Electronic Supplementary Information for:

Bright and photostable nitrogen-vacancy fluorescence from unprocessed detonation nanodiamond

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Nanoparticle solutions

Detonation nanodiamonds:

Detonation nanodiamond powder (Nabond Technologies, China) was purified by $KMnO_4$ (potassium permanganate) by the supplier and used as-received and dispersed in deionized (DI) water at 1 mg/ml. The nanoparticle solution was sonicated for 30 minutes at 125 W using a pulsed horn sonicator with pulse duration of 2 seconds followed by 4 seconds without sonication to allow heat to dissipate. The solution was then centrifuged for 10 min at 1000 rcf to remove large aggregates. The nanoparticles in the supernatant of this solution were found to be colloidally stable and used for experiments.

HPHT nanodiamonds:

120 nm nanodiamond powder (Nabond Technologies, China) was irradiated with with an electron beam (2 MeV) to a total fluence of 1×10^{18} cm⁻¹, annealed in vacuum at 800° C for 2 hours and oxidized in air at 520° C for 4.5 hours. The powder was then dispersed in DI water at 1 mg/ml and sonicated for 1 hour at 125 W using a pulsed horn sonicator as described above for deaggregation. These particles are referred to as "processed HPHT nanodiamonds" throughout the ESI (to distinguish them from the as-received HPHT material) and as "HPHT nanodiamonds" in the main text.

120 nm nanodiamond powder (Nabond Technologies, China) was also used asreceived to exclude the possibility of contamination discussed in the main text. The 120 nm nanodiamond powder was as-received and processed and dispersed in DI water as described above for the detonation nanodiamond material.

Sample preparation

A glass cover slip (22×22 mm, Knittel Glass, Germany) was cleaned using Kimwipes (Kimberly-Clark Professional, USA), absolute ethanol and isopropanol (both Sigma-Aldrich, USA) and placed on a hotplate at 120°C. 10 µL of nanoparticle solution were deposited on the substrate and allowed to dry. Then another 10 µL of nanoparticle solution were deposited on the substrate and allowed to dry. The resulting samples were used for optical imaging experiments. For the experiments shown in Figure 2 and 4 in the main text, a silicon wafer was used instead of a glass substrate.

Dynamic light scattering and zeta potential measurements



Figure S1. Nanoparticle size distributions and zeta potentials for the detonation diamond particles (A-C) and processed HPHT nanodiamonds (D-F). All data were obtained using a Zetasizer Nano ZS (Malvern Instruments, USA).

Sample holder used for ODMR experiments



Figure S2. Sample holder used to deliver the microwave field. The sample was placed inside the white square and imaging was performed inside the loop (black arrow).

Individual ORMD spectra of stable DND particles and comparison with processed HPHT nanodiamonds



Figure S3. ODMR spectra for 9 detonation nanodiamond particle aggregates (A) and HPHT nanodiamonds (B).

Optical properties of processed HPHT nanodiamonds analogous to Figure 2 in the main text



Figure S4. Excitation wavelength and excitation intensity dependence of HPHT nanodiamonds. A: Normalized fluorescence from HPHT nanodiamond particle for excitation wavelengths between 400 nm and 520 nm as indicated in the graph. B: Total fluorescence intensity as a function of excitation wavelength. Line is a guide to the eye only. C: Total fluorescence intensity as a function of excitation power. Line is a guide to the eye only.

TEM images of the detonation nanodiamonds



Figure S5. Transmission electron microscopy images (A-C) and diffraction pattern (D) of the detonation diamond material used in experiments. On all TEM images, only particles of sizes below 6 nm were found as well as larger aggregates of those particles. Assuming a fraction of 0.03% brightly fluorescing particles in the sample as discussed in the main text, several of these are present in images like the ones shown in (A) and (B). HPHT particles are generally well above 20 nm in diameter. Hence, if HPHT particles were the cause of the observed bright NV fluorescence we should find these particles in TEM images as well. The fact that we do not find any particles larger than 6 nm suggests that contamination with HPHT particles can not be the cause of the observed NV fluorescence in DND samples. This in agreement with our optical analysis shown in Figure S9 and S10.

FTIR spectra of the detonation diamond powder and comparison with processed HPHT nanodiamonds



Figure S6. Fourier transform infrared (FTIR) spectra of the detonation diamond particles as received and the processed HPHT nanodiamond particles. The suggested surface functional groups are identified based on references ¹ and ². FTIR spectra were recorded using an Perkin Elmer Frontier FT-IR Spectrometer with a Universal ATR Sampling Accessory (PerkinElmer Inc., USA).





Figure S7. X-ray photoelectron spectroscopy (XPS) spectra of the detonation diamond particles as received. A: survey spectrum identifying carbon, oxygen and nitrogen as the main elements present in the sample. B: Fine scan in the energetic region of C 1s showing a relatively broad peak that points to the presence of numerous forms of carbon in the sample including diamond (sp3) and graphite (sp2).³ This is consistent with the Raman spectra shown in Figure S14. C: Fine scan in the N 1s region. The particles were drop cast onto a silicon wafer. The same sample was also used for the statistical analysis of the optical properties of the DND particles. All XPS spectra were obtained using a Thermo Scientific K-Alpha XPS system (with a aluminum K α X-ray source) (ThermoFischer Scientific, USA)

XPS elemental analysis of the as-received and processed HPHT nanodiamond powder



Figure S8. XPS spectra for as received (A) and processed (B) HPHT nanodiamond particles used in this study. The particles in B were processed as described above under 'Nanoparticle solutions'.

Exclusion of contamination with HPHT nanodiamonds as a cause for the observed NV fluorescence from detonation nanodiamond material.

We excluded contamination with HPHT nanodiamonds by the manufacturer as a possible cause for the observed stable NV emission. First of all, most as received HPHT nanodiamonds show weak NV emission due to the low natural concentration of vacancies and only a small subset of particles show NV emission intensities comparable to the intensities observed in the stable DND particles (see ESI Figure S10). We also analysed the optical properties of 30 of these bright HPHT nanodiamonds. We find that both the fluorescence spectra as well as the fluorescence lifetime of the HPHT particles clearly differ from those obtained from the stable DND particles. The contribution of NV⁰ to the overall spectrum is significantly higher in case of the stable DND particles and the long fluorescence lifetime component of the HPHT particles is found to be 21.7 ns on average, which is markedly different from the lifetime τ_2 of 37.7 ns for the stable DND particles (see ESI Figure S9 B and C). No individual particles above the size of 6 nm were found in TEM images (Figure S5). Assuming a fraction of 0.03% brightly fluorescing particles in the sample as discussed in the main text, several of these are present in images like the ones shown

in Figure 5A and B. The size of HPHT nanodiamonds is generally well above 20 nm. However, no particles of this size can be found in TEM images, suggesting that no HPHT particles are present in the DND sample. As a result of these findings, we can exclude contamination as a cause for the observed NV fluorescence in DND samples.



Comparison of the optical properties of bright detonation and as-received HPHT nanodiamond particles

Figure S9. Comparison of the optical properties of brightly fluorescing detonation (red) and HPHT nanodiamond (blue) particles, both as-received. 30 particles were analyzed for each particles type. A: Averaged and normalized fluorescence spectra. The envelopes indicate the standard deviation between individual spectra. B: Typical time resolved fluorescence decay traces. C: Histogram showing the fluorescence lifetime of detonation nanodiamond particles (red) and HPHT nanodiamonds (blue) obtained from a single exponential fit to 30 fluorescence lifetime decay traces for each particle type between 30 ns and 120 ns. D: Histogram of the brightness of the two particle types in 1000 counts per second (k CPS).

Comparison of fluorescence images of detonation nanodiamond and as-received HPHT nanodiamond particles



Figure S10. Confocal fluorescence images of detonation diamond (A) and HPHT nanodiamond particles (B). Images were acquired under the same conditions: 520 nm excitation at 50 μ W excitation power.

Detonation diamond particles as-received form a second supplier



Figure S11. A: Confocal fluorescence images of detonation diamond from a different supplier (PlasmaChem GmbH, Germany, Product: Purified detonation nanodiamonds/ grade G). Fluorescence spectrum (B) and time resolved decay (C) of the particle shown in a panel A. The image in (A) was acquired using 520 nm laser excitation at 50 μ W excitation power.



Individual particle measurements used to generate Figure 1 C, D and E

Figure S12. Individual particle measurements for 30 detonation nanodiamond particle aggregates. 10 traces are shown in each graph for clarity. Fluorescence spectra (A-C), time-resolved fluorescence decay traces (D-F) and photostability timetraces (G-I).



Statistical analysis of DND particle lifetime and fluorescence brightness

Figure S13. Histograms showing the sort and the long lifetime component distribution (A) and the brightness distribution in 1000 photo-counts per second (k CPS) (B) for 30 detonation nanodiamond particle aggregates



Raman spectra of as received DND and HPHT diamond nanoparticles

Figure S14. Raman spectra for detonation (A) and HPHT (B) nanodiamonds, both asreceived. Both particle types show a clear diamond Raman signal close to 1330 cm⁻¹, while the signal from the HPHT sample is significantly narrower due to a higher crystalline quality of the HPHT particles. The detonation diamond sample also shows a clear peak in the spectral region of the graphite G-band close to 1600 cm⁻¹.¹ The overall signal increase observed with increasing wavenumber may be attributed to the increasing NV fluorescence in this spectral region. The NV⁰ zero phonon line may also contribute to the broadening of the G-band as indicted in graph (A). Raman

spectra were recorded using a Horiba LabRAM HR Raman spectroscopy system (Horiba Ltd, Japan) with a 532 nm excitation laser.

References

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