Purcell enhancement of fluorescence from silicon-vacancy color centers in Mie-resonant luminescent diamond particles

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Abstract. Over the past two decades, nanosized diamond particles with various luminescent defects have found numerous applications in many areas from quantum technologies to medical science. The size and shape of diamond particles can affect drastically the luminescence of embedded color centers. Here we study diamond particles of 250–450 nm in size containing silicon-vacancy (SiV) centers. Using dark-field scattering spectroscopy, we found that fundamental Mie resonances are excited in the spectral range of interest. We then measured the fluorescence saturation curves under continuous excitation to estimate the effects of the excitation and Purcell factor enhancement on the luminescent properties of the studied particles. The results show that the saturation excitation intensity differs by several times for particles of different sizes which is well explained by the numerical model that takes into account both the Purcell factor enhancement and resonant excitation.

1. Introduction
The ability of the environment to influence the spontaneous emission rate has been well known since the middle of the last century and is the essence of the Purcell effect. Recent interest in this field was triggered by the active development of quantum optics and the growing demand for efficient single-photon sources with controllable directionality [1, 2]. Among the most promising candidates for this role are color centers in diamond providing highly stable non-bleaching luminescence at room temperature [3].

A quantitative measure of the Purcell effect, known as the Purcell factor, is defined as the ratio of the spontaneous emission rate of an emitter placed in the environment and the one of the same emitter in an infinite homogeneous medium. For subwavelength particles in the absence of an external resonator, it is usually much less than unity. A number of papers, however, predicted an increase in the Purcell factor at the excitation of fundamental morphological resonances in
the hosting particles [4, 5, 6]. The experimentally observed dispersion in the emission rate of chromium [7] and nitrogen-vacancy [8] color centers in subwavelength diamond crystals was considered to be a manifestation of these resonances.

In this contribution, we report on an experimental study of the Purcell enhancement of fluorescence from silicon-vacancy color centers in Mie-resonant luminescent diamond particles. We characterize our samples using dark-field scattering spectroscopy and measure the saturation power as a function of the particle size. The saturation power, which is determined both by the resonant field enhancement at the pump frequency and the transition rate at the luminescence frequency, is additionally calculated numerically. Finally, we compare the obtained results and discuss their significance for future research.

2. Results and discussion
The studied sample of diamond particles was synthesized from a mixture of adamantane (C_{10}H_{16}) and tetraphenylsilane (C_{24}H_{20}Si) at a mass ratio of 80:1 at a temperature of 1900 K and a pressure of 8–9 GPa. After the purification process, diamonds were dispersed on a glass substrate from a water suspension.

The schematic representation of the luminescence experiments is presented in Figure 1a. For the excitation, continuous-wave laser radiation at a wavelength of 532 nm was used. The excitation beam was directed to the sample from the side of the substrate using an objective lens with a numerical aperture (NA) of 1.2 at an aperture filling factor corresponding to the resulting beam NA of 0.9. The fluorescence was collected in reflection geometry by the same objective and directed into an Ocean Optics QEPro spectrometer. A typical luminescence spectrum is shown in Figure 1b. By recording the luminescence signal at different excitation power values, we obtained the saturation curves for each particle (see Figure 1c). The saturation curves were fitted by the law $I = I_\infty P / (P + P_{sat}) + kP$, where $I$ is the luminescence intensity, $I_\infty$ is the saturation luminescence intensity, $P$ is the excitation power, $P_{sat}$ is the saturation excitation power, and $kP$ represents the background signal. In this way, the saturation power $P_{sat}$ was measured for 17 particles.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** (a) Schematic of the experiment; SiV, silicon-vacancy; PL, photoluminescence. (b) Typical luminescence spectrum of an individual diamond particle. (c) Saturation of SiV centers luminescence. Squares — measured luminescence signal, solid line — approximation.

To reveal the fundamental modes of the studied particles, dark-field scattering spectroscopy was performed. The experimental setup is described in [9], Supporting information. After the measurements were completed, we compared the measured spectra with numerically calculated ones (see Figure 2). Based on this comparison, we have assigned an effective size for each particle (see [10] for details).

To estimate the dependence of the saturation power on particle size, we performed numerical calculations for spherical diamond particles on a glass surface. For each emitter, the saturation
power is proportional to the spontaneous transition rate and inversely proportional to the excitation enhancement. Figure 3 shows the calculated electric field under Gaussian-beam excitation for diamond spheres of three resonant diameters.

The spontaneous transition rate can change due to the Purcell effect. For each sphere diameter, we have simulated an electric dipole oscillating at the frequency of SiV transition. The Purcell factor was calculated for different positions inside the sphere and three orthogonal polarization of the emitter. We have additionally calculated the integral far-field intensity directed into the experimental collection angles. The results of the simulations showing the excitation of the magnetic dipole and magnetic quadrupole resonances by an embedded dipole source are presented in Figure 4.

According to our direct measurements of the excited state lifetime in the studied particles, the spontaneous emission rate varies only for 5% that can be explained by the low quantum yield.
Figure 4. Dipole radiation in spherical diamond particles. (a), (b) — Electric field distribution in spherical diamond particles of diameter 290 and 420 nm. The positions and polarization of the dipoles are marked. The part of non-resonant fields is removed by apodization in the time domain.

of SiV centers. Taking it into account, we can omit the emission rate variations and estimate the saturation power of an individual emitter as

\[ P_{\text{sat}} \propto \text{const} / |E(\lambda_{\text{exc}})|^2, \]

where \( |E(\lambda_{\text{exc}})|^2 \) is the excitation electric field inside the particle at \( \lambda_{\text{exc}} = 532 \text{ nm} \). To estimate the total saturation power of an ensemble of SiV centers, we calculated the averaged saturation power as follows:

\[
\langle P_{\text{sat}} \rangle \propto \frac{\sum_\alpha \int_V I_\alpha(\lambda_{\text{em}}) / |E(\lambda_{\text{exc}})|^2 dV}{\sum_\alpha \int_V I_\alpha(\lambda_{\text{em}}) dV},
\]

where \( I_\alpha(\lambda_{\text{em}}) \) is the far-field intensity of a dipole oscillating at \( \lambda_{\text{em}} = 738 \text{ nm} \) and \( \alpha = \{1, 2, 3\} \) represents the dipole polarization. The term \( I_\alpha(\lambda_{\text{em}}) \) was introduced as a weighting factor.

Figure 5 shows the resulted dependence in comparison with the experimental results. Although experimental data are not consistent with the predicted dependence, the observed dispersion of the measured values is in agreement with the model. We conclude that these measurements reveal the effect of Mie resonances, which is much less apparent in life-time measurements due to the low quantum efficiency of the studied centers. This effect, however, should not be omitted when single-photon emission from isolated particles is studied and the lifetime dispersion is interpreted.

Figure 5. Dependence of the saturation power on the diamond particle size. Circles — experiment, solid line — calculations.
Conclusions
In conclusion, we have experimentally demonstrated the effect of Mie resonances of subwavelength diamond particles on the saturation of fluorescence from their SiV centres. The results demonstrate that the efficiency of diamond-based devices can be improved by choosing particles of a proper size.

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