

# Efficient production of NV colour centres in nanodiamonds using high-energy electron irradiation

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(Dated: September 13, 2009)

Nanodiamond powders with an average size of 50 nm have been irradiated using high-energy electron beam. After annealing and chemical treatment, nanodiamond colloidal solutions were obtained and deposited on silica coverslips by spin-coating. The fluorescence of nanodiamond films was studied by confocal microscopy together with atomic force microscopy. We evaluated the proportion of luminescent nanodiamonds as a function of the irradiation duration and showed that large quantities, exceeding hundreds of mg, of luminescent nanodiamonds can be produced with than one hour of electron irradiation.

PACS numbers:

## INTRODUCTION

In diamond the association of a vacancy with a nitrogen impurity leads to the formation of a luminescent defect, called the NV colour centre [1] and being either neutral ( $NV^0$ ) or negatively charged ( $NV^-$ ). Both of these centres are photostable and can be detected at the individual level using confocal optical microscopy [2–4]. The unique properties of the NV-centres leads to various applications. They have indeed demonstrated their great potential as a reliable single-photon source [5] for quantum optics [6] and for spin-based quantum information processing [7]. When produced in nanodiamonds, they can be used as fluorescent markers for biological applications [8, 9].

Using a top-down approach, the size of diamond particles has been reduced and particles of a few nanometers can be reliably obtained [10]. Though the procedure to produce small and monodisperse diamond particles is now well established, the creation of NV-centres of a given type, either negatively charged or neutral, in nanometer-size diamond particles remains challenging. Recently, Chang *et al.* [11] reported a route to reach mass-production of luminescent nanodiamonds using  $He^+$ -ion irradiation. Parallel to this work, we report on a method which allows us to produce large quantities (few hundreds of mg) of luminescent nanodiamonds using high-energy electron irradiation.

## EXPERIMENTAL SECTION

High-pressure high-temperature (HPHT) commercial diamond nanocrystalline powder (Van Moppes, SYP 0-0.05) was used for this work. Approximately 500 mg

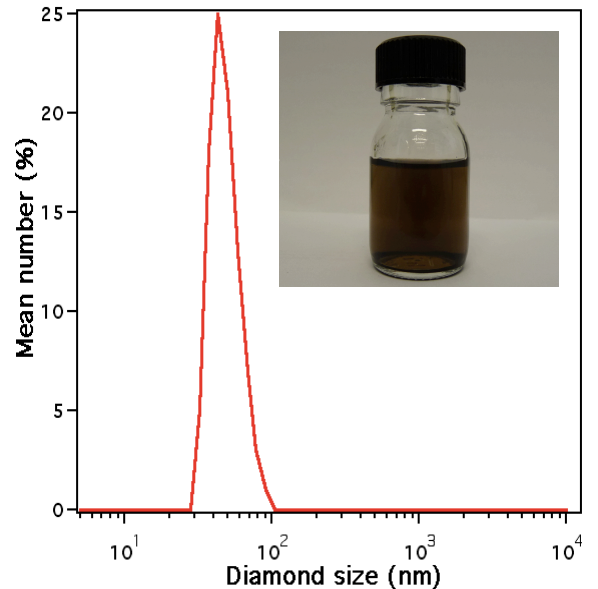


Figure 1: Particle size measurement by DLS for the colloidal solution shown in insert, and corresponding to the SYP 0-0.05 nanodiamond powder after irradiation, annealing and dispersion in an aqueous solution.

of this powder was placed in a glass bottle and irradiated with a 13.9-MeV electron beam (Saphir facility, CEA/Saclay) for various periods of time, corresponding to an irradiation duration  $\Delta t$  varied from 2 to 60 minutes. The irradiated nanodiamond powders were then annealed for 2 hours at 800°C, under vacuum. The annealed powders were treated by a mixture of  $H_2O_2:H_2SO_4$  (1:3 vol) for 15 minutes. After several washing with ultra-pure water using centrifugation, aqueous colloidal solutions of dispersed nanodiamonds were obtained. A few drops of ammoniac were added to the solutions to keep them sta-

ble for several weeks (see insert in Figure 1). The colloidal solutions were characterized in particle size by Dynamic Light Scattering (DLS). After irradiation and annealing, the average size of the nanodiamonds was found to be 45 nm (Figure 1). This value is similar to the specified size of the commercial powder, which proves that the after-annealing chemical process is efficient to remove the aggregates between the processed nanoparticles.

The nanodiamonds were deposited on the surface of silica coverslips following two different methods:

1. The first method consists in directly spin-coating the nanodiamonds on cover slips which were preliminary washed in a  $\text{H}_2\text{O}_2:\text{H}_2\text{SO}_4$  (1:3 vol) cleaning bath. The surface density of nanodiamonds depends on their initial concentration in the colloidal solution.
2. The second method requires the use of a cationic polymer (poly diallylmethyl-ammonium chloride). The coverslips are first washed in a  $\text{H}_2\text{O}_2:\text{H}_2\text{SO}_4$  (1:3 vol) cleaning bath, then dipped in the cationic polymer solution for 10 minutes. Then, the coverslips are washed and dipped in the nanodiamond solution between 1 and 10 minutes. Depending on the dipping duration, the surface density of deposited nanodiamonds varies.

The films were characterized using a Scanning Electron Microscope ( $V=5$  keV,  $5 \mu\text{A}$ ) and were imaged using a home-built confocal microscope associated to an Atomic Force Microscope (AFM, Asylum Research MFP-3D-BIO). For the latter imaging setup, a 532-nm excitation laser beam was focused onto a nanodiamond through an oil-immersion microscope objective (numerical aperture of 1.4), with varying excitation power from 0.1 to 10 mW. The photoluminescence (PL) was detected either by a photon-counting recording system or by a CCD camera mounted at the output of an imaging spectrograph. A Hanbury Brown and Twiss setup was used to record the time intensity correlation function  $g^{(2)}(\tau)$ , allowing the determination of the number of emitting centers per nanodiamond [10].

#### DISPERSION OF NANODIAMONDS ONTO SILICA SUBSTRATES

Starting from a concentrated colloidal solution (see the insert of Figure 1), the nanodiamonds were deposited onto silica coverslips using the two methods previously described. SEM images of the two types of nanodiamond films are shown on Figures 2a and 2b.

The polymer method appears as a method adequate to obtain well-dispersed nanodiamonds on a large scale. However, the particle surface density of the particular sample (see Figure 2b) is too dense for optical studies

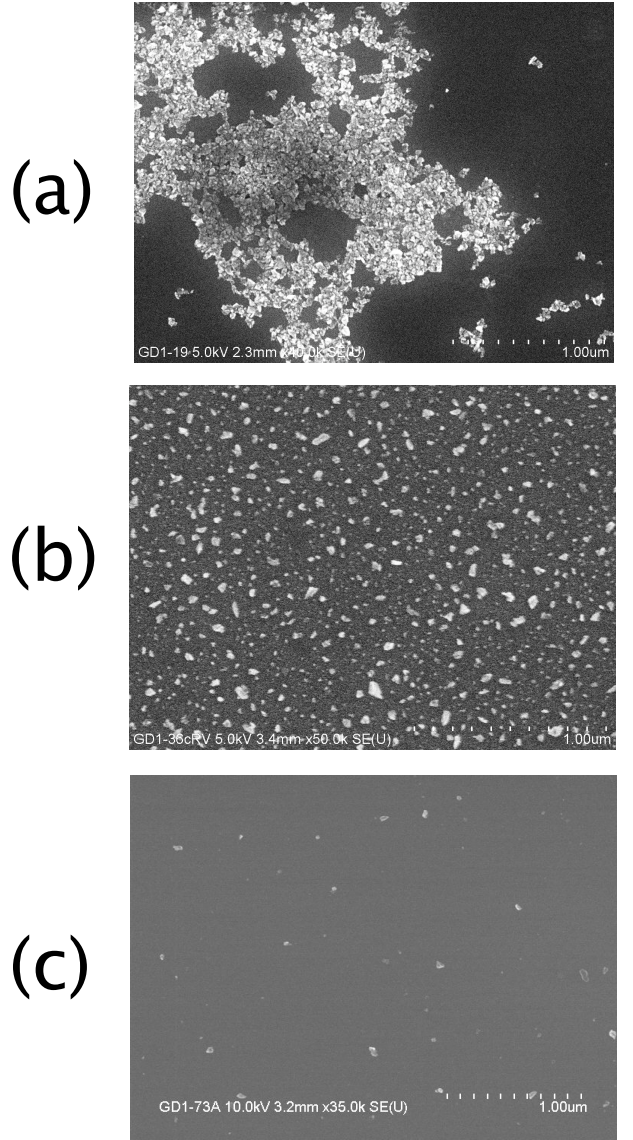


Figure 2: SEM images of nanodiamonds deposited on a silica coverslip. (a) Direct spin-coating of the nanodiamond colloidal solution. (b) Spin-coating realized after preliminary treatment of the coverslip with a cationic polymer. (c) Spin-coating starting with a diluted colloidal solution.

at the level of a single particle, due to the  $\simeq 300$ -nm optical diffraction limit of the confocal microscope. Using diluted colloidal solutions, we prepared other films by spin-coating and using the polymer pre-treatment of the coverslips. Figure 2c shows such a spin-coated film with much less aggregates and in which single particles can be isolated and independently optically addressed. Note that for the photoluminescence experiments reported hereafter, the spin-coating method was used as the presence of the polymer leads to a luminescent background.

Table I: Evaluation of the proportion of luminescent nanodiamonds in  $20\mu\text{m} \times 20\mu\text{m}$  area, as a function of the electron irradiation duration  $\Delta t$ .

| $\Delta t$ | Number of nanodiamonds <sup>a</sup> | Number of luminescent spots <sup>b</sup> | Proportion of luminescent nanodiamonds |
|------------|-------------------------------------|--|--|
| 2 min      | $125 \pm 5$                         | $52 \pm 5$                               | $41 \pm 5\%$                           |
| 10 min     | $170 \pm 10$                        | $79 \pm 5$                               | $47 \pm 8\%$                           |
| 20 min     | $223 \pm 10$                        | $141 \pm 7$                              | $64 \pm 6\%$                           |
| 60 min     | $188 \pm 10$                        | $162 \pm 10$                             | $88 \pm 10\%$                          |

<sup>a</sup>Uncertainties come from the fact that some nanodiamonds are too close to each other to be distinguished by AFM.

<sup>b</sup>Uncertainties come from the fact that there are some weak luminescent spots.

### STUDY OF PHOTOLUMINESCENCE OF NANODIAMONDS AS A FUNCTION OF THEIR IRRADIATION DURATION

Photoluminescence of commercial nanodiamonds that were neither irradiated nor annealed was first studied. A small proportion (about 2 to 5 percent) of nanodiamonds was found to be luminescent. However, we noticed that the photoluminescence of those nanodiamonds was unstable, even after annealing at  $800^\circ\text{C}$  for two hours. Photoluminescence of nanodiamonds which were irradiated by the high-energy electron beam was then investigated. The formation of NV-centres was studied as a function of the irradiation duration  $\Delta t$ .

For 4 samples, respectively corresponding to  $\Delta t = 2, 10, 20$  and  $60$  minutes, the confocal photoluminescence scans and the corresponding AFM scans were recorded simultaneously. As an example, Figure 3 shows the simultaneous AFM and PL images of a diamond film elaborated using a diamond powder irradiated for 20 minutes. On this example, one can notice that it is possible to locate the nanodiamonds on the AFM image and to associate to almost each of them a bright luminescent spot. In the  $20\mu\text{m} \times 20\mu\text{m}$  area of the sample raster scan, we evaluated the number of nanodiamonds via the AFM image and the associated number of luminescent spots in the PL image. We determined that, for this 20-minute irradiated sample, about 70 % of the nanodiamonds were luminescent.

The same study was performed on nanodiamonds which were irradiated for  $\Delta t = 2, \Delta t = 10$  and  $\Delta t = 60$  minutes. The values are reported on Table I. We came to the conclusion that the proportion of luminescent diamond nanoparticles increases with the increase of the irradiation duration, going from about 40 % for the 2-min irradiation time to more than 80 % for the 60-min irradiation time (Figure 4).

In addition to the evaluation of the proportion of luminescent nanodiamonds, the type of emitters (either  $(\text{NV}^0)$  or  $(\text{NV}^-)$ ) and the number of emitters in the nan-

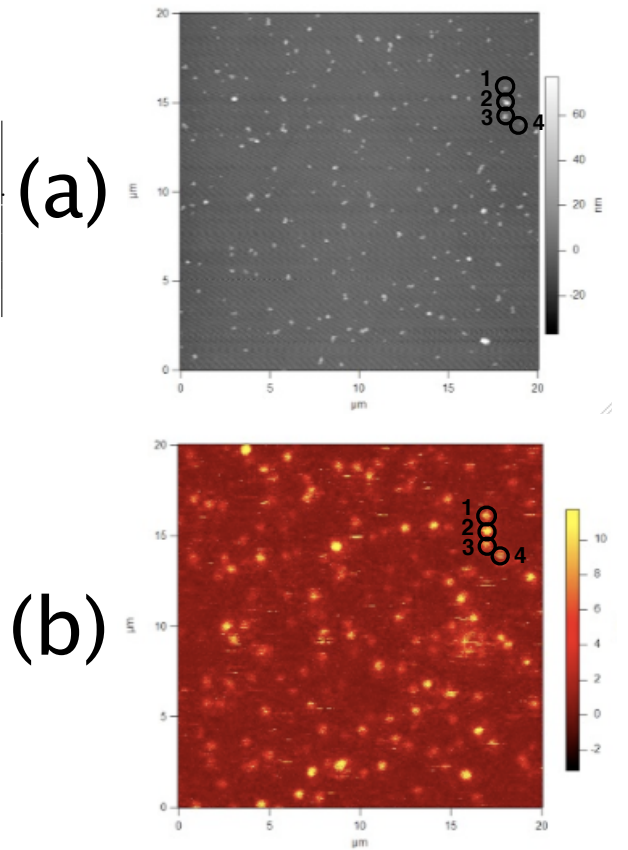


Figure 3: (a) AFM image of a deposited film of nanodiamonds which have been irradiated for 20 minutes using a  $\sim 14\text{-MeV}$  electron beam. (b) Corresponding PL image simultaneously recorded in the raster scan of the sample.

odiamonds can be both determined. In the four samples we found both  $\text{NV}^-$  and  $\text{NV}^0$  centres. We thoroughly studied the sample resulting from the 20-min irradiation time. Out of 25 fully characterized luminescent nanodiamonds, we found 6 single emitters, corresponding to 5  $\text{NV}^0$  centres and 1  $\text{NV}^-$  centre. Considering all nanodiamonds (and not only those with single emitters), a  $\text{NV}^0/\text{NV}^-$  ratio was evaluated to be  $\simeq 60/40$ . In the other samples irradiated for  $\Delta t=2, \Delta t=10$  and  $\Delta t=60$  min, the  $\text{NV}^-/\text{NV}^0$  ratio was found to be similar. Therefore, the duration of the  $\sim 14\text{-MeV}$  electron irradiation does not seem to have any influence on the  $\text{NV}^0/\text{NV}^-$  ratio, at least within this timescale. Contrary to the bulk diamond case where the  $\text{NV}^0/\text{NV}^-$  ratio can be controlled by tuning the  $\text{He}^+$ -ion irradiation conditions [12], the creation of  $\text{NV}^-$  over  $\text{NV}^0$  cannot be favoured in 50-nm sized nanodiamond powder.

### CONCLUSION

High-energy electron irradiation and annealing of 50-nm HTHP nanodiamonds lead to the efficient production

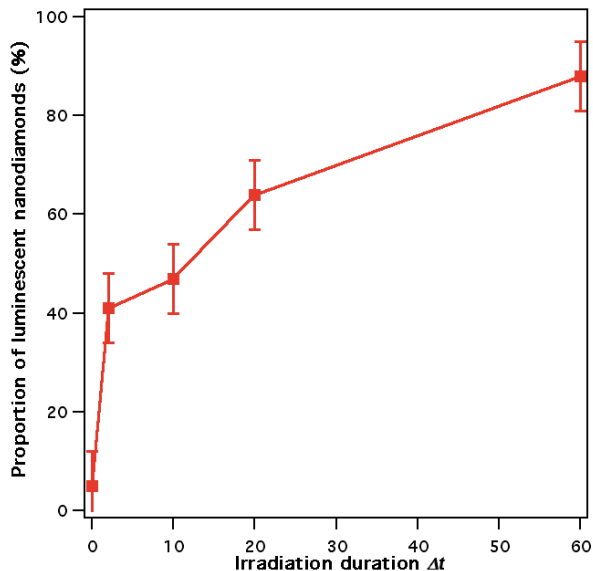


Figure 4: Proportion of luminescent nanodiamonds deposited on a coverslip as a function of the irradiation duration  $\Delta t$ .

of NV-centres on large quantities of nanodiamond powder. We demonstrated that about 500 mg of nanodiamond powder can be irradiated in one shot of a rather short duration, less than one hour. This irradiation results in highly luminescent nanodiamonds with a size smaller than 50 nm.

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