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Effects of the hosting nano-environment modifications on NV centres fluorescence emission☆

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ABSTRACT

The spontaneous emission rate properties of diamond nitrogen-vacancy (NV) centres are largely dependent on the hosting material, especially in nanodiamond. Inside a nanodiamond the fluorescence emission dramatically deteriorates as compared with the case where the defect is embedded in single crystal diamond. In addition the nano-environment, i.e. the hosting nanodiamond, can modify the spontaneous emission properties. It is important to study and identify the mechanisms responsible for these modifications to eventually employ the defect as a sensor of local density of states or to achieve emission enhancement. In this work, we summarize our approach to separate the electromagnetic effects, inducing radiative modification in the spontaneous emission of NV, from other non-radiative effects, these last leading to the quenching of NV emission. We also observe blinking which may be associated with photo-induced charge fluctuations by these additional non-radiative decay channels.

1. Introduction

Remarkable inherent spin and optical properties, such as room-temperature photo-stability and convenient optical manipulation of its electron spin, have led to the emergence of the negatively charged diamond nitrogen-vacancy centre, as a viable candidate for applications in various research fields including quantum optical technologies [1], high-resolution magnetometry [2], sub-wavelength resolution imaging [3,4], and biomedical imaging/tracking [5]. Most of these applications rely on a high signal to noise ratio and photo-stability of the single photon emission from an NV centre as its spin state information, altered by the magnetic field of a nearby object, is read-out optically. In addition, applications that aim to achieve the highest sensitivity in magnetic sensing in material science and biological magnetic resonance imaging are highly dependent on the NV separation from the neighbouring sources of electric/magnetic fields to be sensed [2]. This requires the NV centre to be enclosed inside very small nanodiamonds.

The NV emission is well known to deteriorate drastically in terms of spectral diffusion and photo-stability on moving from a monolithic ultra-pure single crystal diamond host to its counterpart nanosized crystal [6,7]. Despite progress in identifying and characterizing the deterioration of NV spontaneous emission from bulk diamond to nanodiamonds [6,8–10], an observed reduction of the NV spontaneous emission saturation count rate in progressively smaller nanodiamonds cannot be explained by purely electromagnetic arguments [11–13]. It has now been clearly established that nanodiamond NV emission features a significant non-radiative contribution [12,13] and calculations considering purely radiative emission display a large disparity with the observed emission rates [11]. A recent study by Mohtashami and Koenderink also found other experimental evidence of a large distribution in the NV quantum efficiency(QE) related to the nanodiamond size [12]. For single NV centres in bigger 100 nm diamond crystals the QE was observed to be widely distributed between 10% and 90% but for smaller crystals of size around 25 nm, the QE was found to be limited to just 0–20%. The non-radiative factors leading to this discrepancy may include the quenching from the outer graphite shell [14], photo-induced charge conversion between the NV^- and NV^0 charge states [10], surface chemistry [15] and other factors such as spectral diffusion, largely related to NV emission within the nanodiamond lattice. By studying NV emission in a nearly substrate-free aerogel environment of refractive-index close to unity ($n \sim 1.05$), we estimated an upper-bound for the mean QE in nanodiamond ~50 nm as $\eta = 0.7$ [13]. The commonly-used assumption of near-unity quantum efficiency in earlier studies [16,17] is thus no longer appropriate.

It is therefore essential to fully characterise the NV centre spontaneous emission in nanodiamonds and identify the mechanisms responsible for the radiative and non-radiative modifications of the spontaneous

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emission. A number of approaches have been successfully employed to manipulate the rate of radiative spontaneous emission of NV dipole emitters by altering the local electromagnetic environment [18–21]. In this picture, it is possible to model the radiative spontaneous emission changes by treating the NV centre as a dipole radiating inside a nanodiamond crystal via FDTD calculations [11,13,21].

In this work we describe our strategy to separate the modification of the NV spontaneous emission due purely to electromagnetic effects and that due to other effects related to the advent of non-radiative channels.

To more closely identify the mechanisms responsible for the deterioration of NV spontaneous emission, we dynamically studied the spontaneous emission from a single nanodiamond NV centre while shrinking the size of the host diamond crystals via air oxidation from large diamond crystals down to nanodiamond scale [22]. As a guide we also used the modeling of the radiative emission due to the nano-diamond size reduction. As the size of the host crystal shrinks to the nano-regime, the NV emission rate is predicted to be highly suppressed by the Lorenz–Lorentz reduction of the local electric field inside the sub-wavelength dielectric crystal [11,23]. On electromagnetic grounds then, the high refractive index of diamond should favour a strong electromagnetic suppression of the count rate and an increase in the decay lifetime for smaller crystals. Any departure from this behaviour is evidence for changes in the non-radiative dynamics. To track these modifications, we continually monitored the spontaneous emission decay rate, saturation count rate and photon statistics of the single-NV centres. The method of air oxidation is one of the many techniques currently used to control the surface disorder and inhomogeneity of the nanodiamonds surface that can otherwise induce quenching to some of the structural defects, photoluminescence and lifetime modification even in nanodiamonds of 100 nm size. However from our study air oxidation is not immune from introducing other modifications in the NV spontaneous emission. In fact in one case we also observe the onset of blinking with interesting excitation power dependence. We correlate this blinking with the presence of additional non-radiative channels for the NV centre, introduced by the oxidation process at 580 °C. This result suggests other possible causes than electron tunnelling or photo-induced charge conversion as being responsible for blinking which could be worth further investigation.

2. Methods and materials

To identify the radiative modification of NV spontaneous emission we used finite-difference time-domain (FDTD) electromagnetic calculations. Here we show as an example the ideal case of a spherical nanodiamond. Fig. 1(a) shows the continuous suppression of the emission rate with decreasing diamond crystal size for a dipole radiating inside a diamond sphere. For a sub-wavelength diamond sphere of radius $a << \lambda$, the emission rates are drastically suppressed due to the large reduction of electric field within the diamond sphere i.e. Lorentz–Lorenz effect.

According to the analytic results of Chew [23] for the spontaneous emission rate of a dipole inside a sub-wavelength sphere ($a << \lambda$) emitting in air, the emission rate is independent of the dipole location and polarization within the sphere and goes as:

$$\Gamma = \Gamma^{\infty} \frac{1}{\sqrt{\epsilon}} \left(\frac{3}{\epsilon + 2} \right)^2,$$

where $\epsilon = n^2$ and Γ^{∞} is the rate corresponding to a uniform medium density of states in a macroscopic piece of the same material (bulk decay rate). A large suppression in the emission rate and a corresponding increase in the lifetime can be observed. This corresponds to a reduction in the local density of states (LDOS) by an equivalent factor of $9/(n^2 + 2)^2$. As a consequence of the Maxwell boundary condition, the electric field is strongly expelled from within the high dielectric sub-wavelength diamond sphere. This effect is clearly displayed in Fig. 1(c) as an example for the case of an NV dipole emission within a 50 nm diamond sphere. Any increase in the decay rates (measured lifetime^{-1}) with reducing diamond crystal size is therefore expected to result from the non-radiative NV decay contributions. In the experimental case the nanodiamonds' shape is typically non uniform. In our previous work [13], we determined that the large variability of NV lifetime in nanodiamonds of average size 45 nm can be due to the irregular geometry of the host nanodiamonds. Geometries with sharp edges (i.e. cube or trapezoid) will give rise to sharp changes in the dipole electric field patterns nearby, resulting in a broader distribution. However for the specific experiment it was difficult to perform in addition to an AFM/confocal imaging, a SEM image of the nanodiamonds to achieve the shape information needed to implement the computational model. Nanodiamonds of 50 nm indeed at SEM and TEM tend to have an irregular shape, therefore we are limited to a qualitative theoretical analysis by using the analytical expression of the decay rate for a spherical nanodiamond.

For the experiment, we used a commercially available polishing grade HPHT diamond (type Ib) solution in MilliQ water (Van Moppes, SYP-GAF 0.5–1 μm, 60 mg/ml). From the as-received solution we sorted the correct concentration and initial size by Dynamic Light Scattering method, obtaining a solution with average initial size of 500 nm. Agglomeration in this solution was also reduced by ultra-sonication methods. The dispersed solution of diamonds in water was eventually sprayed onto a glass cover slip (Menzer–Glaser) which was laser inscribed with a 5 × 5 grid consisting of 50 × 50 μm squares. This grid facilitated identification of the same diamond crystals over consecutive oxidation steps.

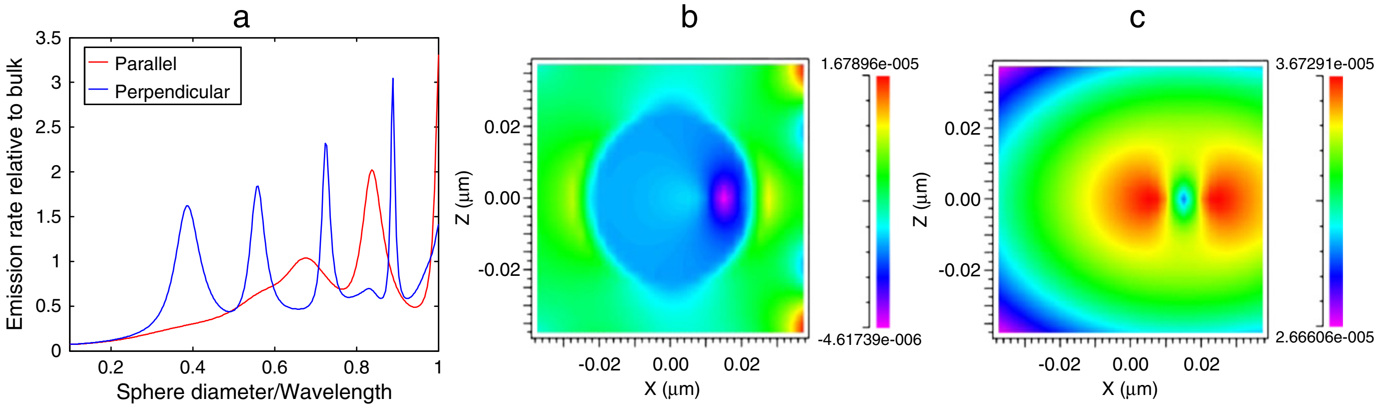

Fig. 1. (a) Emission rates relative to bulk diamond for an NV dipole located inside an isolated diamond sphere as a function of sphere diameter. The dipole is positioned at a distance of 0.6 *a* from the centre. Emission rates are shown for dipole orientations perpendicular and parallel to the radius vector of the dipole from the centre of the sphere. The electric field profile (*Ex*) for an NV dipole radiative emission inside (b) a 50 nm sphere with the dipole being positioned at a distance of 0.6 *a* from the sphere centre and is pointing in the X-direction and (c) a bulk diamond sphere.