

Supporting Information

Stimulated Emission Depletion Microscopy Resolves Individual Nitrogen Vacancy Centres in Diamond Nanocrystals

Silvia Arroyo-Camejo, Marie-Pierre Adam, Mondher Besbes, Jean-Paul Hugonin, Vincent Jacques, Jean-Jacques Greffet, Jean-François Roch, Stefan W. Hell and François Treussart

1 Sample characterization

1.1 Pre-characterization of the nanodiamond sample

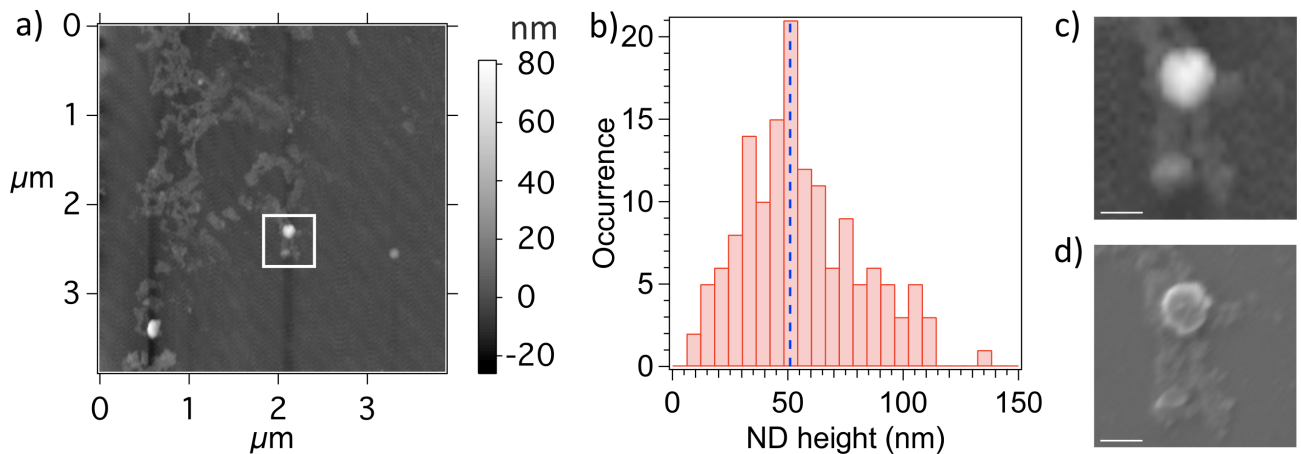


Figure S1: Nanodiamond size measurement. a) $4\ \mu\text{m} \times 4\ \mu\text{m}$ AFM scan around the particle (surrounded by a white square) for which the STED imaging is reported in 3. b) ND vertical dimension distribution as measured by AFM on multiple regions of the sample; the dashed vertical line indicates the median of the distribution. c) AFM image zoom corresponding to the white square in a). d) SEM image of the same ND as in c); scale bars: 100 nm. Note that both AFM and SEM images show the same patterns of the residue of the resin used in the quartz cover slip photo-etching process.

The sizes of the spincoated NDs were first estimated using an atomic force microscope (MFP-3D-BIO, from Asylum Research, USA) placed on top of the fluorescence confocal microscope used to locate FND (inset of Figure 1c). The AFM enabled us to measure the height (*i.e.* the vertical dimension) of the ND with a resolution of approx. 1 nm, but the lateral resolution is practically limited to about 80 nm due to the finite radius of curvature of the AFM tip. Figure S1a shows the AFM scan around the particle for which the STED imaging is reported in Figure 3a,b and d. Figure S1b display the ND height distribution inferred from AFM scans of the same sample, yielding a median value of 48 nm.

1.2 Post-characterization of the nanodiamond sample

For high-resolution SEM images quantifying the lateral dimensions and shape of the investigated nanodiamonds we deposited a 0.3 nm thin layer of palladium-platinum on top of the ND sample to obtain adequate surface conductivity, but not to cover up potential gaps between clustered NDs. The SEM images were recorded together with Felicitas Predel from the group of Prof. P. A. van Aken at the Max-Planck Institute for Intelligent Systems (Stuttgart) on a Zeiss DSM 982 Gemini at a beam power of 1 keV. A comparison of the ND height values (measured by AFM) and the lateral side length values (obtain through SEM) of the same NDs reveals that the NDs were generally at least two times longer than they were high. We may thus conclude that after the spin coating the NDs preferentially stuck to the cover slip with their longest side.

Figure S2 shows the SEM images of the six ND, for which the STED resolution scaling was presented in Figure 2d.

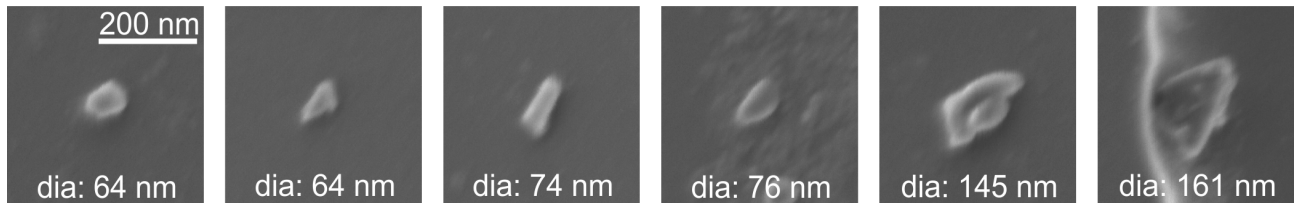


Figure S2: SEM images of the NDs from 2d for different mean dimension (also called “diameter”, denoted “dia”.)

2 Correlation between NV number, fluorescence spots and ESR line pairs

Optically detected ESR spectra were recorded in confocal imaging mode from one ND at a time. The ND ESR spectra were first conducted in continuous wave ESR mode with an external magnet. A second ESR spectrum was recorded in pulsed ESR mode without external magnet to estimate the magnitude of the strain field induced level splittings. This way we could screen the ESR spectra for potential ND aggregates by checking, if the cw ESR lines would or would not group into four line pairs (corresponding to the four possible NV orientations in the diamond lattice) considering the magnitude of the strain splitting.

Due to the reasonably strong strain splitting in NDs of tens of MHz the ESR spectra provided a valuable complementary method for the determination of the approximate number of NV^- centres

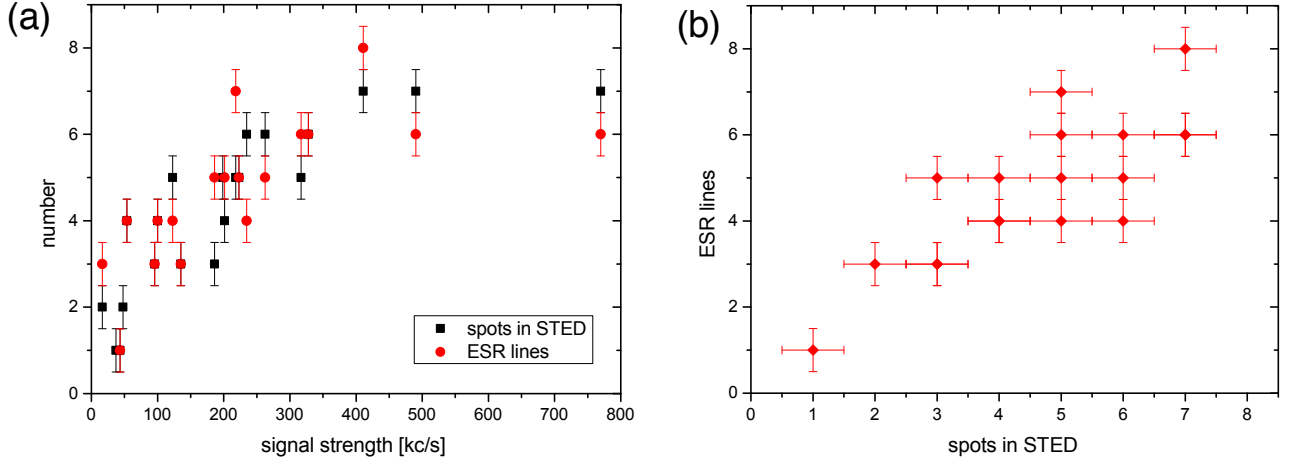


Figure S3: a) Number of NVs identified in the STED images (black points) and number of observed ESR line pairs (red points) versus the total fluorescence intensity of a respective ND confocally recorded with time-gated detection. b) Number of observed ESR line pairs versus number of NVs identified in the STED images showing linear scaling.

inside an ND. Figure S3a displays a comparative plot of the number of NV centres that could be identified in the STED images for each ND (black dots) and the corresponding number of identified ESR line pairs (red dots) *versus* the confocally detected fluorescence signal strength. For ensembles of NV centres in an ND the total fluorescence strength can be considered as a measure for the average number of NV centres incorporated inside the ND, respectively. It is observed, that both the identifiable number of NV centres in the STED images and the number of identifiable ESR line pairs scales nearly linearly for low numbers of NV. At around 6-8 NVs both number scaling shows a saturation behavior due to the finite STED resolution of 10 – 20 nm and the finite linewidth of approx. 10 MHz of the cw ESR lines. A plot of the number of resolved NV centres *versus* the number of identified ESR line pairs in Figure S3b reveals a linear relation between both measures. Note, that the uncharged NV^0 centre does not feature an ODMR line and is thus invisible in the ESR spectra measured here, even though it would be visible in the fluorescence images.

3 Numerical simulations of STED intensity distribution inside bulk diamond

Figure S4 shows the STED intensity distribution of the doughnut beam (z being its axis of symmetry) inside a bulk diamond slab (thickness: 300 μm), and focused 7 μm below the diamond surface. The intensity is normalized to I_{max} which is the STED intensity at the doughnut rim in absence of diamond,

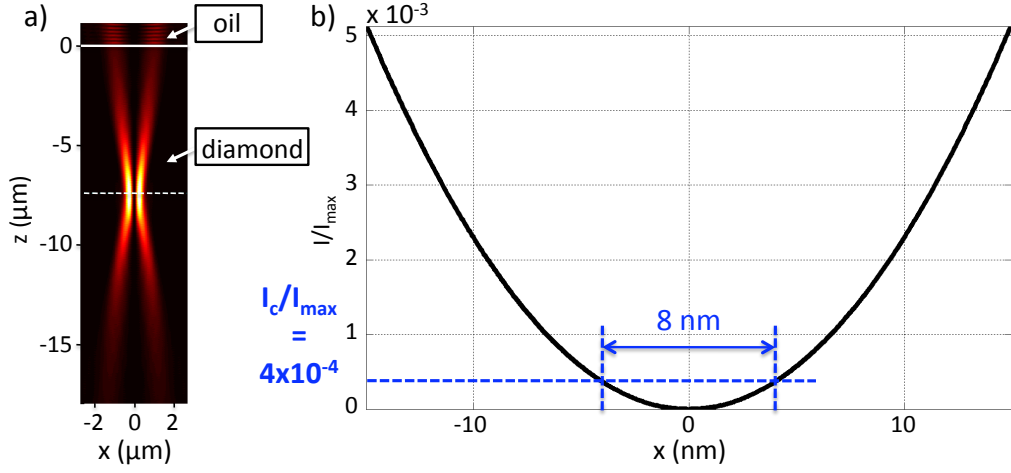


Figure S4: a) Doughnut beam intensity distribution inside a $300 \mu\text{m}$ thick diamond slab, focused at $z = -7 \mu\text{m}$. The beam propagates in the negative z . Optical contact between the microscope objective and the diamond slab is ensured with immersion oil. b) Intensity profile of the STED doughnut along the central dashed white line of a). The STED resolution of 8 nm is associated to a critical intensity $I_c = 4 \cdot 10^{-4} I_{\text{max}}$.

i.e. for the STED beam in vacuum.

The resolution that is achieved for a single NV centre located at this depth with our STED microscope is $\Delta d \approx 8 \text{ nm}$ (see Ref. 5 of the main text). Hence, we propose to use the characteristic STED intensity at $\Delta d/2$ from the doughnut null as a benchmark to evaluate STED resolution for the nanodiamond host. This value is inferred from Figure S4b) intensity profile in the bulk diamond, to be $I_c = 4 \cdot 10^{-4} I_{\text{max}}$. Conversely, this critical intensity can be converted into STED resolution from the simulation of the doughnut intensity distribution in nanodiamond (Figures 5 and 6 of main text).
