

## Bicolour single photon source based on HPHT nanodiamond

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Single-photon fluorescence of the visible and near-infrared ranges in individual diamond nanoparticles of various sizes synthesized at high pressure and high temperature (HPHT) from a mixture of hydrocarbons containing nitrogen and silicon is studied. The fundamental possibility of obtaining diamond crystallites that contain single NV and SiV centers emitting photons at two different frequencies is demonstrated. This research could potentially lead to the controlled creation of dual-frequency room-temperature single-photon sources using individual diamond nanoparticles, which would significantly enhance their functionality in quantum optical technologies.

**Keywords:** HPHT synthesis, nanodiamond, luminescence, single photon source, NV<sup>-</sup>, SiV<sup>-</sup>.

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### Introduction

Negatively charged silicon-vacancy (SiV<sup>-</sup>) and nitrogen-vacancy (NV<sup>-</sup>) complexes that are fluorescent at 738 and 638 nm, respectively, are among the best known color centers in diamond [1]. Unique property of optical initialization of the electron spin of NV<sup>-</sup> center at room temperature ensures practical applications of solid-state quantum bits operating in normal conditions [2,3]. Narrow-band (~ 1 nm) fluorescence of single SiV<sup>-</sup> centers is important for use in quantum data transfer devices [4]. A set of research papers reported about creation of biomarkers and temperature sensors based on microdiamonds and nanodiamonds (ND) containing simultaneously large amounts of nitrogen centers with various structure [5,6], NV and SiV [7], germanium-vacancy (GeV) and SiV [8,9].

As far as we know, until now the literature has not reported that any single fluorescent centers of various types in individual diamond nanoparticles were detected. Recently, an increase in the spontaneous emission rate of single SiV<sup>-</sup> centers in HPHT-ND has been demonstrated thanks to efficient interaction between the emitter and surface plasmons generated on the gold film [10]. The study investigates photoluminescent (PL) properties of individual NV<sup>-</sup> and SiV<sup>-</sup> PL HPHT-ND synthesized from an adamantane-tetrakis-detonation nanodiamond mixture. Single NV<sup>-</sup> and SiV<sup>-</sup> centers were for the first time detected in individual 250–300 nm. ND.

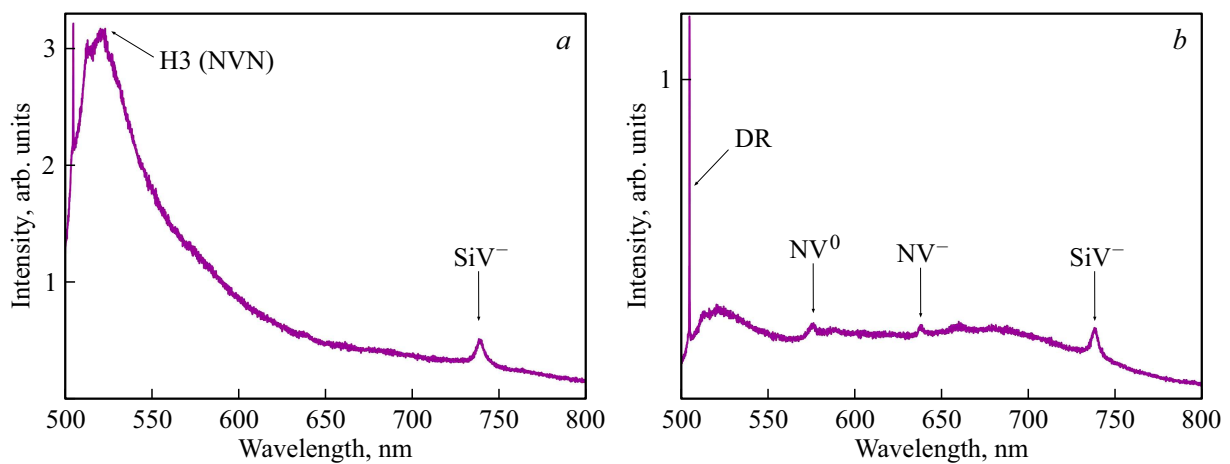
### Experimental methods

Nanodiamonds with typical sizes of individual crystallites within 50–500 nm were synthesized at 7.5–8 GPa and 1550–1650°C from a mixture of adamantane C<sub>10</sub>H<sub>16</sub> (Sigma Aldrich, > 99%), detonation nanodiamond (DND) with particle size 5 nm and tetrakis(trimethylsilyl)silane C<sub>12</sub>H<sub>36</sub>Si<sub>5</sub> (Sigma Aldrich, ≥ 97%). Atomic ratios in the initial growth mixture are assessed at Si/C ~ 1/10 000 and N/C ~ 1/30 000 level considering the nitrogen concentration in DND ~ 1% at [11]. The weight of the prepared diamond powder was approx. 10 mg. The central part of the sample was removed from the growth chamber and dissolved in extra-pure ethanol forming a ND 0.01 g/l suspension. 1 μl of the suspension was applied to a silicon substrate and dried. The resulting layer contained primarily diamond nanoparticles separated from each other to allow optical characterizing of individual ND.

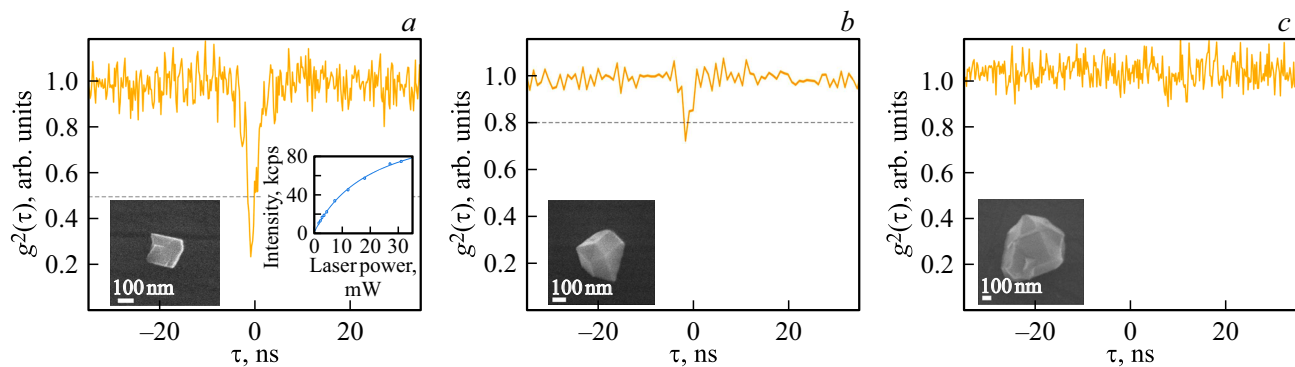
Dimensions and morphology of individual crystallites and crystallite clusters were measured using Jeol 7001F scanning electron microscope (SEM). Distribution of particles by size varies from 100 to 600 nm.

ND fluorescence in a wide spectral range 500–800 nm was studied using NTEGRA Spectra II combined measurement system that incorporated atomic-force microscopy and Raman-scattering spectroscopy. For fluorescence excitation, 473 nm continuous semiconductor laser was used.

Spectral characteristics of NV<sup>-</sup> and SiV<sup>-</sup> centers were examined using a laboratory confocal microscope with two 532 and 660 nm continuous laser excitation sources. fluorescence spectra within 700–800 nm were recorded using Ocean Insight QE Pro spectrometer, SiV<sup>-</sup>-fluorescence



**Figure 1.** Examples of two typical fluorescence spectra of individual HPHT-ND (*a, b*). DR — Raman scattering line of the diamond ( $\sim 504$  nm) at 473 nm laser excitation.



**Figure 2.** Intensity correlation functions of  $\text{SiV}^-$  fluorescence,  $g^{(2)}(\tau)$  measured for individual HPHT-diamond crystallites of various sizes: 500 (*a*), 800 (*b*), and 500 nm (*c*). Each of the figures shows SEM images of the test crystallites (Left-hand details). The right-hand detail in Figure (*a*) also shows a fluorescence saturation curve measured for a single  $\text{SiV}^-$  center (points — experimental data, solid line — approximation curve).  $g^{(2)}(\tau)$  and saturation curve were measured at room temperature and 660 nm continuous laser excitation.

saturation curves were measured using an avalanche photodetector (APDs, Excelitas SPCM-AQR-14-FC) with a bandpass filter (728–749 nm) and Mitutoyo $\times 100$  lens,  $\text{NA} = 0.7$ .

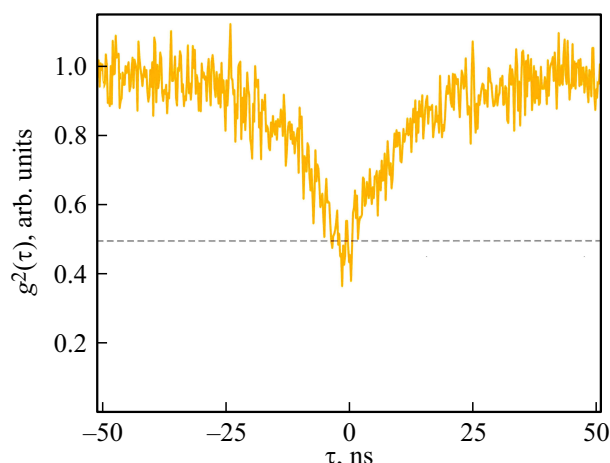
Intensity correlation functions of  $\text{NV}^-$  and  $\text{SiV}^-$  fluorescence,  $g^{(2)}(\tau)$  were defined using an experimental laboratory setup fabricated in accordance with the Brown–Twiss circuit using two APDs.

## Results and discussion

Fluorescent properties of 50 individual ND 200 to 500 nm in size were studied herein. Figure 1 shows two different PL spectra characterizing PL of the nanoparticles in a wide range. It is apparent that for some ND, besides  $\text{SiV}^-$  fluorescence (738 nm), quite weak (relative to the Raman scattering line of diamond (DR) at about 504 nm) PL of centers containing single nitrogen atoms is observed:  $\text{NV}^0$  (575 nm),  $\text{NV}^-$  (638 nm). PL spectra of other ND have a dominating band (520 nm) of more complex nitrogen

centers formed by two neighboring nitrogen atoms in a substituting (carbon atoms) position and by one vacancy (H3 or NVN). Such difference in spectra is associated with uneven distribution nitrogen, delivered from the DND precursor to the growth medium, across the sample. To remove this disadvantage, a technique for homogeneous mixing of DND with adamantane at the precursor preparation stage shall be developed.

To assess the number of  $\text{SiV}^-$  and  $\text{NV}^-$  centers in the ND of interest, we have measured second order autocorrelation functions  $g^{(2)}(\tau)$  for these emitters.  $\text{SiV}^-$  luminescence was excited by continuous laser excitation at 660 nm in order to minimize the noise component from more long-wave radiation of nitrogen centers. Single and double ( $g^{(2)}(0) = < 0.5$ )  $\text{SiV}^-$  centers were detected in many individual nanoparticles ( $> 70\%$ ) during analysis of 30 ND 250–300 nm in size (Figure 2, *a*). ND about 500 nm in size, according to the found value for  $g^{(2)}(0) \geq 0.8$ , contain already at least 5 centers  $\text{SiV}^-$  (Figure 2, *b*). For rare ND crystals about 800 nm in size (Figure 2, *c*), statistics



**Figure 3.** Intensity correlation function of  $\text{NV}^-$  fluorescence,  $g^{(2)}(\tau)$ , measured for an individual diamond crystallite  $\sim 300$  nm in size.  $g^{(2)}(\tau)$  was measured at room temperature and 532 nm continuous laser excitation.

of  $\text{SiV}^-$  emission turns into Poisson statistics, which is proved by the absence of dip in  $g^{(2)}(\tau)$ . For ND with one  $\text{SiV}^-$  center (Figure 2, *a*, Detail), typical saturation curve was shown. From approximation of this dependence, fluorescence saturation power equal to 45 mW and recorded photon emission rate equal to  $10^5$  counts/s were derived.

Analysis of  $\text{NV}^-$  fluorescence in HPHT–ND 250–300 nm in size during excitation by a continuous laser source at 532 nm has shown a wide scatter in the number of centers between particles, which is explained by extremely uneven nitrogen doping of the sample. In one of the ND of interest, fluorescence of a single  $\text{NV}^-$  center was detected (Figure 3). Insufficiently deep dip ( $g^{(2)}(0) \sim 0.5$ ) is explained by background luminescence at 638 nm from the phonon wing of  $\text{NV}^0$  centers excited simultaneously with  $\text{NV}^-$ . Thus, to increase the yield of individual ND 250–300 nm in size containing simultaneously single  $\text{NV}^-$  and  $\text{SiV}^-$  centers, homogeneous initial hydrocarbon mixing technique and further optimization of N/C in them are required.

## Conclusions

Luminescent properties of HPHT–ND synthesized from the mixture of adamantane–tetrakis–DND at atomic ratio Si/C  $\sim 1/10\,000$  and N/C  $\sim 1/30\,000$  were investigated. Using the measurement of second order autocorrelation functions  $g^{(2)}(\tau)$ , emission statistics of  $\text{NV}^-$  and  $\text{SiV}^-$  color centers was studied in individual diamond crystallites of various sizes at room temperature. It has been found that NDs 250–300 nm in size highly likely ( $> 70\%$ ) contain single  $\text{SiV}^-$  centers. Fundamental possibility of preparing diamond crystallites containing single NV and SiV centers that emit photons at two different wavelengths, 638 and 738 nm, respectively, was demonstrated. Such

two-colored sources of single photons have multimodality (possibility to use unique spin properties of  $\text{NV}^-$  centers together with luminescent properties of  $\text{SiV}^-$  centers) and increased selectivity to ensure enhanced functionalities of quantum optical technologies.

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## Conflict of interest

The authors declare that they have no conflict of interest.

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