

Electronic Supplementary information (ESI) for
Hydroxyl Radicals Production Induced by Plasma Hydrogenated Nanodiamonds under X-ray Irradiation

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I. Samples preparation

Detonation nanodiamonds (ND) powder was provided by the PlasmaChem Company (Germany, Grade O2). Particles were manually milled before being modified. Carboxylated NDs (Ox-NDs) were produced by the annealing of 100 mg of NDs placed in an alumina crucible under air for 1h at 550° C. Hydrogenated NDs (H-NDs) were produced by microwave assisted hydrogen plasma treatment ¹. NDs were deposited in a quartz tube and inserted into a plasma Downstream source (Sairem SAS, France). High purity hydrogen gas (>N70) was used with a pressure of 12.5 mbar during the treatment and a flow of 10 sccm. Plasma was generated in the quartz tube at a micro-wave power of 250 W (2.45 GHz). During the plasma, the tube was air-cooled. NDs were exposed to hydrogen plasma for 20 min and cooled down under hydrogen for 10 min, leading to H-NDs. Both types of particles were then dispersed in ultrapure water (18.2 MΩ.cm) and sonicated (Heiilscher UP400s, 300W, 24 kHz) for 30 mins (Ox-NDs) and 1h (H-NDs) under a cooling system. In order to remove highly aggregated particles, the suspensions were centrifuged for 2h (2400g, 4754 rpm) followed by supernatant separation. The final concentration was calculated by measuring the mass of residue with a microbalance after drying a calibrated volume of the initial suspension.

II. Dynamic light scattering (DLS) and zeta potential (ZP) measurements

Hydrodynamic size and ZP of the oxidised and hydrogenated NDs in water suspension were measured using Malvern ZetaSeizer Nano ZS in order to determine the properties of NPs in colloidal suspension. Firstly, the samples were diluted down to 0.1 mg/mL and transferred into 1mL folded capillary cell. Hydrodynamic size and zeta potential analysis were performed with 633 nm laser at 25° C and the scattering angle of 173°. The data obtained are presented below in Fig. S1 and S2.

The hydrodynamic size was measured to be 33 ± 15 nm and 38 ± 14 nm for Ox-NDs and H-NDs, respectively. [Fig. S1] Carboxylated NDs (Ox-ND) possess negative zeta potential equal to -53 ± 10 mV whereas hydrogenated nanoparticles (H-NDs) are positively charged ($+44 \pm 7$ mV). [Fig. S2]

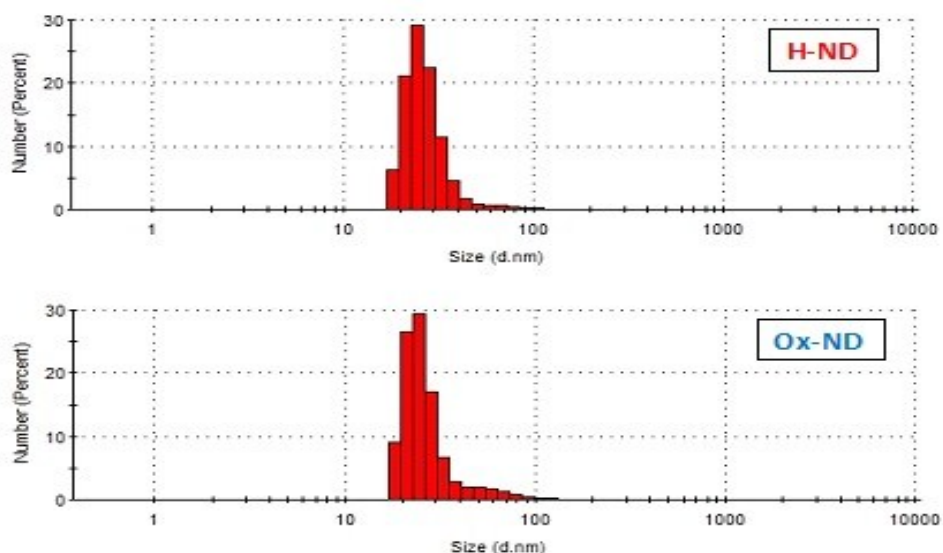


Fig. S1. The hydrodynamic diameter distribution of Ox-ND (bottom) and H-ND (top) in water suspension.

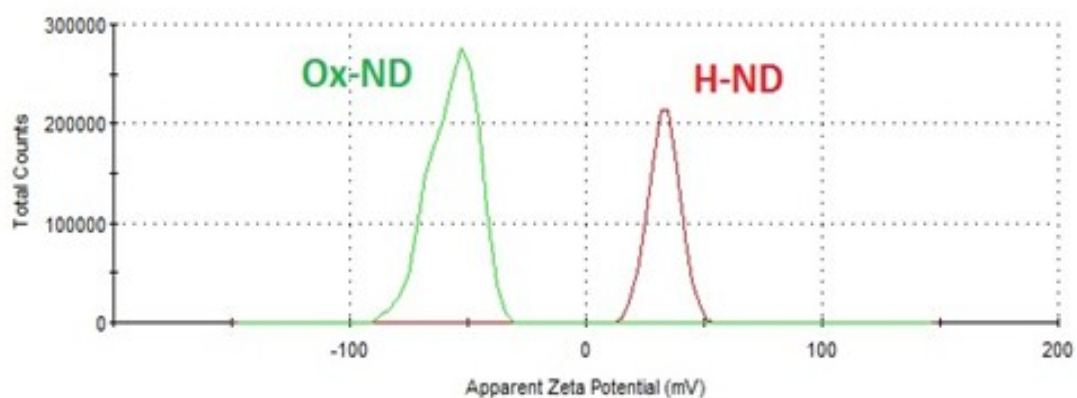


Fig. S2. Zeta potential distribution of oxidised (green) and hydrogenated (red) NDs as measured in water suspension at room temperature.

III. Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra were recorded on a Thermo Nicolet 8700 spectrometer using transmission mode. KBr pellets (1 wt %) were prepared with oxidised and hydrogenated nanodiamonds straight after their surface modifications. In order to minimize the absorbed water content, both pellets were dried in-situ for 24h at 60°C under vacuum before being analysed. Recorded spectra are reported in fig. S3. Ox-NDs are mainly characterized by the presence of a broad band around 1730-1790 cm^{-1} associated with C=O stretching involved in carboxylic acid groups and anhydride functionalities^{2,3}. The small peaks located between 2800 and 3000 cm^{-1} are related to C-H stretching modes, coming from amorphous carbon lying on the surface of the nanoparticles or from a limited carbon contamination. The bands in the range 900 and 1350 cm^{-1} belong to the so-called fingerprint area, in which C-O stretching modes

can be seen (between 1100 and 1200 cm^{-1}) related alcohol or ether-like groups. Note that despite an extensive drying, physisorbed water residues are still visible on the spectrum, with their O-H stretching mode around 3400 cm^{-1} and O-H bending mode at 1630 cm^{-1} .

On hydrogenated NDs, the broad band related to carboxylic groups located around 1750 cm^{-1} completely vanishes, while the C-H stretching modes between 2800 and 3000 cm^{-1} increase, revealing the covering of the surface with C-H terminations. Fingerprint area also evolves with the loss of bands around 1100 and 1200 cm^{-1} (C-O stretching modes) and the appearance of new features around 1450 cm^{-1} associated with C-H bending modes. Here as well, some water residues are still visible on the spectrum around 3400 cm^{-1} and 1630 cm^{-1} related to stretching and bending O-H modes respectively.

This evolution of FTIR spectra from carboxylated to hydrogenated NDs is fully consistent with previously published works on Ox-NDs and H-NDs obtained either by plasma or thermal treatments^{4,5,3}. Ox-NDs and H-NDs exhibit two different spectroscopic signatures, with the clear presence of oxygen-related terminations on Ox-NDs and their absence on H-NDs, the later exhibiting clear stretching and bending modes of C-H features related to hydrogenated terminations.

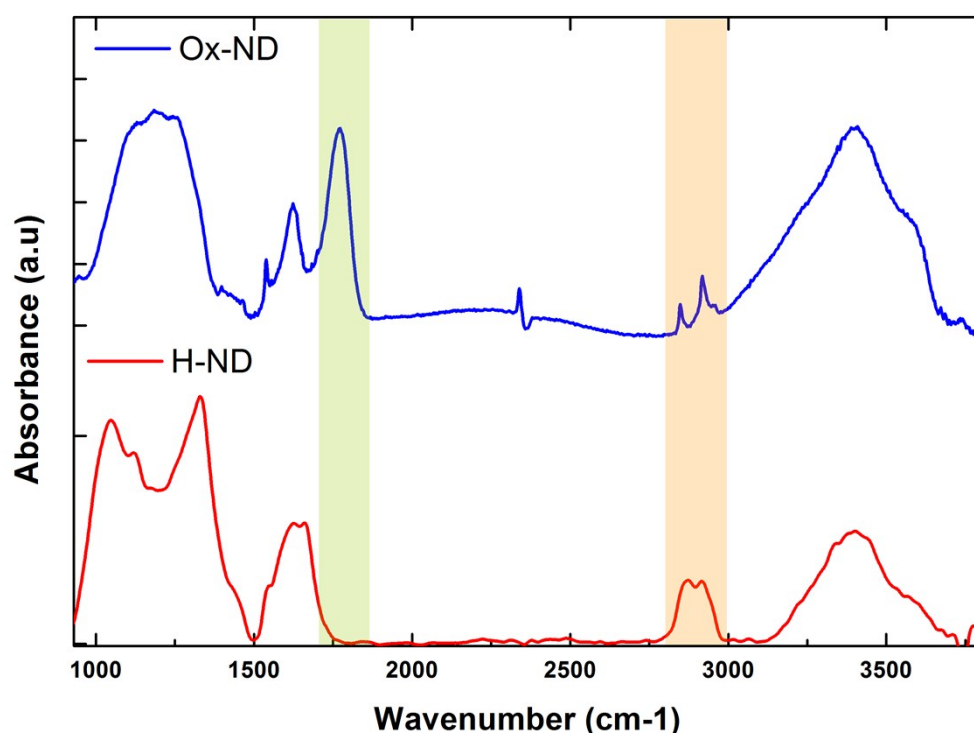


Fig. S3. FTIR spectra of surface-hydrogenated (H-ND) and surface-carboxylated (Ox-ND) detonation nanodiamonds after 24h of drying under vacuum at 60° C, respectively.

IV. Quantification of hydroxyl radical production

NDs suspensions were diluted in water with coumarin (0.5 mM). Conventional X-ray generator (17.5 keV, Enraf Nonius, Mo cathode) was used for sample irradiation with a dose rate of 20 Gy/min. NDs were irradiated with an increasing irradiation dose: 0 Gy - reference, 3.3, 5, 6.7, 8.3, 10, 11.7 and 13.3 Gy. Doses were determined with a Fricke dosimeter⁶.

As nanoparticles often alter fluorescence measurements, we tested different conditions for signal recovery. We mixed ND (100 $\mu\text{g}/\text{ml}$) with 7-hydroxycoumarin (100 nM) in the presence of 0.5 mM coumarin in water to mimic the samples post-irradiation. As can be seen in Fig S4, without treatment, only ca. 70% of expected fluorescence was measured for H-NDs. When NaCl solution (10% w/v, dilution 1:10) was added, the recovery increased to 90%. When an additional centrifugation cycle (18000g, 5 min) was performed, at least 95% of the signal was detected. In all irradiation experiments, samples were treated by addition of salt and centrifugation. Only supernatants were deposited into microplates for reading.

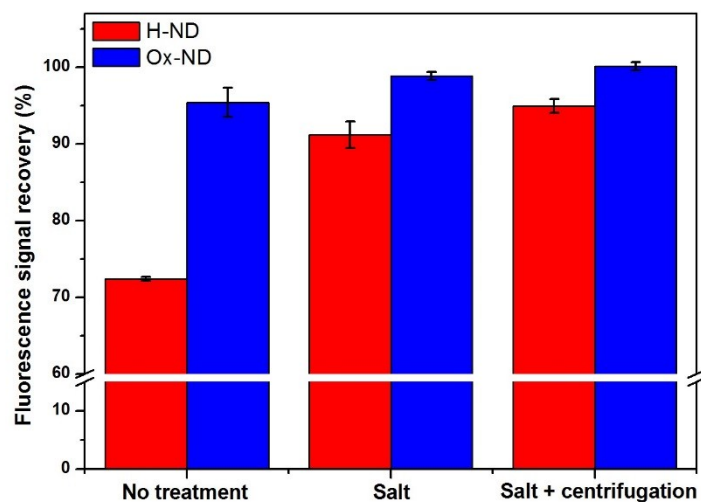


Fig. S4. Percentage of the fluorescence signal measured without treatment (no treatment), after addition of sodium chloride (salt), and for a combined treatment (salt + centrifugation) given for Ox-ND (blue) and H-ND (red).

References

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