

Electronic Supplementary Information

Boosting Nanodiamond Fluorescence: Towards Development of Brighter Probes

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Experimental Section

Chemicals

Sodium hydroxide, nitric acid (65%), and sulfuric acid (96%) were purchased from Penta (Czech Republic). Potassium nitrate was purchased from Sigma-Aldrich (Prague, Czech Republic). All chemicals were *p.a.* quality and were used as received without further purification. Deionized water was prepared with a Millipore Synergy UV Ultrapure water system.

Two types of nanodiamonds were supplied by Microdiamant (Switzerland) (MSY 0-0.05 and MSY 0-0.25). The particles were oxidized by air in a Thermolyne 21100 tube furnace at 510 °C for 5 hours. The nanodiamonds were subsequently treated with a mixture of HNO₃ and H₂SO₄ (85 °C, 3 days).^[1]

Irradiation and annealing

Purified nanodiamond powder (160 mg), containing approximately 100 ppm of natural nitrogen impurities, was pressed in an aluminum target holder and irradiated with a 15.5 MeV proton beam extracted from the isochronous cyclotron U-120M for 70 min (fluence 6 x 10¹⁶ cm⁻²). The irradiated material was annealed at various conditions (for the individual annealing points of the 2D matrix, see Fig. S3). The annealing was performed at normal pressure under an argon atmosphere.

Oxidation of samples

All samples evaluated for the influence of annealing conditions on luminescence intensity were treated with a mixture of HNO₃ and H₂SO₄ (85 °C, 3 days) („standard treatment“).^[1] The sample annealed at 900 °C for 1 hour was selected for further studies, including oxidative treatment by air, oxygen plasma, and heating in melted potassium nitrate. The air oxidation was performed at 510 °C for 1, 2, or 4.5 hours at normal pressure in a Thermolyne 21100 tube furnace calibrated with an external thermocouple (Testo AG 1009). The oxygen plasma treatment was performed for 2 min at 500 °C in an ASTeX AX 5010 series Microwave Plasma Enhanced Chemical Vapor Deposition (MPECVD) reactor. For oxidation in potassium nitrate, 2 mg of ND sample and 1 g of KNO₃ were powdered in an agate mortar. The homogeneous mixture was placed in a quartz boat and placed in a Thermolyne 21100 tube furnace pre-heated to 560 °C for 7, 10, or 20 min. The sample was then cooled down, dissolved in water, and centrifuged. The pellet was resuspended in 3 mL of water, sonicated for 10 seconds in an ultrasonic bath, and centrifuged again. This washing step was repeated five times to remove all salt residue.

Raman and photoluminescence measurements

Although absorption spectroscopy can be used to directly determine the concentrations of defect centers in natural and synthetic single crystal diamonds,^[2] its use is rather limited in the

case of nanodiamond particles (due to high reflection, extreme scattering, and low signal intensity). Instead, we focused on evaluation of NV center formation resulting from annealing using Raman and photoluminescence spectroscopy.^[3,4] If combined with anti-bunching time-correlation spectroscopy,^[5] it does allow us to assess the number of defect centers, *i.e.* quantitative comparison of optically active NV center formation and the related brightness of particles. The photoluminescence normalized to the diamond Raman signal at 1332 cm⁻¹ and compared to a reference sample with known number of NV centers enabled the determination of NV⁰ and NV⁻ center yields. The normalization to the diamond Raman signal served also for the monitoring of particle amorphization (changes in *sp*³ carbon content).^[6]

It should be noted that effects other than the number of NV centers created can be involved in the total luminescent yield, for example, the quenching effect of the surface leading to the “dark state” of NV centers,^[7,8] which is of importance especially for small particles.

Before measurement, all samples were lyophilized from water and diluted in DI water to the concentration of 10mg/ml by high-power ultrasonic horn (Hielscher UP400S, Sonotrode H3) using 400 W at a 1:1 (on/off) cycle for 30 minutes under liquid cooling. The samples were prepared by drop-casting of the aqueous dispersion of NDs on the polished silicon wafer. Raman and luminescence spectra were measured using a Renishaw InVia Raman Microscope; the excitation wavelength was 514 nm (luminescence measurements) and 325 nm (Raman measurements)^[6] with 15 mW laser power, x20 objective, the exposure time was 10 seconds, accumulation 10x. 20 measurements were made on each sample. The Raman and luminescence spectra were taken at room temperature and, to make the luminescence quantitatively comparable, spectra were normalized to the diamond Raman peak. The standard deviation of the normalized luminescence spectra did not exceed 15%. The average of measurements performed on each sample was used for further calculations and comparisons. For results, see Figs. 2, S2, and S3. The NVN centers were examined with the Renishaw InVia Raman Microscope set at an excitation wavelength of 488 nm in combination with an AFM NTEGRA Prima NT MDT system equipped with a soft HA_NC etalon tip. The anti-bunching time-correlation spectroscopy was performed using setup described in reference^[5].

Table S1 Results of repeated annealing experiments performed with 45 and 140 nm particles. The samples were annealed for 1 hour. The standard error (Std. error) was calculated from 5 sample replicates.

Nanodiamond size	Temperature	Average relative fluorescence intensity	Std. error
45 nm	700 °C	0.78	0.093
45 nm	900 °C	1.81	0.133
140 nm	700 °C	5.1	0.131
140 nm	900 °C	12.8	0.098

Figures

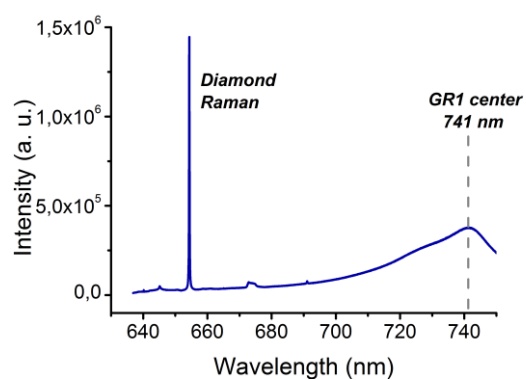
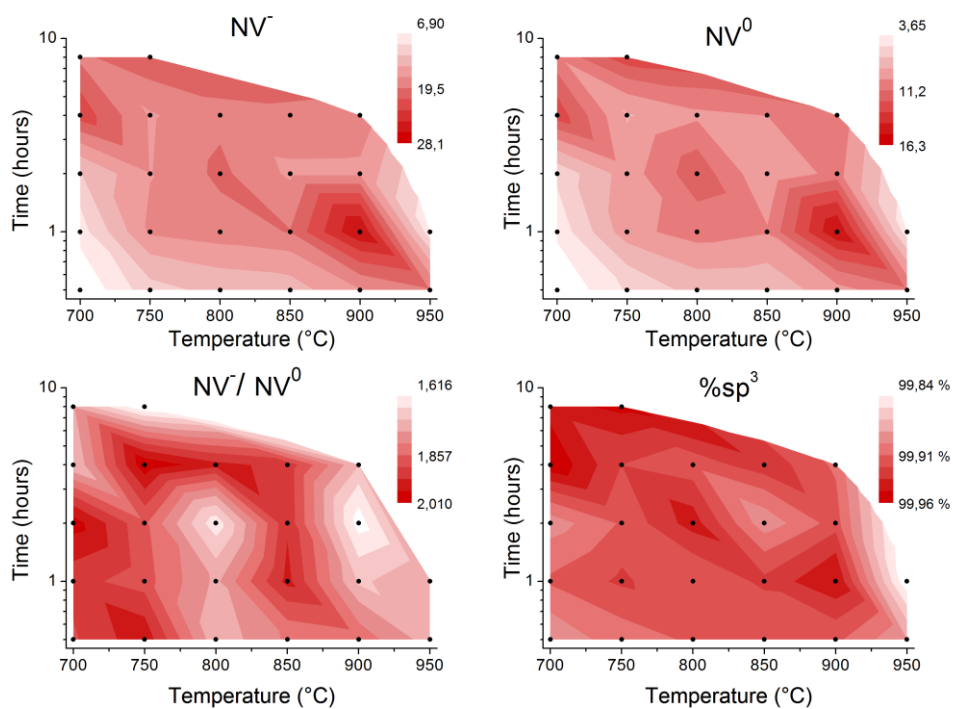


Figure S1 Raman spectrum of GR1 centers observed in samples after proton beam irradiation.

a)



b)

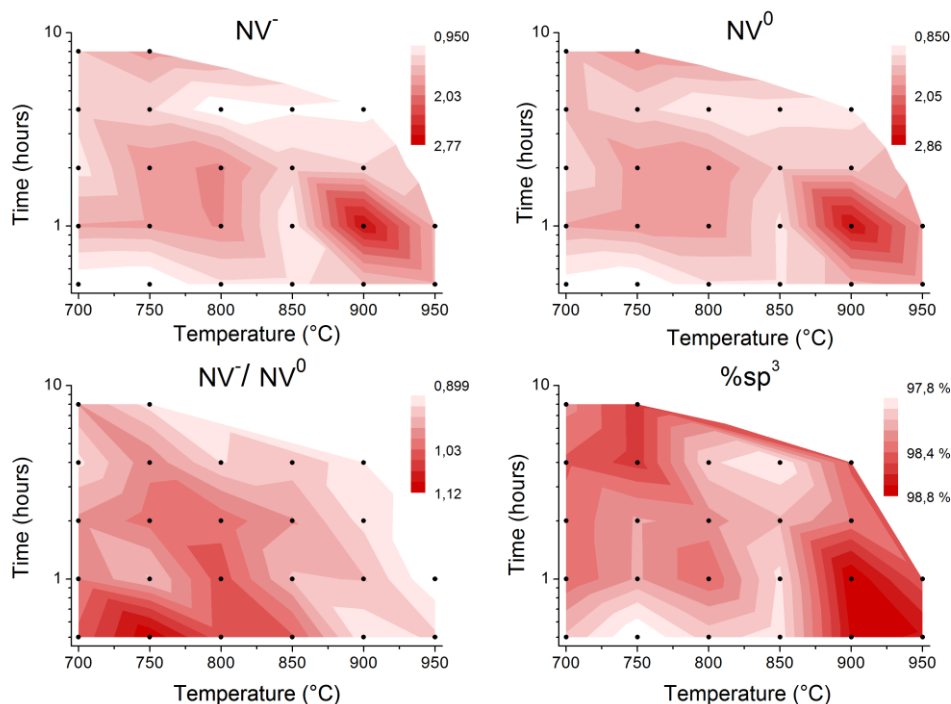


Figure S2 Normalized relative luminescence intensities of NV^- and NV^0 , ratios of NV^-/NV^0 luminescence, and “%” of sp^3 carbons for a) 140 nm and b) 45 nm ND particles as a function of annealing time and temperature. Black dots represent the matrix of annealing conditions, darker color represents brighter samples. Interestingly, the NV^- in 45 nm fNDs are preferentially formed at lower temperatures and shorter times (compare the ratios of NV^-/NV^0 luminescence). This trend is not pronounced in 140 nm fNDs.

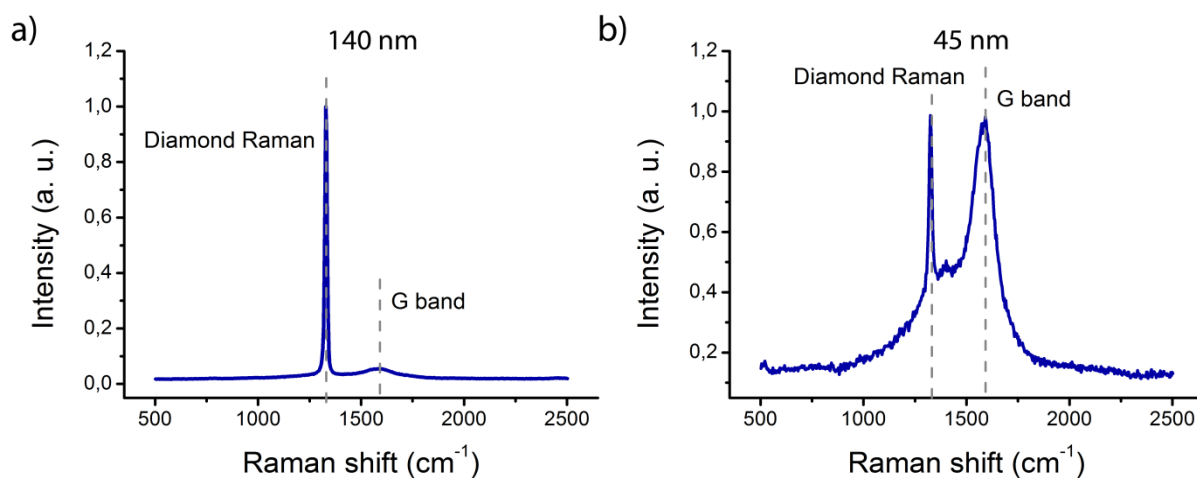


Figure S3 Raman spectra of a) 140 nm and b) 45 nm fND particles after annealing. The intensity is normalized to the diamond Raman band. The G band, corresponding to the amorphized sp^2 carbons, is markedly higher for smaller particles.

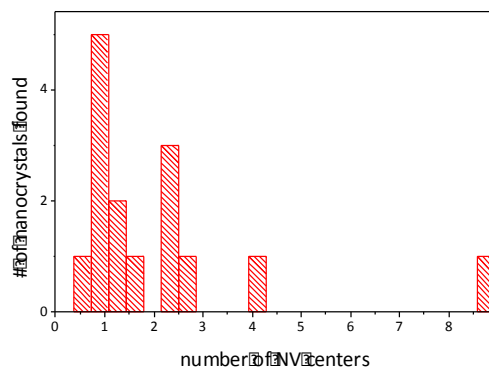


Figure S4 Statistic distribution of NV centers in fND measured using single particle detection fluorescence setup and determined from anti-bunching experiments after laser excitation 532 nm. The measurements were executed on 25 spots.

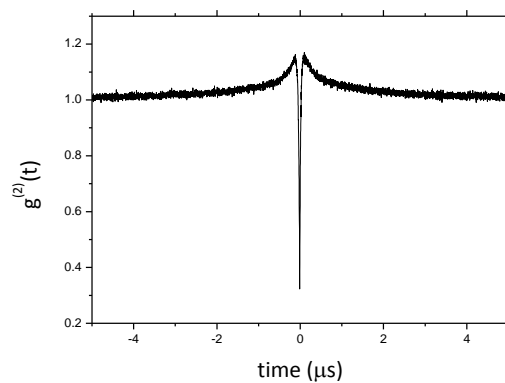


Figure S5 Typical anti-bunching behavior of few emitters as measured from fND used on our study as a reference.

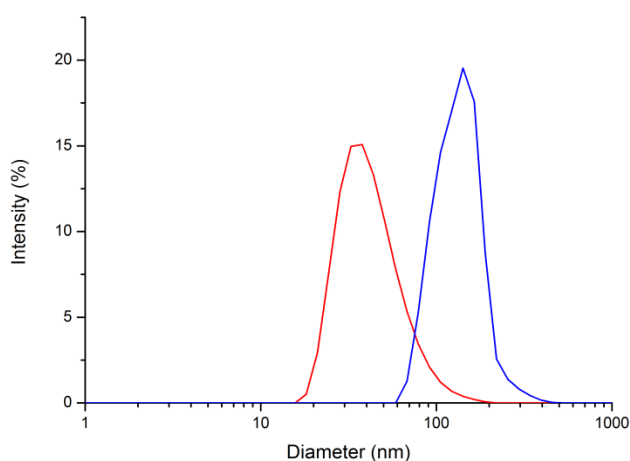


Figure S6 Size distributions by volume of 45 nm (red) and 140 nm (blue) particles in aqueous solution determined by dynamic light scattering.

References

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