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NV-centers in nanodiamonds: How good they are

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ABSTRACT

This paper presents a method for determination of the size distribution for diamond nanocrystals containing luminescent nitrogen-vacancy (NV) centers using the luminescence intensity only. We also revise the basic photo physical properties of NV centers and conclude that the luminescence quantum yield of such centers is significantly smaller than the frequently stated 100%. The yield can be as low as 5% for centers embedded in nanocrystals and depends on their shape and the refractive index of the surrounding medium. The paper also addresses the value of the absorption cross-section of NV centers.

1. Introduction

Recent 20 years have seen explosive increase of publications on nitrogen-vacancy (NV) centers in diamond [1]. A simple search of *Web of Science* reveals that the number of citations on the topic “nitrogen-vacancy” doubles approximately every 3 years and reached ten thousand in 2016 alone. The remarkable popularity of NV centers is based on their extraordinary photo-physical properties such as high photostability, sensitivity to magnetic fields, temperature and pressure, optical polarisation of electronic spin, optically detected magnetic resonance (ODMR) demonstrated even on a single center at room temperature.

Some of the applications of NV centers can profit greatly when the centers are imbedded in nearly perfect isotopically homogeneous crystals but other are feasible only with nanodiamond. An obvious example of the later is labeling for bio-imaging. A less obvious example is temperature measurements on a nanoscale. Application of NV centers for temperature measurements in nano-structures is problematic with bulk crystals because very high thermal conductivity of diamond will inevitably affect the temperature at the location of interest. Nanocrystals of diamond photo activated with NV centers are commercially available from several suppliers. However current methods of production by irradiation, annealing and crashing of high-temperature high-pressure (HTHP) micro-sized crystals result in nanocrystals which are much more inhomogeneous than other common bio-labeling agents such as dye molecules or quantum dots. We will investigate this inhomogeneity in the next section.

A number of reviews are available on sensory applications and photo-physical properties of NV-centers [1–4] but readers should bear in mind that these reviews quickly age except for the parts dealing with

most fundamental characteristics. In the following sections we will focus on some of these fundamentals to see if all the common claims about the NV-centers are sufficiently justified.

2. Brightness of nanodiamonds

Specific brightness (the maximum number of photons which can be detected from a unit volume of the material) is an important figure of merit for many applications. This characteristic of luminescent nanodiamonds has been investigated using commercially available 70-nm fluorescent nanodiamond from Sigma-Aldrich. Product # 798169 is supplied in deionised water at mass concentration of diamond at 1 mg/mL and advertised concentration of NV centers of more than 300 per crystal. For the purpose of this research, the concentration of diamond in the suspension has been decreased to $C_D \approx 5 \times 10^{-4}$ mg mL⁻¹ (2000 times dilution) and a small drop of it (volume $V_{\text{drop}} \approx 8.4 \times 10^{-5}$ mL) has been deposited on a pre-cleaned glass microscope slide. Additionally, a number of water droplets has been placed around the drop of suspension to reduce formation of a coffee ring [5,6]. After drying, the crystals were distributed approximately homogeneously on the slide within an approximately round spot of about 1.2 mm in diameter. The photon count rate for each crystal has been measured under continuous 50-mW excitation at the wavelength of 532 nm (measured at the output of the exciting laser, Coherent Verdi-V5). The luminescence has been collected with a microscope objective, Numerical Aperture (NA) of 0.9 and detected by a photon counting CCD (Andor iXon). The maximum power density of the excitation light beam on the slide has been estimated at about 3.5 kW/cm². The dependence of the detected count rate, $k_r^{(\text{det})}$ on the excitation power P has been measured for 9 nanocrystals and followed a typical saturation curve [7]

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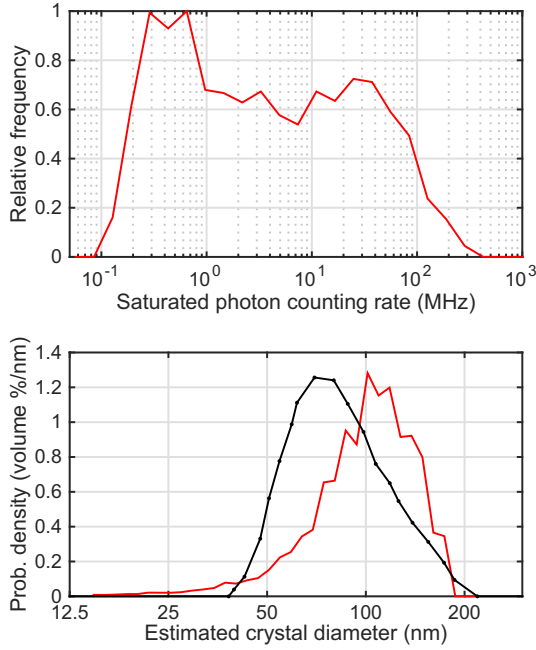


Fig. 1. Distribution of the count rates (top panel) and diameters of the crystals (bottom panel) in a drop of diamond suspension. The bottom panel shows DLS data (filled circles) for comparison.

$$k_r^{(\text{det})} = \mathcal{R}^{(\text{det})} \frac{P}{P + P_s} \quad (1)$$

The average saturation power, P_s for this set has been estimated at the level of 0.9(3) W for the case of a crystal in the center of the illuminated area (the corresponding average saturation intensity is $70 \pm 15 \text{ kW/cm}^2$ in agreement with [8] but the standard deviation in the sample was about 30% of the mean). The value of $\mathcal{R}^{(\text{det})}$, the maximum detectable photon count rate for each crystals can be estimated using the count rates measured at the excitation power of 50 mW and the value of P_s . We have also taken into account the variation of the laser light irradiance across the spot illuminated with the laser. This variation has been determined using weak luminescence of substrate which is proportional to the irradiance. The relatively large uncertainty in the saturation power was a little problem for the following as the observed distribution of the saturated count rates has varied from crystal to crystal by a factor of 1000 as can be seen in the top panel of Fig. 1. If the number of NV-centers per crystal is (as advertised) larger than 300 for each crystals, then some of the crystals should have about a million of such centers (unless many of these centers are very dim in the crystals with low $\mathcal{R}^{(\text{det})}$). To clarify this problem, we will analyse the size distribution of the crystals using the luminescence data.

The total volume of the diamond in the drop can be deduced from the mass concentration of the diamond, the volume of the drop and the density of the diamond. This value should be equal to the sum of $\mathcal{R}_j^{(\text{det})}/\beta_j$ over all the crystals in the drop

$$\frac{C_D V_{\text{drop}}}{\rho} = \sum_{j=1}^N \frac{\mathcal{R}_j^{(\text{det})}}{\beta_j}, \quad (2)$$

where $\rho \approx 3.5 \text{ g cm}^{-3}$ is the density of diamond crystal and β_j is the maximum number of photons detected from j -th crystal divided by its volume. Assuming that $\beta_j \equiv \beta$ is the same for all the crystals, one can find the value of β from Eq. (2) and then determine a diameter of each detected crystal using their volumes $V_j \approx d_j^3 \pi/6$ and the corresponding maximum detectable rates $\mathcal{R}_j^{(\text{det})}$.

$$d_j = \left(\frac{6C_D V_{\text{drop}} \mathcal{R}_j^{(\text{det})}}{\pi \rho \sum_{j=1}^N \mathcal{R}_j^{(\text{det})}} \right)^{1/3} \quad (3)$$

The result of such calculations is shown in the bottom panel of Fig. 1. The distribution of the diameters measured by dynamic light scattering (DLS) is also shown and demonstrates quite a reasonable agreement with the distribution obtained from the luminescence measurements (especially given the assumptions and approximations made in the data analysis). The estimated value of β is 150 Hz/nm^3 . In addition to the inaccuracy of the approximations introduced above, a small mismatch between the position of the maxima in the two distribution (70 and 100 nm) can be explained by the assumption that some of the crystals do not have detectable NV-centers (strictly speaking C_D should refer to detectable diamonds only).

Given that about 10% of emitted photons are detected by our setup (see more details below), the estimated value of β corresponds to an absolute specific brightness of about $1.5 \times 10^3 \text{ photon/nm}^3$. If we take the mean diameter of the crystals (averaged by volume) to be 100 nm (in agreement with the distribution shown in Fig. 1) and the advertised 300 NV centers as the value for such an average size, then the emission photon rate is 2.5 MHz per NV-center.

In summary, this experiment shows that commercially available diamonds can be characterised by a specific brightness. This observation suggests a uniform concentration of NV-centers as a reasonable approximation. The wide inhomogeneity of the overall brightness mainly results from a wide distribution of the crystal volumes in the supplied material.

But does the observed specific brightness matches up with what we know about the photophysical properties of the NV-centers? Note that 2.5 MHz is 16 times smaller than a frequently reported luminescence decay rate of 40 MHz (25 ns lifetime). The answer to this question will be one of the main subjects of the following discussion.

3. Interaction with electromagnetic fields

The interaction of photons with an NV center embedded in a crystal of diamond presents a significant theoretical challenge at the level of microscopic fields inside the crystal. But when these microscopic fields are averaged, one gets macroscopic fields which are much easier to calculate. In principle, identical macroscopic fields can correspond to different microscopic fields but one can assume a one-to-one correspondence between macroscopic and microscopic fields acting on a single NV center in a perfect diamond crystal. If the center resides in a sufficiently large nanocrystal and we can ignore interaction of the NV with any other impurities or defects then equal macroscopic fields in the nanocrystals and in bulk will correspond to equal microscopic fields acting on the NV-center. We will use this equality in the following review of the basic principles of NV-photon interaction and the corresponding dynamics of populations.

3.1. Absorption cross-section

The optical absorption cross-section is defined by the equality

$$k_{lu} = \sigma I \quad (4)$$

where k_{lu} is the excitation rate from the lower electronic state to the upper electronic state and I the photon flux (expressed in units of $\text{photon s}^{-1} \text{ m}^{-2}$). Note that k_{lu} multiplied by the energy difference between the upper and the lower states gives the absorbed power. One should keep in mind that the excitation rate for a typical case of an electric-dipole transition is proportional to $\cos^2 \theta$, where θ is the angle between the microscopic electric field and the direction of the transition dipole. The NV-centers have two mutually orthogonal electrical-dipole transitions due to two electronically excited degenerate states ^{3E}

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