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Control of spontaneous emission rate in luminescent resonant diamond particles

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Abstract.
    We study the properties of luminescent diamond particles of different sizes (up to ~ 1.5 μm) containing multiple NV-centers. We theoretically predict that the average liftetime in such particles is decreased by several times as compared to optically small subwavelength nanodiamonds. In our experiments, samples were obtained by milling the plasma-enhanced chemical vapor deposited diamond film, and characterized by Raman spectroscopy and dark-field spectroscopy methods. Time-resolved luminescence measurements of the excited state of NV-centers showed that their average lifetime varies from 10 to 17 ns in different samples. By comparing this data to the values of the lifetime of the NV-centers in optically small nanodiamonds, known from literature, we confirm a severalfold decrease of the lifetime in resonant particles.

1. Introduction

Resonant high-refractive-index nanoparticles and nanostructures represent a promising platform for effective light manipulation at nanoscale and pave the way for creation of novel photonic devices. Interaction of a quantum emitter with one or several dielectric particles allows to significantly alter its radiation pattern and spontaneous emission rate [1]. Diamond particles containing colour centers such as nitrogen-vacancy, silicon-related and nickel-related centers [2] are of special interest in this context. They can be viewed as a single photonic nanodevice with emitting source embedded inside a diamond particle. Indeed, relatively high refractive index ($n \approx 2.4$) of the diamond and almost zero absorption in visible frequency range make it possible to exploit the morphology- and size-dependent resonance properties of the diamond particles to control the emission properties of luminescent centers [3], which is of particular interest for the development of quantum emitters [4, 5]. In particular, the NV-centers in diamond are of a great importance as sources of single photons, that provide the zero-phonon-line (ZPL) emission in the photoluminescence (PL) spectrum at 637 nm even at room temperature.

    Usually, the NV-centers are coupled to the photonic nanostructures in order to manipulate their radiating properties and decrease the emission into phonon sidebands [6]. As an example, coupling of a single NV-center to a photonic crystal cavity fabricated in a single-crystal diamond provides 70% emission of photons with ZPL wavelength into the cavity mode [7]. However, such systems are hard to fabricate and integrate with other nanophotonic devices. On the other

hand, resonant diamond particles containing light-emitting point defects in fact represent an integral active optical element. Moreover, recent theoretical studies predict the increase of the spontaneous emission rate of quantum sources embedded within the high-index dielectric particles with the Mie modes [8, 9, 3]. Thus, the creation of active nanoantennas based on resonant nanodiamonds with embedded NV-centers is of a high importance not only for nanophotonics in general, but also for different areas of the modern science ranging from quantum information processing to optical bioimaging and sensing.

Here, we study active dielectric nanoantennas made of resonant diamond particles of different sizes up to ∼1.5 μm with incorporated luminescent NV-centers. We study theoretically the emission properties of NV-centers affected by resonance structure of diamond particles. We realize such nanoantennas experimentally and demonstrate the effect of the lifetime reduction of NV-centers due to the presence of resonances in the nanoantenna.

2. Theoretical background
First, we perform a theoretical analysis of optical properties of a spherical diamond nanoparticle. Despite that in our experiments nanodiamonds have complex shapes, such simplified model can provide a good qualitative results. This was demonstrated recently by comparing the theoretical and measured scattering spectra of nanodiamonds with the diameters of 250-450 nm [3].

It is known, that spherical dielectric particles support numerous resonant modes, whose frequencies and mode profiles can be found analytically. The type of resonance depends on the particle size, which in the case of diamond particle should be larger than $R \approx 100$ nm, when the first magnetic dipole resonance appears [3]. Placing the quantum emitter with luminescence frequency that matches the mode resonance frequency near the maximum of the field distribution of the mode can substantially enhance its emission rate, which is known as Purcell effect. Since at resonances the field is enhanced inside dielectric particles, we may expect the enhancement of luminescence rate for the NV-centers embedded inside the diamond particles. The calculation of emission rate can be performed with classical approach developed in Refs. [10, 11]. One can show that in small subwavelength particles (with the size $\lesssim 150$ nm in the case of diamond) the emission rate is substantially suppressed due to low local density of optical states [11], while multipole resonances with high quality factors can significantly enhance the emission rate in larger spheres [8]. In fact, due to a non-spherical shape of real diamond particles, significant roughness and possible contamination of the surface, the quality factors of these resonances and consequently Purcell factor can be reduced. This is confirmed by the absence of high-Q resonances in the experimentally measured scattering spectra. The calculations also predict that the values of the Purcell factor in different locations and for different dipole orientations can differ by several times. To take into account presence of a large number of randomly oriented emitters inside the diamond particle, we average the Purcell factor over all possible orientations of the emitters and the volume of the particle (assuming the uniform distribution of the NV-centers inside the particle), i.e. we calculate the ratio of the average radiative decay rate of the emitter inside the particle to the corresponding rate in the bulk diamond. Furthermore, the luminescence spectrum of NV-centers at room temperature spans over a broad spectral range from about 600 nm to 800 nm due to phonon sideband transitions. Strong spectral variation of the Purcell factor, caused by the resonant nature of nanoparticles, implies the same variation for the emission power. In order to estimate the possible values of the total decay rate we also normalize calculated Purcell factor to the typical luminescence spectrum of NV-centers in spectral range 620-770 nm measured in our experiments. Overall the calculation formula for
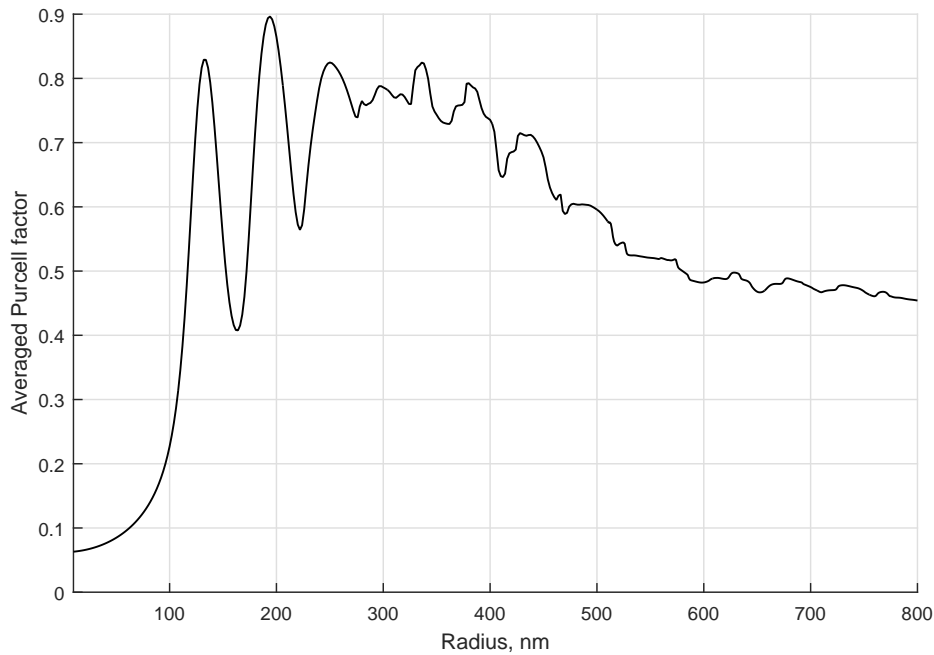
Figure 1. Purcell factor averaged over the volume of the spherical dielectric particle with permittivity $\varepsilon = 5.76 + 0.01i$ and over spectral range 620–770 nm as a function of its radius.

averaged Purcell factor $\overline{F_p}$ is the following:

$$\overline{F_p} = \frac{\int\limits_{\nu_{min}}^{\nu_{max}} \iiint\limits_{V} F_p(\mathbf{r}, \nu)\, dV\, P_0(\nu)\, d\nu}{V \int\limits_{\nu_{min}}^{\nu_{max}} P_0(\nu)\, d\nu},$$

here $F_p(\mathbf{r}, \nu)$ is the Purcell factor that depends on the position of the emitter and the emission frequency, V is the volume of the particle, $P_0(\nu)$ is the typical luminescence intensity spectrum of NV-center. Since in the measured scattering spectra of the studied particles we observed only low-Q resonances, we do not expect high values of the Purcell factor, that are predicted for lossless spherical particles with high-Q resonances. Therefore, in our calculations we introduce small material losses and describe our nanoparticles with constant dielectric permittivity ($\varepsilon = 5.76 + 0.01i$). Note, that losses were introduced only to avoid the appearance of the high-Q resonances, and therefore additional nonradiative decay rate caused by lossy medium was not taken into account. The resulting average Purcell factor is shown in Fig. 1. From these calculations, we can expect that the averaged lifetime of NV-centers in a resonant diamond particle can be reduced by $\gtrsim 3$ times as compared to nonresonant ones.

3. Experimental results
Diamonds particles were made by miling the diamond film fabricated by plasma-enhanced chemical vapor deposition (PECVD) method on a glass substrate [12, 13]. PECVD process was used with a gas source of methane (CH_4). NV-centers formation was achieved due to nitrogen implantation during the PECVD growth. Images of nanodiamonds were obtained using scanning electron microscope (SEM); an example of the nanodiamond is shown in the inset in Fig. 2(a).
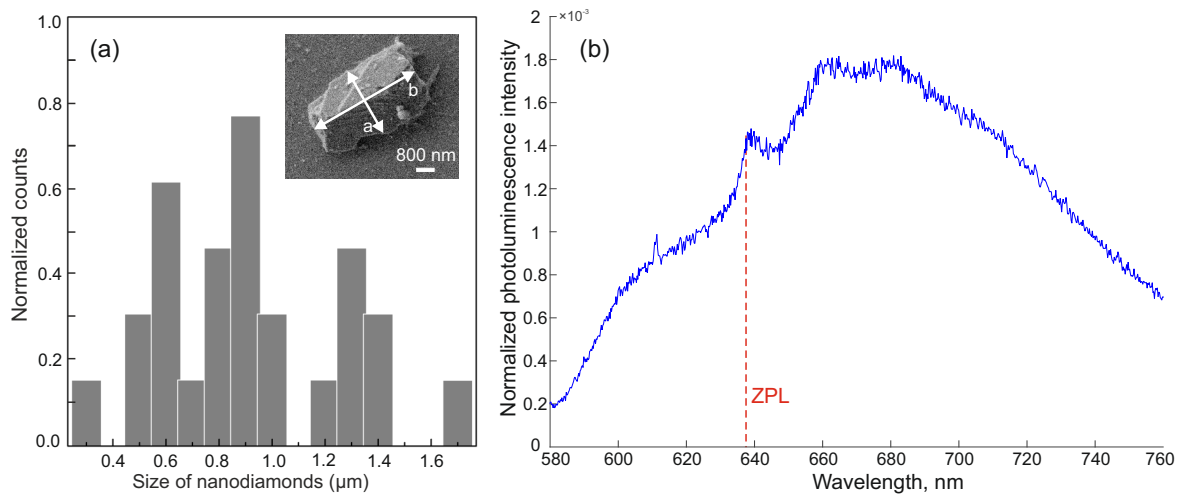
Figure 2. (a) Size distribution histogram (statistics on ∼100 nanodiamonds) measured by SEM; inset — SEM image of a nanodiamond. (b) Typical luminescence spectrum of a diamond particle with NV-centers.

The fabricated nanodiamonds had irregular shapes with rough surfaces, and we measured the characteristic sizes as shown in the insert in Fig. 2. Statistical distribution of the nanodiamond sizes is shown in Fig. 2(a), indicating median size of fabricated particles of 900 nm.

In order to study the phase composition of nanoparticles, we measured Raman scattering spectra for individual particles and applied a Gaussian fit to distinguish the characteristic Raman peaks. The analysis of nanodiamonds revealed that there were two types of nanoparticles: crystalline rough-surface and nearly spherical nanodiamonds. The Raman spectra of rough-surfaced nanodiamonds have a distinct line at 1332 cm^{-1} [14], which indicates a strong Raman scattering at the sp_3 vibrational resonance (C-C pair) of diamond lattice and proves the presence of crystalline phase of diamond. The spherical nanodiamonds that had no zero-phonon line in photoluminescence spectrum exhibited two broad asymmetric peaks at 1332 cm^{-1} and 1590 cm^{-1} — the typical vibrational resonances of surface bounds [15]. This analysis allowed us to eliminate some particles from consideration, and focus only on several particles with the pronounced and intense Raman peak at 1332 cm^{-1}. A further study of the PL spectra of selected nanoparticles reveals that most of them (more than 40 particles) demonstrate a pronounced peak at 637 nm, indicating the presence of NV-centres in the volume of the nanodiamond particle [see Fig. 2(b)].

To characterize luminescence, NV-centers were non-resonantly excited by a 532 nm laser and the lifetime measurements of the excited state were carried out by the time-correlated single photon counting method. Due to the presence of a large number of emitters randomly oriented inside the samples we have observed a nonexponential character of the time dependence of the signal, that indicates that the lifetimes of different NV-centers vary continuously in a wide range, from nanoseconds to tens of nanoseconds. Examples of time-resolved measurements are shown in Fig. 3.

Next, we compare the average lifetime in different resonant diamond particles (44 particles were measured) with the lifetime in subwavelength nonresonant nanodiamonds, for which the data is available from literature. Analytical calculations predict the severalfold enhancement of the Purcell factor for the NV-centers in large diamond nanoparticles as compared to NV-centers in subwavelength nanodiamonds. According to the literature [16, 17, 18, 5] negatively charged NV-centers in optically small ($\lesssim$ 100 nm) nanodiamonds on a glass substrate exhibit the lifetime of at least 20-25 ns. In our experiments the averaged lifetime of emitters in large
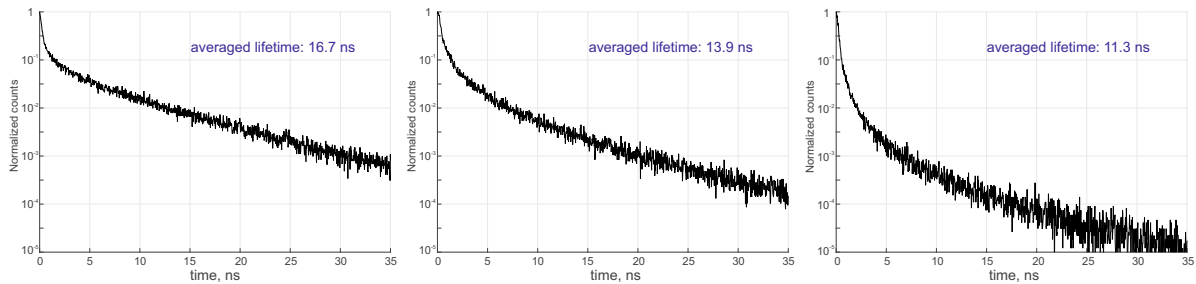
Figure 3. (a-c) Time-resolved PL measurements for three diamond particles in logarithmic scale.

resonant particles lies in the range of 10-17 ns, which is 1.5-2.5 times smaller. We also notice that the lifetime of emitters in large particles is almost unaffected by the presence of a glass substrate, while it is reduced in the case of subwavelength nanodiamonds. NV-centers lifetime in nanodiamonds placed on a porous silica substrate (with the refractive index close to 1), measured in the Ref. [17], demonstrated that the lifetime increases to more than 30 ns without a substrate. Thus, our expermiental results are in good agreement with predictions presented in Fig. 1.

4. Conclusions
We have demonstrated the possibility to control the lifetime of NV-centers via interaction with the eigenmodes of diamond-based optical nanoantennas. We have verified this experimentally for diamond particles having sizes ranging from 300×300 nm to 1.5×2 μm, supporting Mie-type resonances. We have demonstrated that the resonances of large diamond particles affect the photoluminescence properties of the NV-centers providing acceleration of their emission. We have observed a multifold decrease of the lifetime of the NV-centers in the studied diamond particles, as compared to subwavelength nanodiamonds, being in a good agreement with theoretical calculations for the average Purcell factor in the case of multiple NV-centers within a nanoparticle.

Acknowledgments

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