

# Proton Beam Induced Fluorescence in 5 nm Detonation Nanodiamond

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## INTRODUCTION

During the last few decades, nano-scale materials have achieved great success, providing applications in a wide variety of fields. In particular, a strong interest has been focused on the employment of nanoparticles as promising tools in biomedical research, diagnostics and therapy. Among the multitude of novel materials for this kind of applications, diamond nanocrystals (or nanodiamonds) earned a solid reputation and vast interest due to their excellent features, such as inertness, stability, fluorescence, non-toxicity, bio-compatibility and the possibility of modifying their surface termination [1]. Typical nanodiamonds sizes range from ~5 nm to ~250 nm.

Few nanometer (5 – 10 nm) crystals are mainly produced by detonation of carbon-based compounds [2], but the synthesis processes involve, as a side effect, the formation of graphitic and/or amorphous carbon layers on the surface of the nanoparticles. We managed to tune the amount of graphite surrounding the crystals by thermal annealing and/or etching in inert and oxidizing atmosphere, respectively, in order to not affect the optical transparency necessary to take advantage of their luminescence properties. In fact, the diamond lattice can host a large variety of defects that can act as color centres: one of the most appealing is the negatively charged Nitrogen-Vacancy (NV<sup>-</sup>) defect [3], consisting of a substitutional nitrogen atom nearby to a vacancy defect. The system is optically active, with a wide excitation window at 500 – 600 nm and emission spectrum at 600 – 800 nm (main peak at 638 nm).

In this paper we present the development of an effective protocol to induce stable luminescence in detonation nanodiamonds by means of ion implantation and thermal processes, confirmed by optical characterization.

## SAMPLE SURFACE TREATMENTS

The sample under exam is produced by Adamas (NC, USA) and consists of detonation nanodiamonds (DND) synthesized from the carbon contained in high-energy explosives which simultaneously serve as sources of energy and carbon. The characteristic size of primary particles is ~ 5 nm, which can be isolated from large aggregates formed during synthesis and purification. The crystals present single substitutional nitrogen that only

in few percent is involved in the formation of NV centres, due to the low amount of vacancies in the pristine powder: ion-induced damaging represents an effective tool to increase vacancy density and therefore the total amount of luminescent centres upon subsequent thermal annealing.

A first thermal treatment at 800 °C for 8 hours under low vacuum condition (10<sup>-2</sup> mbar) was performed in order to reorganize the surface structure. In an oxygen-free environment, it is anyway necessary to set a temperature below 900 °C to avoid the conversion of the DNDs to carbon onions [4]. The main scope of this treatment consists in the facilitation of the successive surface cleaning step, since the above-mentioned conditions are sufficient to induce only the complete graphitization of the DND amorphous coating.

Thermal oxidation in oxygen environment was then performed at 450 °C for 8 hours at 800 mbar. The process temperature is a crucial parameter to optimize the efficacy of the oxidation allowing a selective removal of graphite, while preserving the nature of the pristine diamond crystal.

Figure 1a shows the modification of the appearance of nanodiamond powders after all the treatments: a pronounced darkening respect to “as-such” DNDs as a consequence of the graphitization is appreciable, while a whitening due to the oxidative surface cleaning is evident. Diffuse Reflectance Infrared Fourier Transformed Spectroscopy (DRIFT), performed at room temperature and environmental humidity, corroborates these assertions as reported in Figure 1b.

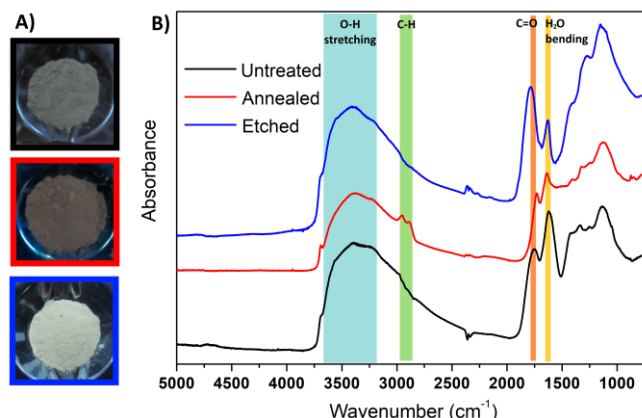


Fig. 1: a) optical images of the processed DND powders b) DRIFT spectra at room temperature performed after all the treatment steps.

The main features of the DRIFT spectrum of untreated sample are represented by:

- 3700-3200  $\text{cm}^{-1}$ , broad absorption associated to O-H stretching modes of hydrogen bonded  $\text{H}_2\text{O}$  molecules due to physisorption of water vapour;
- 1765  $\text{cm}^{-1}$ , due to C=O vibrations of carbonyl and carboxyl groups [5];
- 1630  $\text{cm}^{-1}$ , the water-bending mode.

The spectrum of the annealed DNDs presents a decrease of the C=O groups and a parallel increased number of C-H moieties (2990-2820  $\text{cm}^{-1}$ ) proving the surface graphitization. This result concerns with a lower affinity of the surface towards environmental water, as indicated by the evident decrease in intensity of the water related signals. Finally, the spectrum of etched batch shows both an increase of the C=O moieties and the disappearance of the graphitic features due to the efficacy of the oxidation process.

## ION BEAM IMPLANTATION

Powders were deposited onto silicon substrates as a thin layer by drop-casting (DNDs/ethanol solution). The samples were then implanted at room temperature with a 2 MeV  $\text{H}^+$  ion broad beam at the AN2000 accelerator facility of the INFN Legnaro National Laboratories (INFN-LNL). An implantation fluence of  $10^{16} \text{ cm}^{-2}$  was achieved. The penetration depth of 2 MeV proton is sufficient to pass through all the thin ( $\sim 20 \mu\text{m}$ ) deposition, guaranteeing a nearly-uniform vacancy creation over the totality of the nanoparticles. After ion implantation, thermal treatment at 800 °C for 8 h in low vacuum environment ( $10^{-2}$  mbar) was performed to further promote the coupling of nitrogen and vacancy sites into NV centres. The definition of the annealing parameters in this phase is crucial since it determines radical structural modifications: vacuum environment avoid carbon oxidation and, moreover, promote the reduction of the surface carbonyl and carboxyl termination, maintaining an optimal transparency of the nanocrystals, essential for luminescence evaluation.

## OPTICAL CHARACTERIZATION

Raman and Photoluminescence (PL) spectra were acquired with a Raman micro-spectrometer. The optical excitation was provided by a continuous 532 nm laser focused with a 100 $\times$  air objective. The excitation radiation was filtered out from the CCD detection system by a narrow-band notch filter. Laser power intensity was setted at 1.21 mW avoiding powder puffing. The employed magnification allowed to probe the entire volume of thin DND deposition, since the laser spot is  $\sim 2 \mu\text{m}$  both in diameter and in focal depth.

Figure 2 shows the spectra collected after the above described procedures. The untreated material presents the characteristic D ( $\sim 1345 \text{ cm}^{-1}$ ) and G ( $\sim 1580 \text{ cm}^{-1}$ ) Raman

bands associated to amorphous and graphitic carbon respectively. No evidence of the Raman diamond peak or colour centres luminescence are appreciable at this stage.

The Raman and PL spectra of the intermediate batches, after oxidation and proton implantation, do not report any significant feature.

The efficacy of the overall treatments is finally confirmed by the rising of the Raman peak of diamond ( $1332 \text{ cm}^{-1}$ ) and by the characteristic Nitrogen-Vacancy emissions. NV colour centre presents two charge states associated to two different emission features, neutral state  $\text{NV}^0$  (575 nm) and negatively charged state  $\text{NV}^-$  (638 nm), as clearly highlighted in Figure 2. As widely observed, the zero phonon line of the  $\text{NV}^-$  is associated with a broad phonon sideband in the 650-750 nm spectral range.

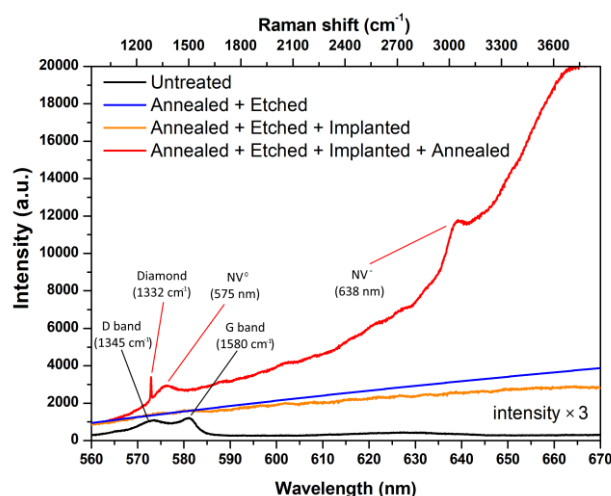


Fig. 2: Raman/photoluminescence spectra collected at 1.21 mW laser excitation power from processed DNDs. Significant features are highlighted and labelled (note: the curves are vertically displaced for sake of readability).

## CONCLUSIONS

In the present paper the procedure for the realization of fluorescent detonation nanodiamond with 5 nm mean size was presented. The DNDs were extensively characterized by means of DRIFT and Raman/PL after each treatment, monitoring the surface chemistry of the nanocrystals. These results represent an effective alternative to common strategies based on milling of micrometric diamond [6] offering stable and bright optically active nanoparticles employable as nanosensors in biophysics or single photon emitters in quantum photonics.

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