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1 **Milled Nanodiamonds Overproduce Solvated Electrons while Scavenging Hydroxyl**
2 **Radicals under Gamma Irradiation**

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9 Keywords: nanodiamonds, HPHT milling, irradiation, solvated electrons, hydroxyl radicals

10
11 **Abstract**

12 Among the different nanodiamonds, milled nanodiamonds (MNDs) from high pressure high
13 temperature (HPHT) synthesis exhibit a crystalline quality close to the bulk diamond, making it a
14 serious candidate for quantum or energy-related fields. In this study, MNDs aqueous suspensions
15 with oxidized (MND-Ox) and hydrogenated (MND-H) surface chemistries were irradiated with
16 gamma-rays. Using optimized nanoparticle-compatible methods, we revealed that MNDs in
17 suspension enhance the production of solvated electrons under irradiation, with a higher yield for
18 MND-H. Also, for the first time, a surface chemistry-dependent scavenging effect of hydroxyl
19 radicals was highlighted for this type of nanodiamonds.

20 **Introduction**

21 Among all carbon nanostructures, nanodiamonds (NDs) exhibit promising properties for
22 biomedical and energy-related applications¹ as their thermal², electrical³, and hardness⁴ hallmarks

1 come along with chemical stability⁵ and biocompatibility⁶. The major route for high-scale
2 production of NDs is detonation of carbon-containing explosives, leading to quasi-monodisperse
3 particles around 5 nm with a defectuous crystalline core. However, over the last five decades,
4 mechanical milling has evolved from a standard technique in metallurgy to a novel synthetic route
5 for a wide variety of materials including nanocrystalline or nanocomposite ones⁷. To date, it is also
6 one of the main methods to obtain commercial NDs, by milling of natural or synthetic diamond,
7 the latter being obtained by high pressure high temperature (HPHT) or chemical vapor deposition
8 (CVD) growth. Milled NDs (MNDs), commercially available with the smallest average particle
9 size around 20 nm, even if more polydisperse than detonation nanodiamonds (DNDs), present a
10 better crystallinity, closer to bulk diamond, and exhibit clear crystallographic facets⁸. That's why
11 till now they garnered researchers' interest for very specific uses such as highly stable fluorescent
12 biomarkers⁹, magnetic sensors¹⁰ or single photon emitters for quantum information processing¹¹.

13 To envision new applications to MNDs, in nanomedicine or energy-related fields for example, it
14 is of interest to investigate their behavior towards radical species, such as hydroxyl radicals (HO•)
15 or solvated electrons (e^-_{solv}). In fact, MNDs¹² (from natural source) or DNDs¹³ are able to enhance
16 the production of solvated electrons into water under UV or visible illumination when their surface
17 is hydrogenated. In previous work, higher energy photons were used to irradiate DNDs aqueous
18 suspensions and in the presence of hydrogenated DNDs, but not oxidized, hydroxyl radicals and
19 solvated electrons were available in solution in equivalent and higher amounts than in water only¹⁴.

20 This leads us to study how MNDs react under gamma irradiation, depending on their surface
21 chemistry.

22

23 **Experimental Section**

24 ***Materials***

1 Milled nanodiamonds (MNDs) were purchased from Van Moppes (SYP 0-0.05, purity > 99,9%).
2 The polydispersity of the powder was assessed by particle size measurement on cryo-electronic
3 microscopy observations (Figure S1).
4 Coumarin (purity > 99%), 7-hydroxycoumarin (7-OHCou, purity 99%) and 2,3-
5 diamionaphthalene (2,3-DAN, purity > 95%) were purchased from Sigma Aldrich. Sodium
6 nitrate and sodium nitrite (purity 98.5%) were purchased from Acros Organics.
7 2,3-DAN aqueous solution was prepared in 0.63 N HCl with 0.16 mM final concentration.
8 All aqueous solutions and dilutions were made with ultra-pure water (18.2 MΩ.cm) and kept
9 refrigerated between experiments.

10

11 ***Modifications of nanodiamond surface and aqueous suspension preparation***

12 Oxidized MNDs (MND-Ox) were obtained by annealing as-received particles for 4h30 at 410°C
13 under atmospheric pressure of air. Hydrogenated MNDs (MND-H) were obtained by annealing
14 MND-Ox under H₂ (50 SCCM, atmospheric pressure) for 5h, at 750°C. All the annealing
15 treatments were performed using a Carbolite Gero tubular furnace.

16

17 ***Aqueous NDs suspension preparation***

18 Annealed powders were collected in a 15 mL plastic tube and the volume was completed to 4 mL
19 with ultrapure water. Powder dispersion was obtained by a sonication step of 30 min with a 1 s
20 on/off period and an amplitude of 60% (Cup Horn Bioblock Scientific 750 W, equipped with a
21 cooling system with a programmed temperature of 10°C). Finally, MNDs suspensions were
22 collected after centrifugation at 2400 g for 40 minutes, to isolate the dispersed MNDs from the
23 aggregates/agglomerates.

24

25

1 ***X-Ray Diffraction analysis (XRD)***

2 Crystalline structure and average sizes of nanodiamonds were identified using a D2-Phaser
3 diffractometer (Bruker) equipped with a CuK α X-rays source. The recorded range of 2 θ angles
4 was 10° to 100°. Analyses were realized on *ca.* 10 mg of powder deposited onto a silicon substrate.
5 Diffractogram of the substrate alone was subtracted from the sample's signal. FWHM
6 measurement and subsequent crystallite size determination was realized on the diamond (111)
7 diffraction peak at 44°.

8 9 ***Specific surface area measurements***

10 The specific surface area was determined by N₂ adsorption using the single point B.E.T. (Brunauer,
11 Emmett and Teller) approach and a 3Flex instrument (Micromeritics, France). 20 to 60 mg of
12 MNDs were degassed under vacuum for 6h at 180°C (VacPrep06, Micromeritics) for removal of
13 impurities and then analysis was realized under N₂ at -196°C.

14 15 ***Size determination by microscopy***

16 Diameters distribution of MNDs particles was realized by manual analysis of cryo-EM
17 observations (Figure S1). Microscopy equipment and observation parameters were already
18 described in a previous study¹⁵. The statistics were realized on 300 particles.

19 20 ***Fourier Transform Infrared (FTIR) measurements***

21 Infrared spectra were recorded with a Bruker Vertex 70 spectrometer equipped with a diamond
22 ATR system (MIRacle, PIKE Technologies). 2 μ L of MNDs suspension in water were deposited
23 and dried on the ATR crystal before analysis. The acquisition represents the average of 128 scans
24 recorded with a 4 cm⁻¹ resolution at room temperature and ambient atmosphere with a nitrogen-

1 cooled MCT detector. A break was applied in the 2240–2400 cm^{-1} region to avoid the contribution
2 of atmospheric CO_2 absorption bands.

3

4 ***X-Ray Photoelectron Spectroscopy (XPS)***

5 10 μL of MNDs suspension were deposited on a silicon substrate covered by a gold coating made
6 by evaporation to limit the charge phenomenon during analysis. The substrates were dried at
7 ambient temperature and pressure before analysis. XPS measurements were performed on a Kratos
8 Analytical Axis Ultra DLD spectrometer equipped with a monochromated Al $\text{K}\alpha$ (1486.6 eV) X-
9 ray source and a charge compensation system (Manchester, UK). The take-off angle was set at 90°
10 relative to the sample surface. Spectra were acquired at a pass energy of 160 eV for the survey and
11 40 eV for core levels (O_{1s} , C_{1s}). C_{1s} spectra shown in this study were acquired at 10 eV to reach a
12 higher energy resolution. Binding energies were referenced to the $\text{Au}_{4f7/2}$ peak located at 84 eV.
13 After the background subtraction by a Shirley correction, a curve fitting procedure was carried out
14 to extract the components of the C_{1s} core level using Voigt functions with a Lorentzian to Gaussian
15 ratio of 30% (Figure S2).

16

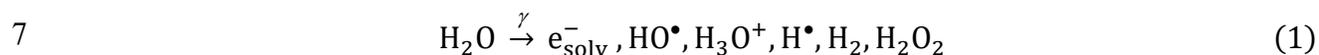
17 ***Dynamic Light Scattering (DLS) and zeta potential measurements***

18 Hydrodynamic diameters and zeta potentials (ZP) were measured by a Malvern NanoZS in
19 DTS1061 cells. Acquisitions were realized on $0.5 \text{ mg}\cdot\text{mL}^{-1}$ suspensions at 25°C with a 173°
20 backscattered angle. For size measurements, a refractive index of 2.417 was used. For ZP
21 measurements, 150 V was applied (Smoluchowski equation). Both sizes and ZP results are the
22 average of 30 independent measurements.

23

24 ***Irradiation of nanodiamonds aqueous suspensions***

1 Irradiation experiments were performed using a panoramic ^{60}Co source (IL60PL Cis-Bio
2 International, photons of 1.17 and 1.33 MeV) with dose rates between 0.5 and 1.5 Gy.min $^{-1}$
3 depending on the chosen distance from the gamma source. Dosimetry was determined using a
4 Fricke dosimeter¹⁶. For each MNDs concentration, independent samples were irradiated at
5 different doses between 0 and 8 Gy. Gamma irradiation of water leads to the formation of radical
6 and molecular species, among which hydroxyl radicals and solvated electrons (Eq. 1).



8 For ^{60}Co disintegration, the formation yields of HO^\bullet and e_{solv}^- are 0.28 $\mu\text{mol.J}^{-1}$ at neutral pH.

9 For irradiation experiments, coumarin or sodium nitrate solutions were added to MNDs
10 suspensions. Their respective final concentrations were comprised between 0.2 and 1.5 mM for
11 coumarin or equal to 2 mM for sodium nitrate.

12 After irradiation of MNDs suspension in the presence of coumarin or nitrate ions, NaCl (1% w/v
13 final) was added to each sample to induce aggregation and samples were centrifuged (20000 g, 5
14 min) to remove MNDs and collect the supernatant for further analysis. Two different aqueous
15 suspensions of MND-H were used in this study.

16

17 ***Quantification of hydroxyl radicals***

18 Quantification of hydroxyl radicals was realized using coumarin as a probe. HO^\bullet can add to several
19 positions of coumarin rings and among the hydroxylated products, 7-hydroxycoumarin (7-OH
20 Cou) is fluorescent¹⁷. 7-OH Cou formed during irradiation was quantified by spectrofluorometry
21 with a microplate reader (Synergy H1 microplate reader, Biotek, excitation 326 nm, emission 450
22 nm). Calibration curves were made with commercial 7-OHCou in the presence of coumarin at the
23 same concentration as in the irradiation experiments to take into account the intern filter effect¹⁸.

1

2 ***Quantification of solvated electrons***

3 Post-irradiation, supernatants were mixed with 2,3-DAN solution in a (2:1) v/v ratio. After
4 incubation for 10 min in the dark at room temperature, NaOH solution (final concentration 0.44
5 M) was added. Fluorescence was detected with excitation at 360 nm and emission at 403 nm.
6 Calibration curves were made using the same protocol with sodium nitrite solutions.

7 ***High-Performance Liquid Chromatography (HPLC)***

8 Coumarin and hydroxycoumarins were analyzed by HPLC (HP 1100 Series, Agilent) and
9 hydrophobic separation was performed on a C18 column (25 cm length, 4.6 mm intern diameter).
10 100 μ L of supernatants were injected. Mobile phases were A: (89 % water, 10 % methanol and 1
11 % acetic acid) and B: (89 % methanol, 10% water and 1% acetic acid). Gradient elution was 0 %
12 B during 5 min, 0-30 % B in 5 min, 30-50 % B in 20 min and 50-100 % B in 5 min, with a flow
13 rate of 0.8 mL.min⁻¹. Chromatograms were plotted with absorbance detection at 280 nm. Peaks
14 were attributed as labeled by comparison to standard hydroxycoumarins injected under the same
15 chromatographic conditions. Chromatograms were realigned to 6-hydroxycoumarin peak and
16 baseline corrections were applied when necessary.

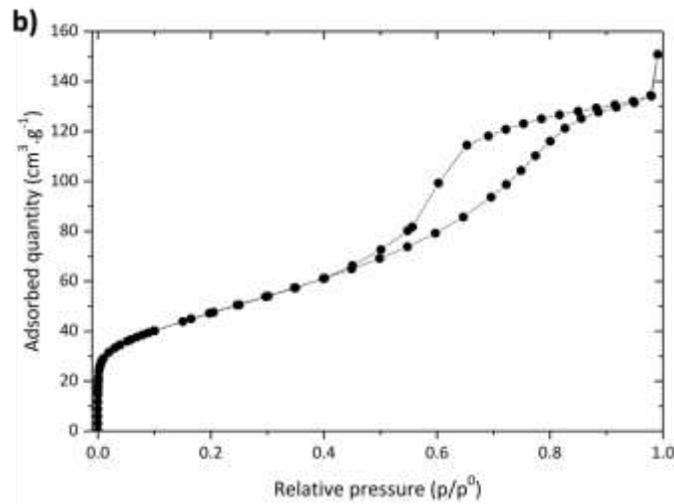
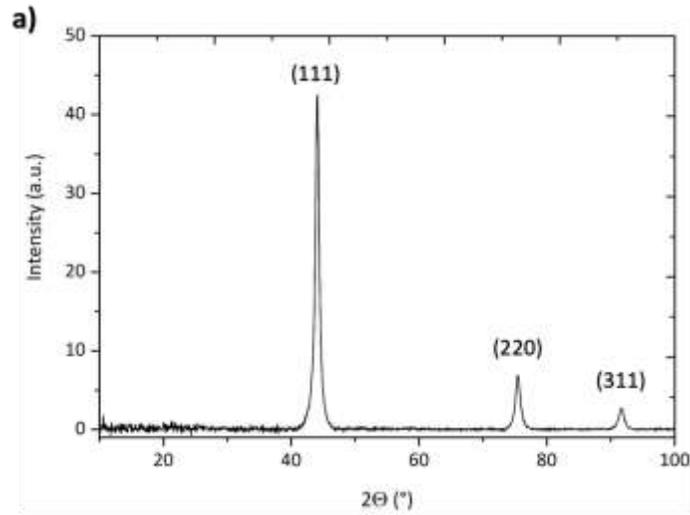
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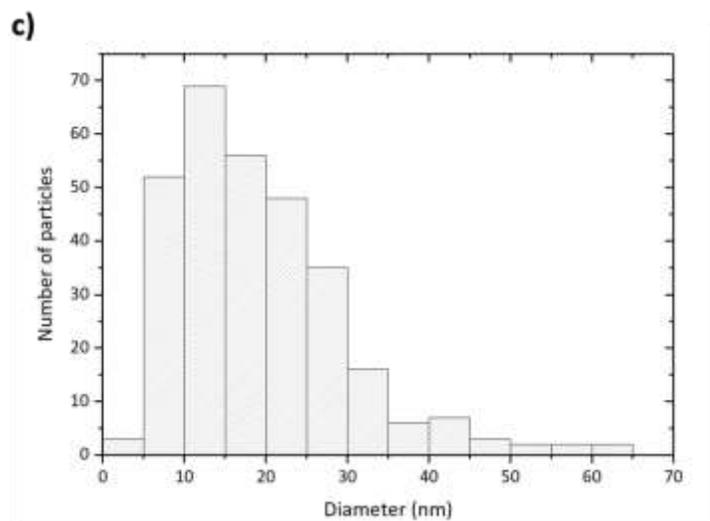
18 **Results**

19 This work aims to quantify solvated electrons and hydroxyl radicals available in solution when
20 MNDs aqueous suspensions were submitted to ionizing radiation. As surface chemistry was shown
21 to play a decisive role for other NDs¹⁹, we decided to focus on hydrogenated (MND-H) and
22 oxidized (MND-Ox) MNDs. Starting from a commercial powder, we analyzed the particles before
23 and after treatments to obtain an exhaustive characterization of our samples.

1 **Characterization of nanodiamonds**

- 2 First, the commercial powder was analyzed by XRD, N₂ adsorption and microscopy to confirm
3 the crystalline structure and obtain the specific surface area of untreated (as-received) MNDs.
4 Results are presented in Figure 1.



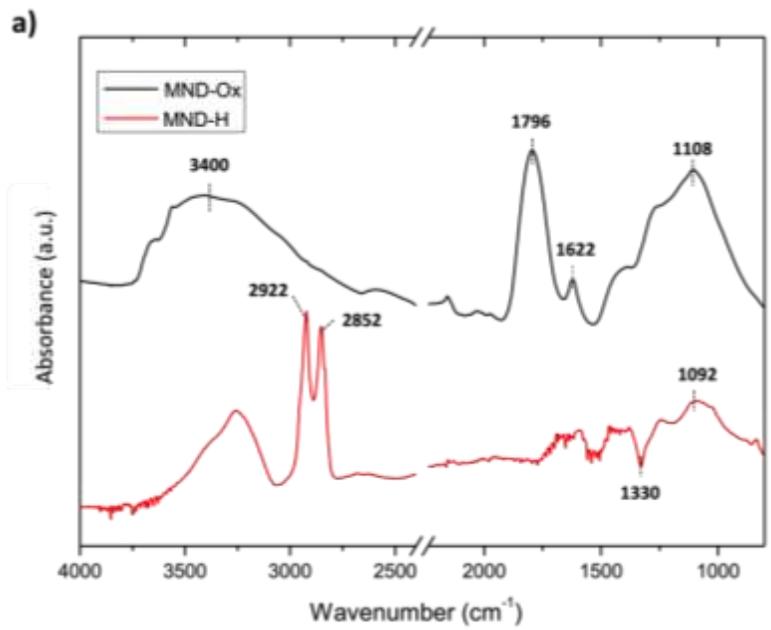


1
 2 **Figure 1: Characterization of untreated MNDs powder. a) XRD diffraction pattern, b) N₂**
 3 **adsorption-desorption isotherm and c) Size distributions of untreated MNDs obtained by**
 4 **analysis of cryo-EM images**

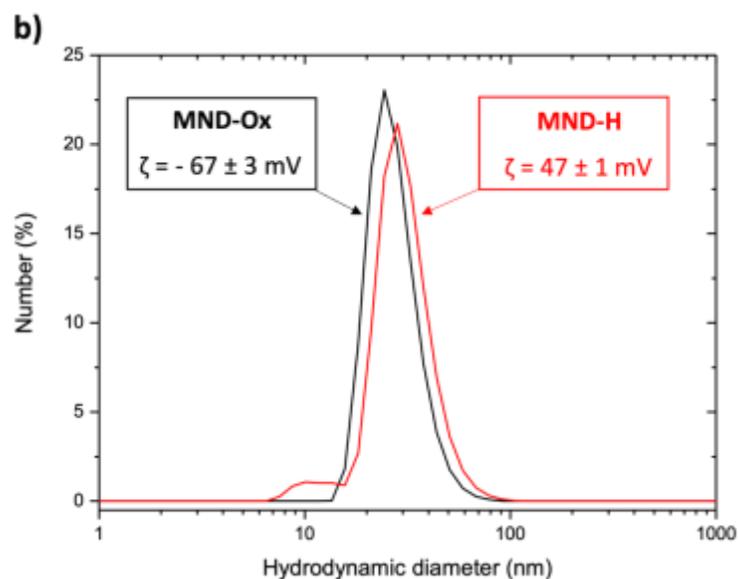
5 The diffraction pattern of as-received MNDs particles revealed the presence of three different
 6 peaks associated with (111), (220) and (311) cubic diamond planes at respectively $2\Theta = 44^\circ$, 75.4°
 7 and 91.6° . The analysis of the (111) diffraction peak (FWHM) allowed the determination of the
 8 average size of the crystalline core, which was *ca.* 12 nm. No signal was detected at $2\Theta \approx 25^\circ$
 9 corresponding to (002) graphite planes, confirming that these particles have a negligible content
 10 of sp²-organized carbon at their surface²⁰. Figure 1b depicts the N₂ adsorption-desorption isotherm
 11 of untreated MNDs. A type IV hysteresis isotherm can be observed, corresponding to mesoporous
 12 materials²¹ with pores of 2-50 nm³. B.E.T. calculations allowed the determination of an average
 13 specific surface area of 170 m².g⁻¹ which supports other values from the literature²². Considering
 14 a spherical geometry for MNDs, the corresponding diameter would be *ca.* 10 nm which is in close
 15 agreement with XRD results. In addition, the diameter distribution was also evaluated by cryo-
 16 electronic microscopy. According to manual measurements on 300 particles, the mean diameter
 17 was 19 ± 10 nm, and the median was 17 nm. This size is slightly higher than the one estimated by

1 XRD and N₂ adsorption, but since the observations used for this distribution were made without
2 high resolution, the smallest particles may not be detected, leading to an overestimation of the
3 mean diameter.

4 A post-treatment is necessary for the homogenization of the MNDs' surface chemistry. Oxidation
5 and subsequent hydrogenation treatments were performed on MNDs by annealing under air and
6 H₂, leading to MND-Ox and MND-H, respectively. A temperature of 750°C was chosen for
7 thermal hydrogenation to ensure an optimized reduction of oxidized functions¹⁵. These thermal
8 treatments did not significantly affect the specific surface area of the powders as verified with N₂
9 adsorption experiments (Figure S3). Annealed powders were then dispersed in ultrapure water by
10 sonication and centrifugation steps. MND-Ox and MND-H suspensions were characterized by
11 FTIR, DLS, zetametry (Figure 2) and XPS (Table 1).



12



1
 2 **Figure 2 : Characterization of MND-H and MND-Ox suspensions in water. a) FTIR**
 3 **spectra obtained on dried suspensions, b) Hydrodynamic diameter distribution (in number)**
 4 **obtained from DLS analysis for MNDs particles. Associated zeta potentials are presented in**
 5 **each insert.**

6 Fourier Transform Infrared (FTIR) spectroscopy is a reference method for the characterization of
 7 NDs' surface chemistry²³. The spectrum of MND-Ox presents a prominent band at 1796 cm^{-1}
 8 corresponding to C=O stretching vibrations of carboxylic acids and anhydrides. The broad band
 9 from 1000 to 1250 cm^{-1} with a maximum at 1108 cm^{-1} corresponds to C-O stretching involved in
 10 hydroxyl and ether groups and confirms that MND-Ox present an oxidized surface chemistry. For
 11 MND-H, the effective hydrogenation can be assessed by the presence of C-H stretching bands at
 12 2922 and 2852 cm^{-1} , associated with hydrogen terminations on (100) and (110) facets²⁴. A shoulder
 13 is also noticeable at 2830 cm^{-1} corresponding to (111) facets. Only for MND-H, a dip in the
 14 absorbance is visible at 1330 cm^{-1} . This particularity is the focus of recent studies, attributing this
 15 phenomenon to a surface conductivity of MND-H in water^{15,25-27}. Note that for both MND-H and
 16 MND-Ox samples, bands located at *ca.* 3300 cm^{-1} and 1620 cm^{-1} associated respectively to O-H

1 stretching and bending modes may be partially or totally related to the presence of water molecules
 2 since infrared measurements were performed under air at ambient temperature.

3 To obtain information on the colloidal behavior and stability of these suspensions, DLS and ZP
 4 measurements were realized (Figure 2b). For MNDs particles, the average hydrodynamic diameter
 5 was around 30 nm whatever the surface chemistry. Meanwhile, their zeta potentials were good
 6 indicators of the success of the different treatments, with opposite charges detected, ranging from
 7 – 67 mV for MND-Ox to + 47 mV for MND-H, in agreement with the literature²⁸.

8 We then evaluated the impact of annealings on the atomic composition and carbon binding states
 9 through XPS analysis of MNDs suspensions (Table 1).

<i>Atomic %</i>	MND-Ox	MND-H
Carbon	91.5	98.5
Oxygen	8.5	1.5
Nitrogen	ND	ND

<i>% of the C_{1s} area</i>		
sp³-C	61	82.5
sp²-C	7	3
Defects	17.5	8
C-O-C	7.5	5
C=O	7	1.5

10

11 **Table 1 : Atomic percentages of carbon, oxygen and nitrogen in MND-Ox and MND-H and**
 12 **results of the C_{1s} core fit of each sample. ND = Not Detected. Estimated error on values is *ca.***
 13 **2.5%.**

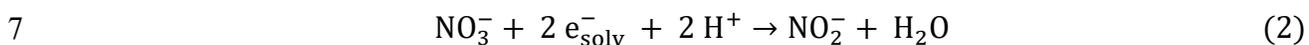
1 For each sample, carbon is, as expected, the predominant component of MNDs with atomic
2 percentages higher than 91 %, followed by oxygen. MND-Ox particles have the highest oxygen
3 atomic percentage (8.5 %) corroborating the oxidized functions detected by infrared analysis. This
4 percentage drops to 1.5 % when these particles are hydrogenated. It is noticeable that nitrogen is
5 below the XPS detection limit (< 0.5 at %²⁹) which is usually not the case for DNDs due to their
6 synthesis precursors³⁰.

7 To investigate the types of carbon bonding present in these MNDs, deconvolution of the C_{1s} core
8 levels of each spectrum was realized using previously described methodology¹⁵ (Figure S2). For
9 both samples, the vast majority of carbon atoms are of sp³ configuration, which reflects the high
10 quality of the crystalline diamond core in HPHT synthesized diamond. This percentage is slightly
11 higher for MND-H than for MND-Ox. The contribution of sp²-carbon was estimated at 7 % of the
12 C_{1s} area for MND-Ox particles, and drops to 3 % after hydrogenation, suggesting an etching of
13 sp²-C by the H₂ treatment. “Defects” in Table 1 refers to carbon atoms not directly bonded to
14 oxygen, including sp³-C close to structural defects. For MNDs particles, the content of defects is
15 quite low, 17.5 % for MND-Ox and 8 % for MND-H, which is in line with the long-range order
16 of sp³ carbon in diamond crystalline lattice. Finally, at the highest binding energies of the C_{1s} core,
17 carbon linked to oxygen atoms can be found, simply (C-O-C) and doubly linked (C=O). These
18 percentages are higher for oxidized MNDs than for hydrogenated ones, as expected. This XPS
19 analysis confirms the preservation of sp³-C and the modification of the atomic composition of
20 MND-H and MND-Ox after surface treatments.

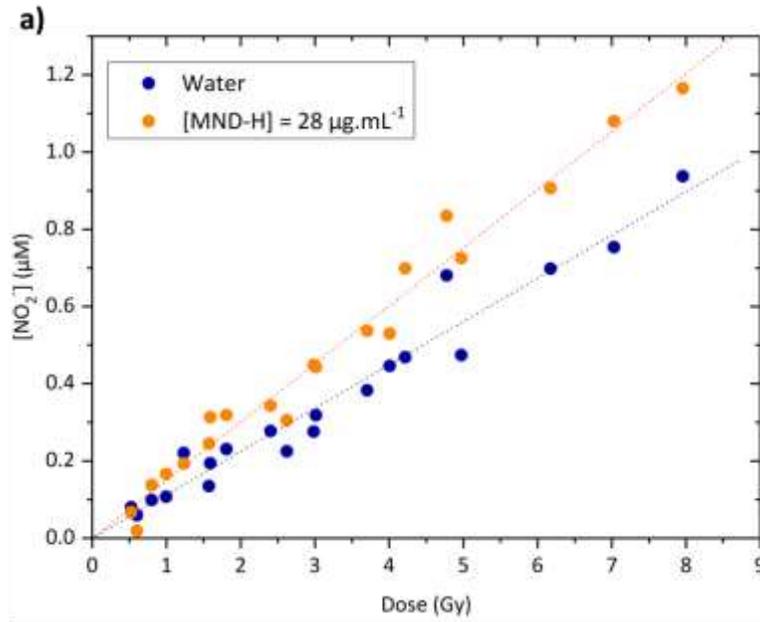
21 According to these complementary techniques, not only the effective oxidation and hydrogenation
22 of MNDs were confirmed, but also the colloidal stability of each suspension, making them suitable
23 for further irradiation experiments.

1 *Quantification of solvated electrons*

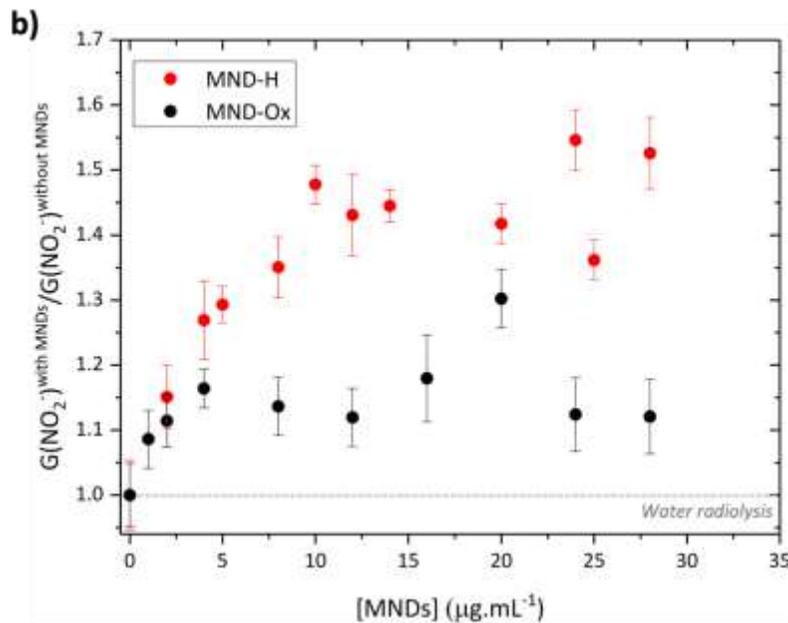
2 Our concern in this study was to evaluate the impact of MNDs on the formation of solvated
3 electrons and hydroxyl radicals during γ -radiolysis. As these radical species have very short
4 lifetimes, probes were needed for their quantification. For e^-_{solv} quantification, the indirect
5 detection we implemented was based on the reduction of nitrate ions by solvated electrons, leading
6 to the formation of nitrite ions^{31,32} (Eq. 2).



8 The first step of this reaction is the monoelectronic reduction of NO_3^- into $\text{NO}_3^{\bullet 2-}$ that occurs with
9 a rate constant³³ of $9.7 \times 10^9 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$. Therefore, a 2 mM initial concentration of nitrate ions
10 corresponds to a reaction time with solvated electrons of *ca.* 52 ns. The diazotation reaction
11 between nitrite ions and 2,3-diaminonaphthalene (2,3-DAN) produces 2,3-naphtotriazole (2,3-
12 NAT), whose fluorescence signal is linear over a large range of nitrite concentrations, allowing
13 the indirect quantification of electrons over a large dose range. The protocol was adapted and
14 optimized from previous works³⁴⁻³⁶, resulting in a simple process, compatible with samples
15 containing nanoparticles³⁷. The slope of the fit always presented a linear evolution, as can be seen
16 in Figure 3a, and represents the formation yield of NO_2^- , or G-value, usually expressed in $\text{mol}\cdot\text{J}^{-1}$.
17 We plotted in Figure 3b the ratio of the G-values for nitrite ions with and without MND-H and
18 MND-Ox, allowing an easier comparison with water radiolysis.



1



2

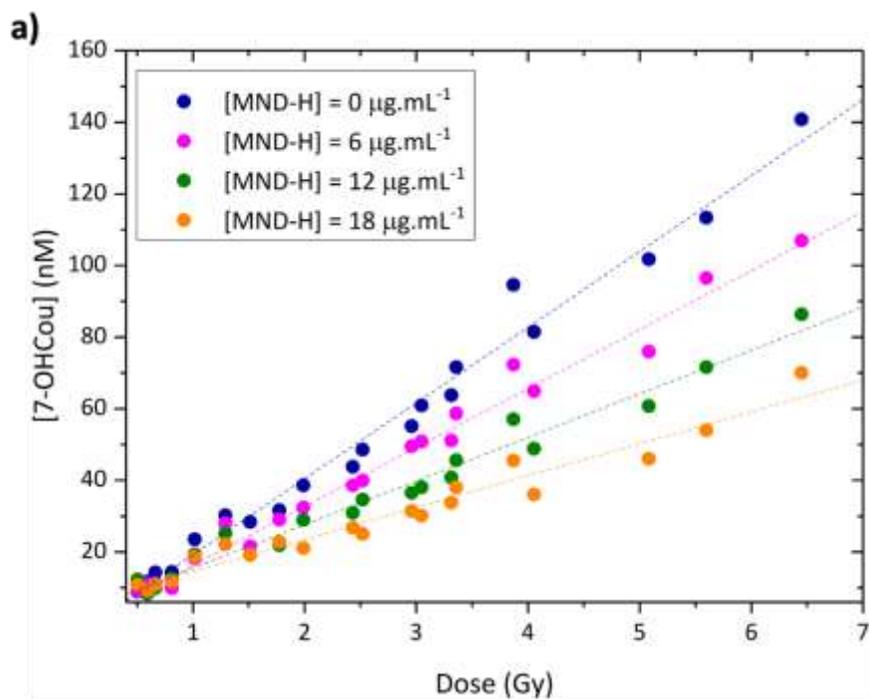
3 **Figure 3: a) Evolution of NO_2^- concentration as a function of the dose for water and MND-**
 4 **H (28 $\mu\text{g}/\text{mL}$). b) Ratio of the formation yields of nitrite ions in solution under irradiation as**
 5 **a function of MNDs concentration for both surface chemistries. The dotted line represents**
 6 **the values when only water is irradiated.**

1 The apparent formation yield of nitrite ions increases with MND-H concentration till
2 approximately $10 \mu\text{g.mL}^{-1}$ where a plateau begins, attributed to competition reactions. Such a trend
3 was already observed for DND-H particles¹⁴. This progression is linear for the lowest
4 concentrations, with a 30% increase in nitrite ions for $5 \mu\text{g.mL}^{-1}$, reflecting a corresponding
5 increase in solvated electrons production. To our best knowledge, this is the first experimental
6 evidence of an increase in solvated electrons, available for subsequent reductions, when
7 hydrogenated MNDs aqueous suspensions are irradiated by high-energy photons. For MND-Ox, a
8 moderate increase of $G(\text{NO}_2^-)$ was also observed. For concentrations below $5 \mu\text{g.mL}^{-1}$, the ratio
9 rises quite similarly as with MND-H but it reaches its limit at *ca.* 15 % of the value for water within
10 the explored concentration range ($4\text{-}30 \mu\text{g.mL}^{-1}$ max).

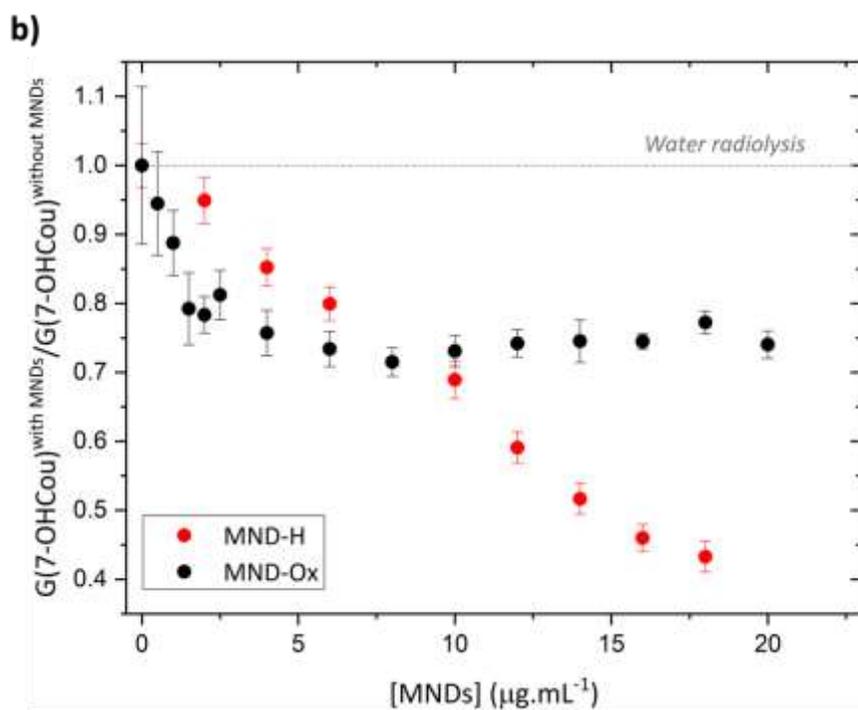
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12 ***Quantification of hydroxyl radicals***

13 To study the reactivity of MND particles towards hydroxyl radicals, the coumarin probe was used.
14 It reacts with HO^\bullet with a constant rate³⁸ of $1.05 \times 10^{10} \text{ L.mol}^{-1}.\text{s}^{-1}$ to give several hydroxylation
15 products, among which 7-hydroxycoumarin (7-OHCou) is fluorescent. Before deploying this
16 protocol, a preliminary experiment consisting in checking if the particles modify the
17 regioselectivity of coumarin hydroxylation was required³⁹. Figure S4 presents HPLC separation of
18 the oxidation products in irradiated samples containing coumarin only, or in the presence of MND-
19 H or MND-Ox for similar doses. The HPLC profiles are very similar as the same
20 hydroxycoumarins are detected in all three conditions with the same relative proportions, meaning
21 that regioselectivity is not impacted significantly by the presence of MNDs. 7-OHCou is thus
22 representative of all hydroxylation reactions, and so of hydroxyl radicals. Concentrations and G-
23 values of 7-OHCou were then quantified from fluorescence measurements after irradiation.



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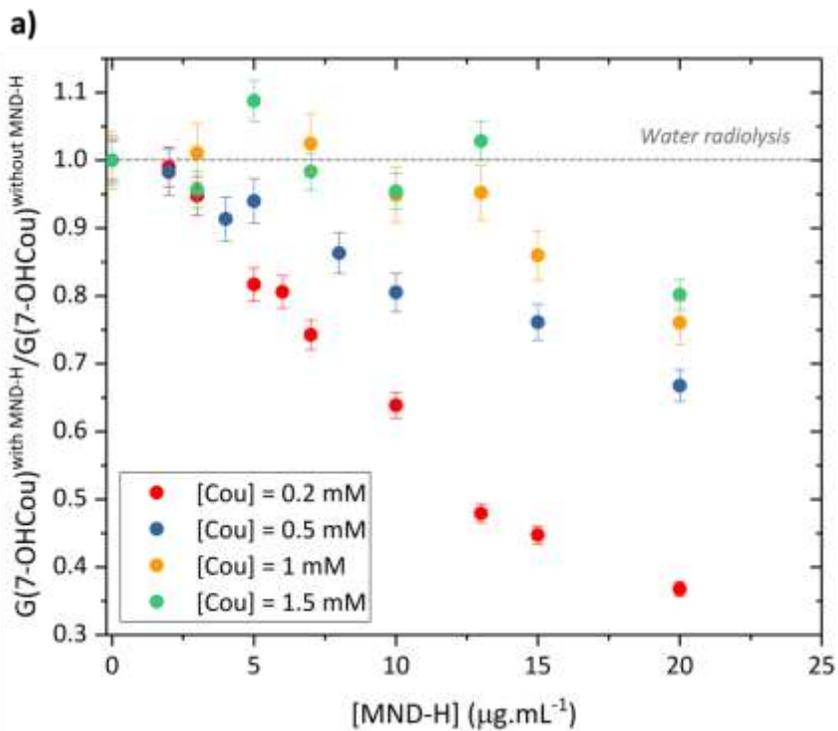


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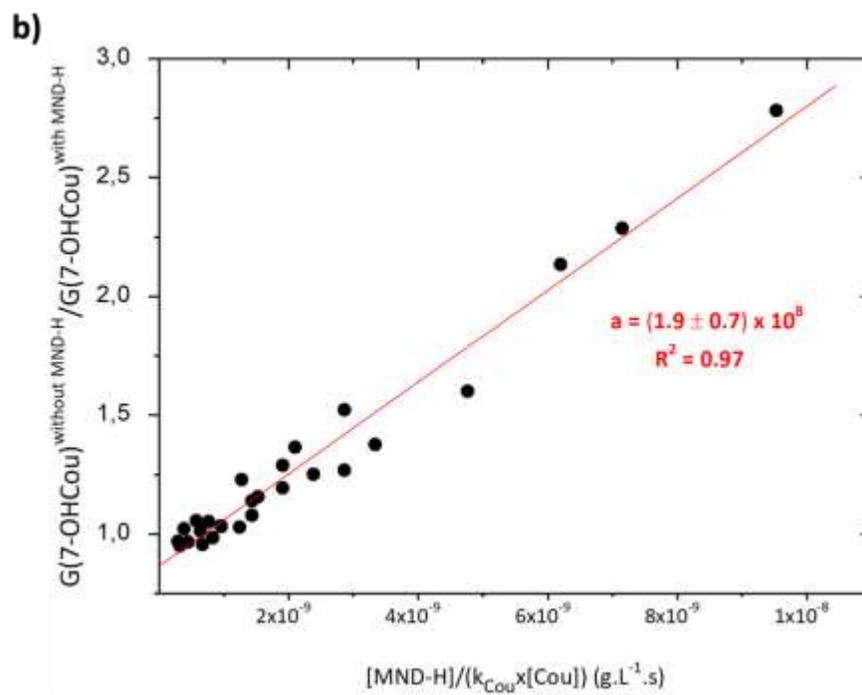
Figure 4 : a) Evolution of 7-OHCou concentration as a function of the dose for several MND-H concentrations. b) Evolution of the apparent formation yields of 7-OHCou in presence of MND-H and MND-Ox compared to water alone. Initial coumarin concentration: 0.5 mM

1 Figure 4a presents the evolution of the concentration of 7-OHCou as a function of the dose for
2 different MND-H concentrations. For each condition, the concentration of 7-OHCou increases
3 linearly with the dose, but when calculating the 7-hydroxycoumarin formation yield a decrease is
4 obtained with increasing MND-H concentration. This means that fewer HO• radicals are scavenged
5 by coumarin in solution in the presence of nanoparticles than for water alone. While a 7-OHCou
6 apparent formation yield of 21 nmol.J⁻¹ was found without MNDs, this value went down whatever
7 the concentration of MND-H particles. In Figure 4b, the ratio of G-values of 7-OHCou with or
8 without MNDs is plotted. For MND-H, the decrease seems linear with the massic concentration
9 of particles whereas MND-Ox particles present a different evolution of the formation yield of 7-
10 OHCou. Up to 2.5 µg.mL⁻¹, a decrease of the G(7-OHCou) is observed, which is more pronounced
11 than for MND-H. Then, it remains unchanged till the highest tested concentration of 20 µg.mL⁻¹.

12 Possible kinetic competitions are thus to be considered. That is why we performed similar
13 irradiation experiments, using another MND-H aqueous suspension, varying coumarin
14 concentration between 0.2 and 1.5 mM. Indeed, given the rate constant of the reaction between
15 coumarin and hydroxyl radicals³⁸ ($k = 1.05 \times 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$), a 0.2 mM coumarin solution reacts with
16 HO• in *ca.* 480 ns after the initial transfer of energy to water compared to *ca.* 60 ns for a 1.5 mM
17 coumarin solution. Under continuous irradiation, the system can be considered in steady-state as
18 regards HO•, therefore increasing coumarin concentration increases the fraction of HO• reacting
19 with it. The results of this competition for MND-H are presented in Figure 5.



1
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4



5

1 **Figure 5: a) Evolution of the formation yield of 7-OH coumarin with MND-H**
2 **concentration for different initial coumarin concentrations, b) Determination of the**
3 **apparent rate constant of HO• radicals with MND-H.**

4
5 Comparing the results for 0.2 and 0.5 mM concentrations, higher coumarin concentration results
6 in a higher G-value of 7-OHCou. For 1 and 1.5 mM, a G-value equivalent to the one of water
7 radiolysis is measured for MND-H concentrations up to 7 µg.mL⁻¹. For higher concentrations,
8 scavenging by MNDs is again visible. This evidences a competition between coumarin and MND-
9 H for scavenging hydroxyl radicals. It is important to note that even at the higher coumarin
10 concentrations, the G-values are equal to or smaller than the G-value of pure water solution,
11 revealing the absence of supplementary HO• when MND-H are irradiated. Also, these experiments
12 allowed us to extract the rate constant for the reaction between MND-H and HO• (k_{MND-H}) using
13 Eq. 3 adapted from previous studies^{40,41}:

14
$$\frac{G(7-OHCou)^{without\ MND-H}}{G(7-OHCou)^{with\ MND-H}} = 1 + k_{MND-H} \times \frac{[MND-H]}{k_{cou} \times [Cou]} \quad (3)$$

15 The fit of the plot presented in Figure 5b gives us an estimate k_{MND-H} of $1.9 \pm 0.7 \cdot 10^8$ L.g⁻¹.s⁻¹.

16
17 As HO• is known to react with any molecule due to its high redox potential, this scavenging could
18 be caused by the presence of any contaminant in or at the surface of MND-H samples, reacting
19 more rapidly with HO• than coumarin. To assess this hypothesis, NaCl salt was added to MNDs
20 samples to increase ionic strength, resulting in MND-H precipitation and the release of weakly
21 bound species at the particles' surface. The supernatant was then irradiated and results, presented
22 in Figure 6, showed an identical G(7-OHCou) for coumarin alone or irradiated with the
23 supernatant. This shows that MND-H particles by themselves present scavenging properties
24 towards HO•.

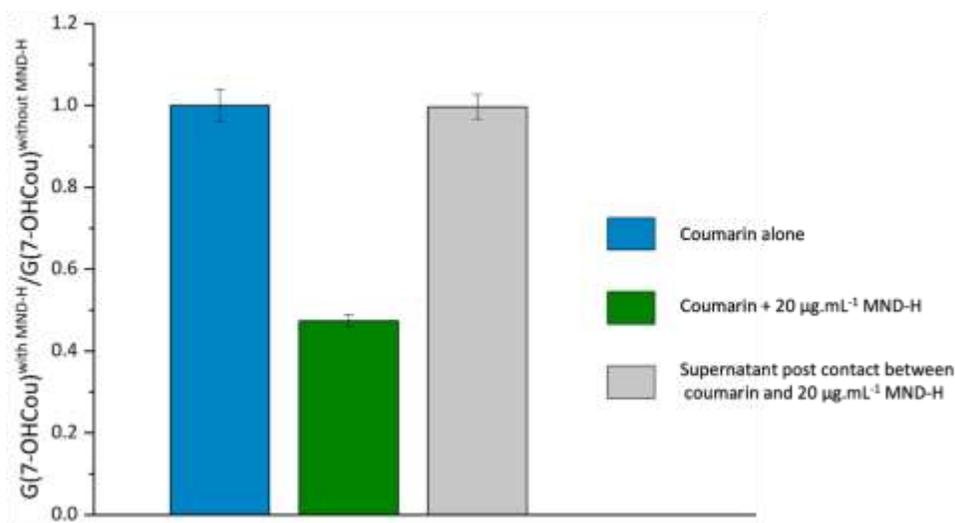
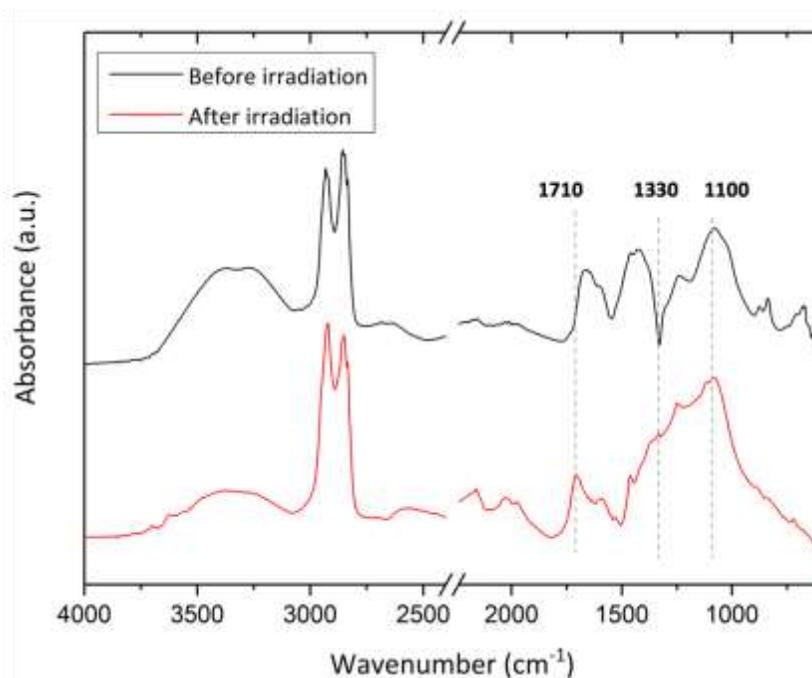


Figure 6 : Comparison of the yield of 7-OHCou production for coumarin (0.5 mM) irradiated in water, in the presence of 20 µg.mL⁻¹ MND-H and with MND-H supernatant.

The supernatant was obtained after incubation with 1% (w/v) final NaCl and centrifugation.

To detect any HO[•]-induced modification of MND-H surface, concentrated suspensions were irradiated at higher dose and analyzed by XPS and FTIR (Figure 7). The dose was chosen to keep the ratio between concentrations of radicals and particles in the same order of magnitude for this experiment and the ones with coumarin. The main observation was that colloidal stability was lost after irradiation, leading to a visible precipitate of MND-H. XPS analysis revealed that the oxygen atomic percentage went from 1.5 to 2.5 at % after irradiation.



1
 2 **Figure 7 : FTIR spectra of MND-H suspensions before (top, black) and after (bottom, red)**
 3 **irradiation. A concentrated suspension of MND-H (5.6 mg.mL^{-1}) was irradiated at 1200 Gy.**

4
 5 As can be seen in Figure 7, irradiation also induces modifications in the MND-H infrared spectra.
 6 Signatures of C-H bonds are still present but a new band is visible at 1710 cm^{-1} , usually associated
 7 with C=O bonds of ketones and aldehydes. Also, the C-O stretching modes at $1100\text{-}1200 \text{ cm}^{-1}$
 8 seem more prominent. These analyses confirm that the irradiation induced an oxidation of MND-
 9 H surface. Besides, one can notice that the dip in the absorbance at 1330 cm^{-1} is lost after
 10 irradiation. It is in agreement with previous observations where this optical phenomenon is only
 11 present for MND-H stable in suspension¹⁵.

12
 13 **Discussion**

14 Recently, optimal hydrogenation conditions to obtain stable suspensions of MND-H in water over
 15 months were reported^{15,42}, which opens the way for new investigations as presented in this paper.

1 With stable suspensions, we were able to study how MNDs behave under gamma irradiation
2 through the quantification of hydroxyl radicals and solvated electrons available in solution.

3 We focused on MND-H particles as a hydrogenated surface is required for negative electron
4 affinity (NEA), enabling a facilitated electron emission when electrons are excited into the
5 conduction band⁴³. A set of complementary techniques documented that H₂-annealing led to the
6 reduction of oxygenated functions, etching of non-diamond phase, and creation of C-H bonds on
7 the different facets. Submitted to high-energy photons, MND-H increased the available quantity
8 of solvated electrons but not of hydroxyl radicals. On the opposite, they scavenged hydroxyl
9 radicals very efficiently. These results could be compared with previous studies realized with
10 DNDs¹⁴. Under gamma irradiation, colloids of hydrogenated DNDs exhibit an equal
11 overproduction of hydroxyl radicals and solvated electrons while in the case of MNDs, for similar
12 coumarin concentrations, no overproduction of HO• radicals was detected. We previously
13 proposed, as for other nanomaterials⁴⁴, that interfacial water could play an essential role in radicals'
14 production in solution when DND-H were irradiated¹⁴. This hypothesis is supported by
15 experimental data revealing different structures of water molecules surrounding detonation
16 nanodiamonds when the surface chemistry is varied⁴⁵ and simulation results on gold
17 nanoparticles⁴⁶. The possible weakening of O-H bonds in water molecules near the DND-H surface
18 could locally amplify water radiolysis, leading to hydroxyl radicals and solvated electrons in the
19 same proportions. Obviously, mechanisms for milled nanodiamonds are different as only electrons
20 seem to be overproduced.

21 As solvated electrons are among the most reductive species in aqueous environment, they arouse
22 lively interest. In previous studies, we used to quantify solvated electrons available in solution
23 under deaerated atmosphere, a method based on the transformation of electrons into hydroxyl
24 radicals by N₂O, and subsequent detection by coumarin³⁹. In this work, samples were irradiated

1 under air, and electrons were quantified based on the reduction of nitrate into nitrite ions, detected
2 by 2,3-DAN. On the one hand, this protocol presents the main advantage that samples do not need
3 to be degassed before irradiation; on the other hand, as a preliminary step, colloidal stability must
4 be studied as a function of nitrate ions concentration to determine working concentration. 2 mM
5 was chosen as it preserves colloidal suspensions and allows to capture electrons twice more rapidly
6 than dissolved dioxygen. Indeed, electron scavenging is favored by higher nitrate concentration
7 but as ionic strength increases, it can cause flocculation and sedimentation of particles. For a
8 concentration as low as 20 $\mu\text{g}\cdot\text{mL}^{-1}$, MND-H led to 45 % supplementary electrons in solution
9 compared to water, while DND-H at the same massic concentration led to 50%, which is of the
10 same order of magnitude. Saoudi *et al.* proposed that such MND-H must behave like bulk diamond
11 as they observed the shift of their valence and conductive bands¹⁵. Their NEA would facilitate
12 electron transfer from the particle onto the solution if their electrons are excited with energies
13 higher than 5.5 eV, which is the bandgap of diamond. In our case, MeV photons, as well as
14 Cerenkov light, have enough energy to trigger this phenomenon. Regarding the absence of
15 coumarin hydroxylation, either these emitted electrons are not energetic enough to cause secondary
16 radiolysis, or secondary radiolysis occurs very locally at the surface of MND, the resulting HO \bullet
17 being then scavenged by the diamond surface. As demonstrated by numerous complementary
18 characterizations, MNDs are different from DNDs in many points such as crystalline quality, large
19 crystallographic facets, polydispersity or surface chemistry and they present different behaviors
20 under irradiation. Further investigations are needed to assign to these different features a role, if
21 any, in the mechanisms of radical production.

22 Another striking fact for MND-H suspensions is the loss of colloidal stability following
23 irradiation. FTIR spectra and XPS analysis confirmed the oxidation of the irradiated MND-H as
24 well as the induced loss of the surface conductivity, the latter being probed by the dip of absorbance

1 which is peculiar to stable colloids. Co-existence of C-H terminations, that confer positive zeta
2 potential, with irradiation-induced oxygenated groups could result in a modified zeta potential,
3 and eventually flocculation of the samples. This is also in agreement with the study from Zhang
4 and Hamers who demonstrated that H-terminated MNDs, in the absence of an electron donor, show
5 clear signs of oxidation and aggregation under illumination¹². So destabilization seems also to
6 occur for hydrogenated particles of high crystallinity of smaller sizes.

7 Surprisingly, MND-H do not present any overproduction of hydroxyl radicals as DND-H did,
8 but scavenging properties. The main reactions of hydroxyl radicals are additions and hydrogen
9 abstraction^{47,48}. Given the C-H bonds at the MND-H surface, hydroxyl radicals can abstract some
10 surface hydrogen atoms, to form water molecules, generating carbon-centered radicals. The latter
11 can react with dissolved oxygen or water molecules to form oxidized functions, which is supported
12 by the infrared and XPS analyses after irradiation. HO[•] can also add on remaining C=C bonds
13 though sp²-C content on MND-H is only 2 % of the whole carbon content. Varying coumarin
14 concentration, we obtained an estimated rate constant of MND-H with hydroxyl radicals of $k_{\text{MND-H}} = 1.9 \pm 0.7 \times 10^8 \text{ L.g}^{-1}.\text{s}^{-1}$. Because of the polydispersity of MNDs, it is unreliable to convert
15 massic into molar concentrations to obtain a value comparable to those available for other
16 antioxidant species. Nevertheless, Que *et al.* recently applied the same methodology to investigate
17 the antioxidant properties of MXenes, which are nanosheets containing carbon and nitrogen atoms
18 as well as early transition metals⁴⁹. They found a rate constant of $1.58 \times 10^8 \text{ L.g}^{-1}.\text{s}^{-1}$ which means
19 that both material rate constants are in the same order of magnitude. It is also possible to convert
20 the mass concentration into the solid surface area to solution volume ratio as in Li *et al.*⁴¹, which
21 gives $k_{\text{MND-H}} = 1120 \pm 400 \text{ m.s}^{-1}$, a 50-fold higher value than the one reported for carbon black.
22 For MND-Ox, the reactivity is different. As confirmed with HPLC analyses, this behavior is not
23 due to different coumarin hydroxylation patterns. It can be noticed that these oxidized particles
24

1 present three times more sp^2 -carbon than MND-H, according to the XPS analysis. Some rare
2 hydrogen terminations might also subsist at MND-Ox surface, even if not visible by FTIR. But
3 overall there are fewer attack sites on MND-Ox than MND-H, which could explain why they are
4 less efficient to scavenge HO^\bullet (for concentrations above $10 \mu\text{g.mL}^{-1}$).

5 Also, a limited enhancement of the available quantity of solvated electrons is noticed for MND-
6 Ox. This differs from what was observed for DND-Ox for which we previously reported no
7 overproduction of solvated electrons¹⁴. Recent literature reports also this observation for UV
8 illumination of HPHT synthesized NDs with an oxidized chemistry¹³. As mentioned before, while
9 hydrogenated surface chemistry would induce an overproduction of electrons, photons from
10 gamma irradiation have enough energy to trigger the emission from an oxidized surface. Given
11 these observations, the question of using MNDs as antioxidants and electron emitters is open.
12 Since the scavenging of hydroxyl radicals leads to an oxidation of the MNDs surface, a decrease
13 in the scavenging and overproducing efficiencies might happen. Given the strong interest in
14 photocatalysis perspectives of HPHT synthesized nanodiamonds, a main challenge could be then
15 to prevent MNDs surface oxidation while maintaining electron emission. The addition of
16 sacrificial donors, as it was proposed elsewhere¹², could be a wise approach.

17 **Conclusion**

18 The radical species reactivities towards nanodiamonds are crucial for considering applications in
19 radiomedicine or (photo)catalysis. In the present study, we brought new insights on milled
20 nanodiamonds (MNDs) behavior under irradiation by revealing opposite reactivities of MNDs
21 towards hydroxyl radicals and solvated electrons. Using nanoparticle-compatible and optimized
22 methods, we put into light that the irradiation of MNDs aqueous suspensions with MeV photons
23 leads to an overproduction of solvated electrons, more pronounced for hydrogenated than oxidized

1 MNDs. In contrast, for the first time, we evidenced a HO• scavenging behavior of MNDs whose
2 intensity is also surface chemistry dependent. Our results suggest that MND particles, especially
3 hydrogenated, can be considered either as photocatalysts or as antioxidant agents.

4 ASSOCIATED CONTENT

5 **Supporting information**

6 Supporting information consists of cryo-EM observation of untreated MNDs, N₂ adsorption
7 isotherm of MND-AsR, MND-Ox and MND-H powders, XPS C_{1s} spectra and deconvolutions of
8 MND-Ox and MND-H, HPLC profiles of irradiated coumarin (0.5 mM) solutions alone and in the
9 presence of 20 µg.mL⁻¹ MND-H or MND-Ox.

10

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4 **Authors Contributions**

5 All authors participated in the investigation, analysis and writing draft.

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