, which may act as radical or electron scavengers. Such effect may significantly affect the expected photocatalytic or radiolytic properties of NDs. This work aims to warn about the formation of these ionic species during the deagglomeration of NDs by sonication. Our investigation reveals for the first time that for oxidized detonation NDs, such treatment promotes the formation of additional NO_2^- ions and hydroxyl radicals, suggesting an increase in cavitation bubbles formation. Hydrogenated particles on the opposite present no overproduction of nitrite ions. Our results also show that these species can be avoided in suspension by sonicating under controlled atmosphere with no significant perturbation of NDs colloidal stability or surface chemistry.

Keywords : nanodiamonds, sonication, nitrite ions, colloids, scavengers

Introduction

Among the nanocarbon family, nanodiamonds (NDs) constitute a promising material for nanomedicine¹, quantum² and energy³ fields. Colloidal dispersion of NDs in water is often required to fully exploit their properties, for instance when NDs are studied for drug delivery, biomarkers or photocatalysis purposes. In water, very stable colloids of NDs were reported without addition of any surfactant, through a fine tuning of their surface chemistry to generate either carboxylic functions⁴ or hydrogenated terminations^{5,6,7,8}, giving rise at neutral pH to negative or positive zeta potentials, respectively. Most of the time, the dispersion is realized by ultrasonic treatment in ultra-pure water. The quality of the dispersion also relies on disaggregation techniques carried out by manufacturers, and several strategies were developed like the bead-assisted sonic disintegration (BASD) method⁹ and more

recently, the salt-assisted ultrasonic deaggregation (SAUD) protocol¹⁰, both conducted in water.

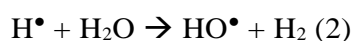
These recent years, NDs have attracted a rising attention for their unique properties under irradiation or illumination, for which their surface chemistry and subsequent organization of water molecules at their surface seem to play a major role¹¹. For instance, an overproduction of hydroxyl radicals and solvated electrons during water radiolysis (under X- or gamma-rays) in presence of hydrogenated detonation NDs (DND-H) was measured¹². Recently, the emission of solvated electrons was also measured for DND-H under visible illumination¹³. Moreover, first proofs of concept of CO_2 photocatalytic reduction was reported using ND-H suspended in water illuminated under UV¹⁴. All these processes rely on reactions involving radical species generated at the vicinity of NDs surface, which support the particular attention that needs to be paid to the preparation of NDs suspension. Indeed, the

presence of unwanted ionic species arising from the dispersion protocol may significantly affect the expected photocatalytic or radiolytic properties of NDs if they are radical or electron scavengers.

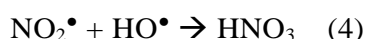
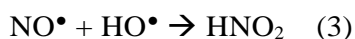
According to literature, when high-powered sonication is performed, cavitation bubbles are generated in aqueous medium, which causes a variety of subsequent chemical reactions¹⁵. If the energy delivered is in the range or superior to the dissociation enthalpy of water, then H₂O molecules are thermally dissociated leading to the formation of hydroxyl and hydrogen radicals (1).



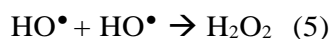
These radicals, created in the gas phase of cavitation bubbles, can enter the liquid phase while H[•] radicals can also react in the gas phase with water vapour to form hydroxyl radicals and dihydrogen¹⁶ (2).



When the sonication is performed under air, the dissolved nitrogen and oxygen gas undergo the same excitation which leads to their dissociation and reaction of the transient species formed^{17,18}. In presence of all these reactive intermediates, nitrous (3) and nitric (4) acids are formed.



At almost neutral pH, these acids dissociate, forming nitrite and nitrate ions and increasing the solution acidity^{19,20}. Also, hydroxyl radicals can recombine to form hydrogen peroxide (5).



As sonication is required for NDs disaggregation and dispersion, such sonochemical reactions are likely to occur. Consequently, nitrite and nitrate ions may be present in NDs aqueous suspensions, their amount mostly depending on the sonication experimental conditions. Therefore, the present study aims to quantify these ionic species post-sonication of aqueous suspensions of DNDs, with a special focus on nitrite ions for which a sensitive and selective detection by fluorescence was optimized. Influences of the atmosphere, the surface chemistry and mass concentrations of DNDs are investigated.

Experimental

Materials

2,3-diaminonaphthalene (2,3-DAN, purity > 95 %), coumarin (purity > 99 %) and 7-hydroxycoumarin (7-OH Cou, purity 99 %) were purchased from Sigma-Aldrich. 2,3-DAN aqueous solution was prepared in 0.63 N HCl with 0.16 mM final concentration. NaNO₂ (purity 98.5 %) was purchased from Acros Organics. All aqueous solutions and dilutions were made with ultra-pure water (18.2 MΩ.cm) and kept refrigerated between experiments.

Modification of nanodiamond surface

Detonation nanodiamonds (DNDs) were purchased from Adamas Nanotechnologies (ND5nmN, carboxylated, Raleigh, NC, USA). For DNDs with an oxidized surface (DND-Ox), as-received powder was used without further modification.

Hydrogenated DNDs (DND-H) were obtained by annealing under H₂ of as-received particles (5h, 750°C, 50 SCCM, atmospheric pressure). All the annealing treatments were performed using a Carbolite Gero tubular furnace.

Sonication of nanodiamond powders

Nanodiamond powders, up to 200 mg, were collected in 15 mL plastic tubes and the volume was made to 4 mL with ultrapure water. Dispersion of the powder was obtained by a sonication step of 30 min (unless specified otherwise) with a 1 s on/off period and an amplitude of 60 % (Cup Horn Bioblock Scientific 750 W 20 kHz). The Cup Horn temperature was maintained at 10°C during sonication treatments by a cooling system. In the Cup Horn system, ultrasonic power delivered to water was estimated to 30 W by calorimetry using a standard calibration protocol²¹.

The sonication step was performed under air or oxygen (purity > 99.9991 %). To ensure saturation with oxygen, samples were degassed for one hour before the sonication step and the gas flow was maintained during the ultrasonic treatment. For experiments with controlled atmosphere, a stopper with septum was used, increasing the distance

between the source of ultrasounds and the sample. This longer distance led to a diminution of nitrite ions concentration formed for the same sonication parameters but did not interfere with the overall trends.

After sonication, 150 μL of each sample were collected. NaCl (1% w/v final concentration) was added to each sample to induce agglomeration and samples were centrifuged (20000 g, 5 min) to remove DNDs and collect the supernatant.

Dynamic light scattering and zeta potential measurements

Hydrodynamic diameters and zeta potentials were measured by dynamic light scattering and laser Doppler electrophoresis using a Horiba Nanopartica SZ100 system. Acquisitions were realized at 25°C with a 173°C backscattered angle on diluted suspensions (0.025 wt %) in ultrapure water (18.2 M Ω .cm). Size distributions and zeta measurements result from the average of 10 independent measurements.

Fourier-transformed infrared spectroscopy

Infrared spectra were recorded with a Bruker Vertex 70 spectrometer equipped with a diamond ATR system. 2 μL of DNDs suspension in water were deposited and dried on the ATR crystal (MIRacle, PIKE Technologies) before analysis. Acquisition represents the average of 128 scans recorded with a 4 cm^{-1} resolution at room temperature and ambient atmosphere with a nitrogen-cooled MCT detector.

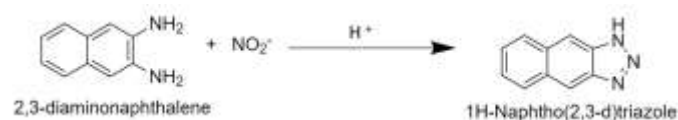
Quantification of hydroxyl radicals

For quantification of HO \bullet radicals, coumarin was added to samples at 0.5 mM final concentration. Formation of 7-hydroxycoumarin was quantified post-sonication in the supernatants by fluorescence with excitation at 326 nm and the maximum of emission detected at 450 nm. Fluorescence measurements were realized with a Synergy H1 microplate reader (Biotek).

Quantification of nitrite ions

Nitrite ions quantification was realized using the 2,3-diaminonaphthalene (2,3-DAN) molecule

which reacts with NO $_2^-$ in acidic medium to form 1H-naphtho(2,3-d)triazole (2,3-NAT):



The protocol was adapted from previous works²²⁻²⁵ to be compatible with our experimental procedure. Supernatants were mixed with 2,3-DAN solution in a (2:1) v/v ratio. After incubation for 10 minutes in the dark, NaOH solution (final concentration 0.44 M) was added. Each quantification was realized on supernatants after sonication and precipitation of DNDs particles to avoid any interaction between DNDs with 2,3-DAN and 2,3-NAT molecules. 2,3-NAT was quantified with excitation at 360 nm and the maximum of emission detected at 403 nm using a Synergy H1 microplate reader (Biotek). Calibration curves were made using the same protocol with sodium nitrite solutions. The evolution of 2,3-NAT was linear with the nitrite concentration in the studied concentration range.

Liquid Phase Anionic Chromatography

Ionic species formed by sonication treatment were analysed using anionic chromatography (Dionex Integron) equipped with an AS 19 column (Thermo Fisher) and a gradient of KOH with a 1 $\text{mL}\cdot\text{min}^{-1}$ flow rate. Detection of nitrate and nitrite ions was made by conductimetry. Quantification was realized by analysing a Dionex Seven Anion Standard II (Thermo Fisher) with known concentrations of nitrite and nitrate ions.

Irradiation of DNDs aqueous suspension

Irradiations were performed with a panoramic ^{60}Co gamma-rays source (IL60PL Cis-Bio International). Dose rate, assessed by Fricke dosimetry, was 1.3 $\text{Gy}\cdot\text{min}^{-1}$.

Results and discussion

Evidencing the formation of nitrite and nitrate ions during sonication

This work aims to study the formation of nitrite and nitrate ions during sonication of DNDs powders to prepare stable aqueous colloids. First, to attest the generation of both species in our

sonication conditions, anionic chromatography was performed on ultra-pure water after 30 minutes of sonication. Results are presented in Table 1.

	[NO ₂ ⁻] (μmol.L ⁻¹)	[NO ₃ ⁻] (μmol.L ⁻¹)
Reference	0	0
Sonicated water	4.9	18.4

Table 1: Concentrations of nitrite and nitrate ions determined by anionic chromatography on a reference (ultra-pure water before sonication) and on water sonicated for 30 minutes.

The sonication treatment not only induced the formation of both NO₂⁻ and NO₃⁻ ions but it can also be noticed that the concentration of nitrate ions is 3 to 4 times the one of nitrite ions. This result couldn't be expected since the formation ratio of NO₂⁻ and NO₃⁻ varies among the literature^{19,26,27}.

To determine the concentration of nitrite and nitrate ions when the sonication is performed in the presence of detonation nanodiamonds (DNDs), an addition of salt (NaCl) after sonication is necessary to separate the aqueous phase from the particles. However, anionic chromatography is incompatible with such a high concentration (1% w/v) of ionic content. Therefore, for the next experiments, the focus was made on the quantification of nitrite ions by a chemical titration using 2,3-diaminonaphthalene (2,3-DAN) molecule.

As can be seen on Figure 1, with the selected sonication parameters, the evolution of NO₂⁻ concentration is linear with time at least for one hour of sonication. It can be noticed that for 30 minutes of sonication, a concentration of 4.2 μmol.L⁻¹ is determined with the 2,3-DAN protocol, which is in agreement with the concentration determined by anionic chromatography. The same experiment was realized in presence of oxidized DNDs (DND-Ox) with a mass/volume ratio of 2.5 %, in the same final volume. After removing particles from the solution, NO₂⁻ concentrations for each sample were measured. The evolution of the concentration is also linear with the sonication time but surprisingly an enhancement of the concentration

by almost a factor 4 is measured. The presence of DND-Ox seems to lead to an overproduction of nitrite ions.

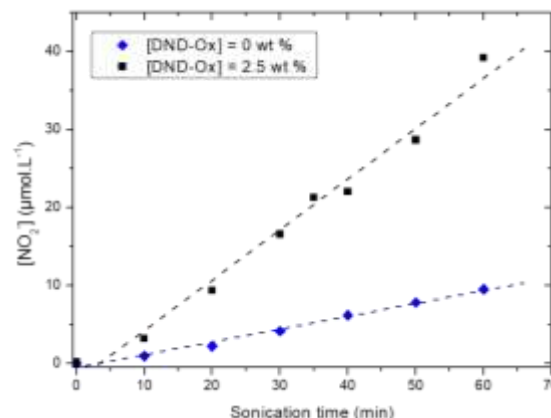


Figure 1 : Influence of the sonication time on the formation of nitrite ions in presence or absence of DND-Ox.

As expected²⁰, a decrease of pH was observed. For longer sonication times, this phenomenon may affect the colloidal stability of DND-Ox that is related to the formation of carboxylates in water.

Investigating the overproduction of nitrite ions by DND-Ox

DND-Ox particles were sonicated in ultra-pure water for 30 minutes at different mass concentrations under air atmosphere. Results are depicted in Figure 2. Without DND-Ox in solution, a concentration of nitrite ions of 1.2 μmol.L⁻¹ is obtained, lower than the previous experiment due to a change in distance from the ultrasound source (see Materials). When DND-Ox are added to ultra-pure water, an increase of the nitrite concentration occurs, up to almost 15 μmol.L⁻¹ for 4 wt. %.

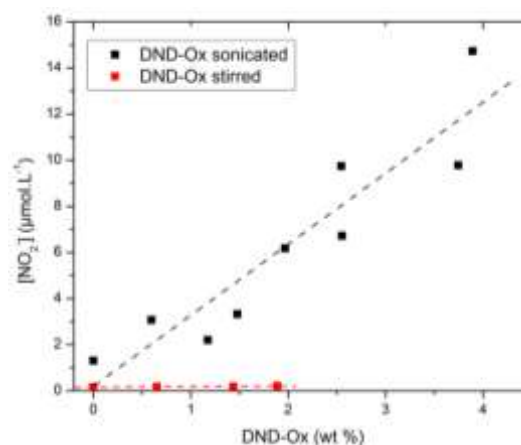


Figure 2 : Influence of the DND-Ox

concentration on the formation of nitrite ions during sonication.

To explain this raise of the nitrite ions formation in the presence of DND-Ox, two possibilities could be considered: (i) nitrite ions are brought by DND-Ox and desorbed from their surface when NaCl is added to the suspension for nitrite titration or (ii) an enhancement of the sonochemical formation of nitrite ions due to the presence of DND-Ox occurs. Concerning the first hypothesis, the loading of negatively charged DND-Ox by anions such as NO_2^- is unlikely to happen due to electrostatic repulsion. Nevertheless, to definitely refute this option, the concentration of nitrite ions was measured for different concentrations of DND-Ox, up to 2 wt %, simply dispersed in water by mechanical stirring, all other parameters being similar to sonication experiments (Figure 2). Whatever the amount of DND-Ox in solution, NO_2^- concentration remains below $0.20 \mu\text{mol.L}^{-1}$ invalidating the first hypothesis.

If the presence of DND-Ox during the sonication increases the formation of cavitation bubbles, a similar effect on the formation yield of HO^\bullet could be expected since hydroxyl radicals are witnesses of their formation¹⁵⁻¹⁷. Indeed, the formation of hydroxyl radicals by sonolysis is a well-known process and coumarin has already been investigated as a chemical probe of these radicals under sonication²⁸. Then, sonication experiments with increasing concentration of DND-Ox were realized in the presence of 0.5 mM coumarin solution. Coumarin is a specific scavenger of hydroxyl radicals with a high rate constant²⁹ ($k = 1.05 \times 10^{10} \text{ L}^{-1}.\text{mol}.\text{s}^{-1}$) and among the hydroxylated products, 7-hydroxycoumarin (7-OH Cou) is fluorescent. Quantification of 7-OH Cou allows the indirect quantification of HO^\bullet generated during the sonication. Results of this experiment are presented in Figure 3.

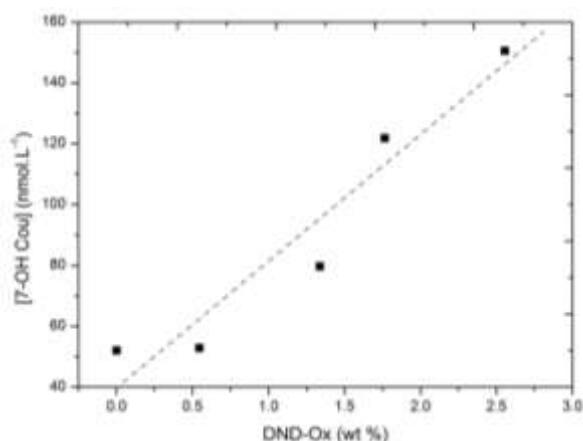


Figure 3 : Evolution of 7-hydroxycoumarin concentration as a function of DND-Ox concentration.

As expected, sonication of ultra-pure water without DNDs gives rise to the formation of 7-OH Cou with a concentration of 52 nmol.L^{-1} . When DND-Ox are added, an increase of the 7-OH Cou is measured with the DND-Ox concentration, up to 150 nmol.L^{-1} for a DND-Ox concentration of 2.5 wt %. As for nitrite formation, in the presence of DND-Ox, an enhancement of the sonication effect on HO^\bullet formation occurs.

To determine the origin of such higher yields in the presence of DND-Ox, cavitation phenomenon has to be discussed. When water is irradiated with ultrasounds, cavitation promotes the formation, the oscillation and the implosion of bubbles¹⁵. During collapsing, shockwaves are produced and high pressure and temperature are reached (about 1900 K for a 20 kHz irradiation³⁰), which are at the origin of the water thermolysis and the formation of hydroxyl and hydrogen radicals. The formation of cavitation bubbles is facilitated if nucleation sites are present in the media. Such nucleation sites can be found at the surface of nanoparticles dispersed in the irradiated liquid. This phenomenon of bubble formation has already been described for gold³¹, silica³² or alumina³³ nanoparticles. Similar effect may happen with DND-Ox, explaining the raise of the HO^\bullet and nitrite concentrations observed in their presence. Another hypothesis can also be considered. As it was proposed for other particles³⁴, the presence of DND-Ox may also disturb the propagation of ultrasonic waves, leading to modified formation yields of hydroxyl radicals and nitrite ions.

Effect of DNDs surface chemistry on nitrite ions formation

As DNDs exhibit very different properties according to their surface chemistry and are valued either with an oxidized surface but also with a hydrogenated surface³⁵, the effect of the surface terminations of DNDs on the nitrite formation was also investigated. Thanks to their carbon-based chemistry, DNDs surface can be easily tuned by gas-phase treatments. Annealing of DNDs under hydrogen atmosphere promotes the desorption of carbon-oxygen surface groups and the saturation of dangling bonds with hydrogen⁶ (see Figure S1). When dispersed in water, such hydrogenated DNDs (DND-H) exhibit excellent colloidal properties with a positive zeta potential.

Ultra-pure water was sonicated under air atmosphere with increasing concentrations of DND-H, in the same conditions than for oxidized ones.

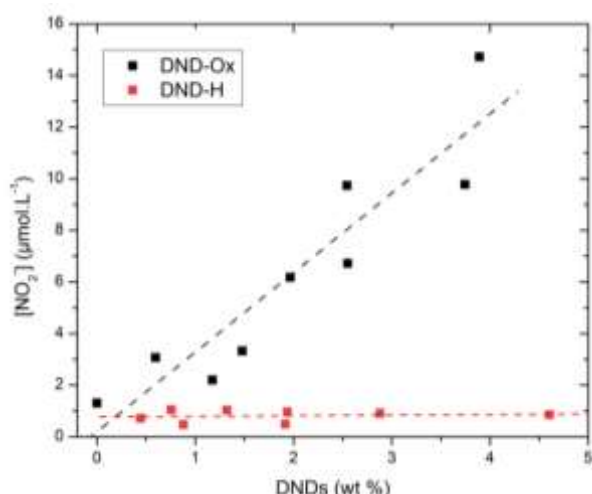


Figure 4 : Influence of the DNDs surface chemistry on the formation of nitrite ions during sonication.

Surprisingly, in the presence of DND-H, no increase of the nitrite concentration is observed as a function of DND-H concentration (Figure 4). Starting from 1.2 µmol.L⁻¹ without DND-H, the nitrite ions concentration remains almost constant around this value whatever the concentration of DND-H in the solution up to 5 wt % tested.

To explain this completely different behaviour of DND-H, we may consider two possibilities: (i) nitrite ions are formed the same way as with DND-Ox but remained strongly adsorbed at the DND-H

surface due to favourable interactions or (ii) DND-H interfere with the reaction pathway leading to the formation of NO₂⁻ ions and inhibit their formation. In the former possibility, the positive surface charge of DND-H would favour the adsorption of nitrite ions at their surface. However, concentrated NaCl (final concentration 1% w/v) was added to the sonicated DND-H solution before NO₂⁻ titration, initially to induce flocculation and easier separation of the DNDs from the aqueous phase. Such an important increase of the ionic strength should also ensure an efficient desorption of any anionic species from DNDs surface. Nevertheless, to verify the effective desorption of NO₂⁻ from DND-H, nitrite ions were intentionally added at different concentrations to a suspension of DND-H and mechanically stirred for one hour. Then, NaCl was added in a similar manner than after sonication and the solution was centrifuged. Nitrite concentration was then measured in the supernatant.

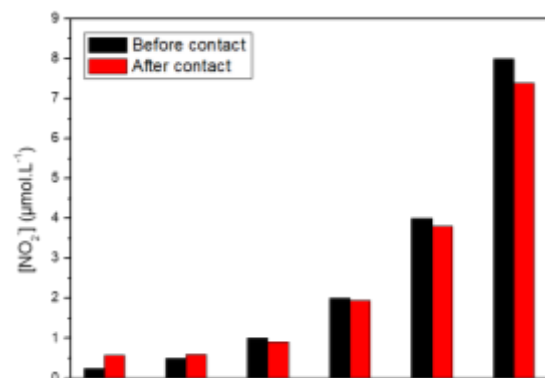


Figure 5 : Quantification of nitrite ions before and after contact for one hour with a suspension of DND-H.

As can be seen in Figure 5, for each concentration of NO₂⁻, almost all ions are titrated after precipitation, meaning that the addition of salt is efficient to desorb nitrite ions from DNDs surface if adsorption occurs. Considering this observation, the interaction of DND-H surface with the reaction pathway of NO₂⁻ formation is then more likely to be at the origin of the invariance of nitrite concentration during sonication. As reported in the literature, hydroxyl radicals react predominantly with hydrogenated surfaces resulting in hydrogen atoms abstraction^{36,37}. This scavenging of the hydroxyl radicals by DND-H may explain the invariance of nitrite concentration.

Avoiding the formation of nitrite ions during sonication

Since NO_2^- ions are formed thanks to atmospheric nitrogen dissolved in water, one way to avoid their formation is to suppress this nitrogen source during sonication. Previous works already demonstrated that sonication under a controlled atmosphere leads to the diminution or the total avoidance of the formation of nitro content^{17,26,27}. To explore this possibility, ultra-pure water previously degassed with pure O_2 was sonicated in presence or not of DND-Ox. NO_2^- concentrations resulting from sonication under air or O_2 are compared in Figure 6.

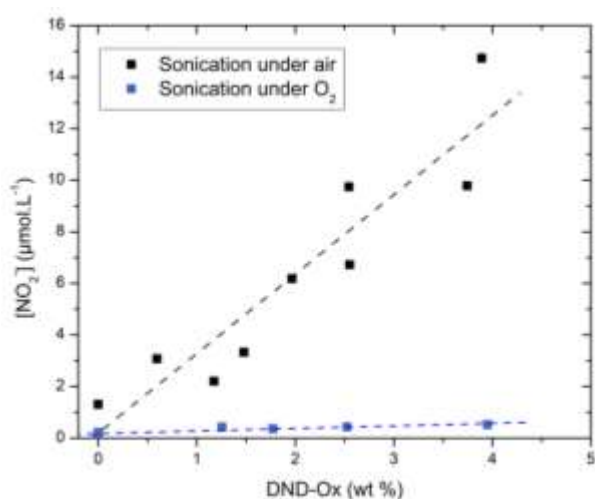
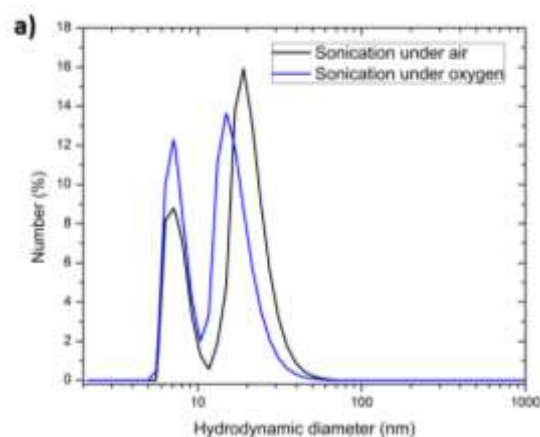


Figure 6 : Evolution of nitrite concentration as a function of DND-Ox concentration depending on the sonication atmosphere.

When ultra-pure water is sonicated under O_2 atmosphere, the formation of NO_2^- is drastically reduced compared to a similar sonication under air, from $1.2 \mu\text{mol.L}^{-1}$ to $0.1 \mu\text{mol.L}^{-1}$. When DND-Ox are introduced at increasing concentrations, no further increase in the generation of nitrite ions is observed. Degassing suspension with oxygen is thus an efficient way to avoid the formation of nitrite ions. Not only the nitrogen source is avoided but it was also demonstrated that degassing under pure O_2 atmosphere may induce the quenching of excited species by molecular oxygen³⁸. This affirmation would also explain that the sonochemical processes that allow the formation of nitrite ions are inhibited while the physical effects (deagglomeration and dispersion of DNDs) are still effective. Also, this experiment also

demonstrates that NO_2^- ions are definitively not brought by DND-Ox but are formed *in situ* and only in the presence of both dissolved nitrogen and oxygen.

Colloidal behaviour of DNDs sonicated in these particular conditions was then investigated. For DND-Ox, DLS measurements performed on DNDs sonicated at 1 wt % under air or under pure O_2 evidence almost similar colloidal size distribution whatever the sonication atmosphere as shown in Figure 7a. In both cases, isolated particles (hydrodynamic diameter of 7 nm) and small clusters (15 nm for oxygen sonication and 20 nm for air sonication) are present with no significant difference. Note that equivalent zeta potentials were also measured with $-53 \pm 2 \text{ mV}$ and $-56 \pm 3 \text{ mV}$ for the air- and oxygen saturated samples, respectively. FTIR spectra of these DND-Ox are also shown in Figure 7b, exhibiting in both cases an intense band of C=O stretching modes at 1780 cm^{-1} attributed to carboxylic functions and anhydrides and C-O stretching modes between 1000 and 1200 cm^{-1} . O-H stretching and bending modes are also visible at $3000\text{-}3500 \text{ cm}^{-1}$ and 1630 cm^{-1} respectively³⁹. These O-H groups are partly due to the carboxylic acids and to ambient humidity. Here, the atmosphere of sonication did not induce any noticeable modification, at least at the detection limit of FTIR. Note that if nitrite ions formed in presence of air during sonication are adsorbed at the surface of DND-H, they are not visible on these IR spectra. However, one has to take into account the sensitivity of FTIR and the rather low concentration of nitrite ions formed.



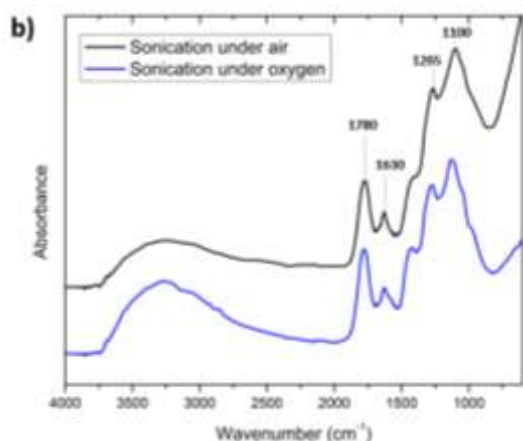


Figure 7: a) DLS measurements of DND-Ox sonicated under air and under oxygen and b) FTIR spectra of DND-Ox suspensions sonicated under air and under oxygen.

Therefore, sonication under oxygen is an effective alternative to avoid the presence of nitrite ions in the suspension while keeping colloidal stability and similar surface chemistry.

Presence of nitrate ions and electron scavenging

Nitrate ions, as nitrite ions, may be prejudicial depending on the targeted application of DNDs aqueous suspensions. Particularly, nitrate ions are good electron scavengers, with a rate constant⁴⁰ of $9.7 \times 10^9 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$. As NDs are nowadays investigated for radiosensitization¹² and photocatalysis¹⁴, an accurate control of the species that could scavenge hydroxyl radicals and solvated electrons are mandatory. To investigate the impact of our sonication conditions, two suspensions of DND-Ox, sonicated under air or oxygen, were irradiated with a final dose of 9 Gy with gamma-rays using a ⁶⁰Co source. After NaCl addition, nitrite ions were quantified. Results are presented in Figure 8.

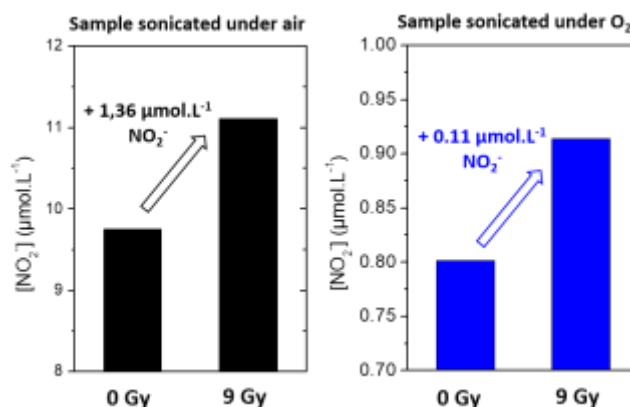


Figure 8 : Quantification of nitrite ions before and after gamma irradiation of DND-Ox samples sonicated under air or oxygen.

It can be noticed that both non-irradiated samples (0 Gy) exhibit different NO_2^- concentrations depending on the atmosphere of sonication, as described before (Figure 6). As shown on Figure 8, the concentration of NO_2^- increased after irradiation. This is due to the presence of NO_3^- ions and their two electrons reduction reaction (6) :



This increase for both samples confirms the formation of nitrate ions during the sonication treatment in the presence of DND-Ox, as observed with anionic chromatography for water alone. This experiment also demonstrates that degassing under O_2 is effective not only to avoid the formation of NO_2^- but also NO_3^- ions since the increase in NO_2^- formation is lower for the sample sonicated under oxygen. Literature supports this observation for water alone^{17,26,27} but here the same trend is observed in the presence of DNDs.

Considering a formation yield of solvated electrons of $0.28 \mu\text{mol}\cdot\text{J}^{-1}$ for gamma radiolysis of water⁴¹, a 9 Gy irradiation should generate ca. $2.5 \mu\text{mol}\cdot\text{L}^{-1}$ electrons. In this experiment, for the sample sonicated under air, an increase of $1.36 \mu\text{mol}\cdot\text{L}^{-1}$ of nitrite ions is measured. Considering (6), it means that ca. $2.7 \mu\text{mol}\cdot\text{L}^{-1}$ electrons were engaged in the reduction of nitrate ions, which is in the same range considering the uncertainty of the nitrite titration. This experiment reveals that nitrate ions introduced by the sonication under air may scavenge a wide proportion of the electrons that are generated under irradiation, in the absence of a better electron scavenger. Therefore, if we

consider the example of photocatalytic CO₂ reduction using NDs, since the rate constant of carbon dioxide with solvated electrons⁴⁰ (7.7 x 10⁹ L.mol⁻¹.s⁻¹) is lower than the one of nitrate ions, a part of the electrons generated by NDs may not participate in targeted reduction when the corresponding NDs aqueous suspension was sonicated under air. Consequently, as the presence of these ionic species may be prejudicial, the choice of the sonication atmosphere must not be underestimated.

Conclusions

We have investigated the formation of nitrite and nitrate ions generated by sonication of DNDs with different surface chemistries. The introduction of DND-Ox seems to promote the formation of cavitation bubbles, assessed by the increase in the formation of hydroxyl radicals and nitrite ions. The surface chemistry plays a major role since no overproduction of nitrite ions is observed for DND-H. A reactivity of the hydrogenated surface towards radical species formed during sonolysis is proposed, leading to a constant concentration of NO₂⁻ in solution. Finally, to avoid the formation of these ionic species, a precise control of the sonication atmosphere represents an easy experimental alternative. Ejecting the N₂ by an intense degassing with pure O₂ leads to a drastic diminution in nitrite and nitrate ions formation, while maintaining the same colloidal properties and surface chemistries. This study highlights an unexplored part of the composition of DNDs suspensions and present a sonication method that needs to be applied for applications of aqueous nanodiamonds for which an interaction with these ionic species would be prejudicial like photocatalysis or radiosensitization.

Author Contributions

Conceptualization, F.D., H.A.G., E.B., C.S.R. and J-C.A.; methodology, F.D., H.A.G., E.B., C.S.R., S.P.P. and J-C.A.; validation, F.D., H.A.G., E.B., S.P.P., C.S.R. and J-C.A.; formal analysis, F.D., H.A.G., E.B., S.P.P., C.S.R. and J-C.A.; investigation, F.D., H.A.G., S.P.P., T.J.; resources, F.D., H.A.G., E.B., C.S.R., S.P.P. and J-C.A.; data curation, F.D., H.A.G., E.B., C.S.R., S.P.P. and J-C.A.; writing—original draft preparation, F.D.,

H.A.G., E.B., C.S.R. and J-C.A.; writing—review and editing, F.D., H.A.G., E.B., C.S.R., S.P.P., T.J. and J-C.A.; visualization, F.D.; supervision, H.A.G., E.B., C.S.R. and J-C.A.; project administration, H.A.G., E.B., C.S.R. and J-C.A.; funding acquisition, H.A.G., E.B., C.S.R. and J-C.A.

All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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