Spontaneous emission of a nanoscopic emitter in a strongly 
scattering disordered medium

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Abstract

Fluorescence lifetimes of nitrogen-vacancy color centers in individual diamond nanocrystals were measured at the interface between a glass substrate and a strongly scattering medium. Comparison of the results with values recorded from the same nanocrystals at the glass-air interface revealed fluctuations of fluorescence lifetimes in the scattering medium. After discussing a range of possible systematic effects, we attribute the observed lengthening of the lifetimes to the reduction of the local density of states. Our approach is very promising for exploring the strong three-dimensional localization of light directly on the microscopic scale.

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The behavior of electromagnetic waves in disordered media has been a subject of intense studies in the past decade [1–6]. In particular, the regime of strong scattering where the mean free path of a photon becomes comparable to its wavelength has fascinated scientists. In such systems, constructive and destructive interference can lead to the modification of the local density of states (LDOS) in various spatial modes and to the localization of light [7–9]. In an ideal “gedanken” experiment, one might imagine to map the fluctuations of LDOS directly at the subwavelength level. However, so far, light scattering phenomena have been studied via transmission and reflection intensity measurements on macroscopic samples, where separation of the effects of absorption and scattering has posed a challenge [1–3, 6, 10]. In this work, we probe the variations of LDOS by measuring the modification of the spontaneous emission rate of individual nanoscopic emitters. Our experimental strategy is to characterize the fluorescence decay of each emitter first and then trace its change after covering them by a scattering disordered medium.

As emitters, we used nitrogen-vacancy (NV) color centers in diamond nanocrystals (DNC). The size of the DNCs ranged between 10 and 500 nm with an average size of 60 nm, as measured by electron microscopy. The DNCs were treated by irradiation with 1.5 MeV electrons during 8 hours with a total dose of $3 \times 10^{18} \text{ e/cm}^2$. Annealing at 850°C for 4 hours resulted in approximately 1-10 NV color centers in each DNC. Aside from having a high quantum yield, our choice of emitter has two crucial advantages. First, NV centers in diamond are indefinitely photostable so that repeated quantitative measurements can be performed. Second, the color centers are well protected in the diamond lattice against surface effects upon contact with other material [11].

Our scattering sample consisted of a powder of rutile TiO$_2$ particles (DuPont, Ti-Pure R706) with a mean size of 250 nm and a distribution of 150-350 nm as revealed by electron microscopy. Particles were coated with silica (SiO$_2$, 3 wt %) and alumina (Al$_2$O$_3$ 2.5 wt %) and had a refractive index of 2.8 [3]. We produced a disordered medium in half space by sprinkling the powder on a cover glass carrying the DNCs. We then compressed the powder manually by applying a gentle pressure via another glass cover slide. The final thickness of the medium was typically about 0.4 mm. Based on the volume and weight of the material that was deposited, we estimated the volume fraction occupied by particles in the compressed powder to be about 30%.

The schematics of the experiment are shown in Fig. 1. The sample was placed on a
three-dimensional piezoelectric stage of a home-built microscope. Laser pulses at a wavelength of 532 nm, duration of 13 ps, and repetition rate of 3.8 MHz were used to excite the NV centers. This light was sent to a microscope objective (NA=1.4) via a 50/50 beam splitter. The scattering and fluorescence from the sample were collected through the same objective, separated via a dichroic mirror and two 540 nm long pass filters, and directed to a photomultiplier tube and an avalanche photodiode, respectively. Fluorescence lifetimes were determined with a time-correlated single-photon counter by recording the time delay between the excitation pulses and the detected photons. The intensity \( I \) measured on the photomultiplier tube resulted from the interference of the light reflected by the sample interface and that scattered by a given nano-object in the focus spot. The details of this interferometric scattering (iSCAT) detection method are described in our previous work [12, 13]. The added value of the iSCAT signal is to visualize nano-objects without the need for a fluorescence signal.

In a first step, the DNCs were spin coated on a glass cover slide (see Fig. 1b) and simultaneously imaged in fluorescence and iSCAT by scanning the sample across the focus of the excitation laser beam. Figure 2a shows an example of a fluorescence map of DNCs while Fig. 2b displays the simultaneously recorded iSCAT image. The latter locates the same DNCs as well as a few other nonfluorescent nanoparticles which are most likely DNCs without color centers.

The second step of the experiment involved the measurement of the excited state lifetime \( \tau \) for each fluorescent DNC. For NV centers in bulk diamond, \( \tau \) has been measured to be about
12 ns \[14\]. It is known, however, that the spontaneous emission rate is slowed down, and thus \(\tau\) becomes larger in subwavelength dielectric media \[15\]. Furthermore, as the size of the dielectric medium is decreased, the dependence of the spontaneous emission rate on the shape of the medium as well as the emitter orientation and position becomes less significant \[16\]. Figure 3a displays a typical example of measurements on a single DNC. This measurement is fitted using a background and a double exponential with 1/e times of \(4.2 \pm 0.3\) ns and \(22.8 \pm 0.3\) ns, respectively. We attribute the deviation from a simple exponential decay to the inhomogeneity of emitting transitions in a single DNC. In particular, the shorter lifetime component is most likely due to quenching effects for some NV centers. A plausible cause of this might be the presence of a thin graphite layer on the DNCs \[11\]. Another source of inhomogeneity can stem from the coexistence of a transition at 575 nm, which is attributed to the neutral charge state of NV centers, and the usual transition of the negatively-charged center at 637 nm \[17\]. Indeed, we confirmed the presence of both lines by measuring the emission spectra of individual DNCs. To our knowledge, no data are available on the fluorescence lifetime of the neutral color centers. A third phenomenon that can cause different fluorescence lifetimes in a DNC is the orientation of the transition dipole moments of the individual NV centers with respect to the glass substrate \[18\]. To examine this effect, we have performed rigorous finite-difference time-domain (FDTD) calculations to compute

FIG. 2: Fluorescence (a,c) and iSCAT (b,d) images of the same diamond nanoparticles on a glass cover slide in air (a,b) and covered with scattering particles (c,d).
the variation of the radiative decay rates of emitters in a dielectric nano-object placed on a glass surface [19]. It turns out that for the parameters (indices of refraction, particle size) of relevance to our measurements, $\tau$ could vary within a factor of three, depending on the orientation of each emitter and its distance from the interface.

The details of the inhomogeneities in $\tau$ are not important to our current work because we will be only interested in its modification when the scattering medium is added. In fact, in what follows we will only investigate the changes of the long-lifetime component of the measurements. As explained below, while several systematic effects could cause shortening of the fluorescence lifetime, its increase provides a robust evidence for the modification of the density of states in the scattering medium. Fig. 3b displays the histogram of this component for DNCs placed on a glass cover slide in air. The variation from 8 ns to 37 ns is in agreement with previous reports [11, 20]. We checked the validity of this attribution by measuring the fluorescence lifetime $\tau_w$ of the same DNCs after adding water on top of the sample (see Fig. 1c). The change in the radiative lifetime of an emitter is inversely proportional to the refractive index of the environment so we expect $\tau$ to be reduced under water. Figure 3c shows a histogram of the resulting values normalized to the lifetimes of each DNC in air. The mean value of $\tau_w/\tau_a$ amounts to 0.9, where $\tau_a$ denotes the fluorescence lifetime at the air-glass interface. This outcome is in very good agreement with the expected value of 0.88 if one considers the refractive index of the surrounding environment to be the average of the refractive indices of the media in the lower and upper halves of the glass-air or glass-water interfaces. Note that we do not have to account for local field effects since the NV centers embedded in the diamond matrix do not experience a change of environment at the
FIG. 4: a-f) Data collected on the fluorescence lifetimes of many individual DNCs in three different samples (First row, sample 1; second row, sample 2; third row, sample 3.) measured in air and in the scattering medium. We examined 49, 33, and 33 DNCs in the three studies, respectively.

molecular level [15].

Once the DNCs were characterized, the water was removed with a micro-pipette and the substrate was left to dry overnight under a gentle stream of nitrogen. In the last phase of the experiment, TiO$_2$ particles were placed on the sample (see Fig. 1d). Figures 2c and d show the fluorescence and iSCAT images in the scattering medium. The individual DNCs are still easily identified via fluorescence, while the scattering image now displays a “speckle” pattern. Figures 4a-f present the measured lifetimes of many DNCs from three different scattering samples (the step with water was omitted for samples 2 and 3). Let us label the fluorescence lifetime in the scattering medium by $\tau_s$. As in the case of water immersion, we found a distribution of the normalized fluorescence lifetimes $\tau_s/\tau_a$, indicating both reduction and enhancement of the spontaneous emission rate. However, while in the previous case the average value $\langle \tau_w/\tau_a \rangle < 1$, here we find $\langle \tau_s/\tau_a \rangle > 1$. In sample 1, for example, fluorescence lifetimes are longer than in air by up to a factor of 1.4 with an ensemble average of 1.1. The histograms of Figs. 4b, d, f reveal variations in the measurements from the three samples.
A possible cause of this might be different qualities of powder compression and nanoparticle packing.

The observation of lifetimes longer than in air indicates the reduction of LDOS in the scattering medium. We believe this conclusion is robust against systematic effects. First, opening of non-radiative decay channels, e.g. as a result of contact with the medium, cannot be responsible for this effect since it could only increase the total decay rate $\gamma = \gamma_r + \gamma_{nr}$ and therefore lower the lifetime. Second, lengthening of the fluorescence lifetime cannot be explained in the context of a homogeneous medium with an effective index of refraction because addition of high-index TiO$_2$ particles could only increase such an effective refractive index with respect to that of the air-glass interface, and thus, reduce the lifetime. Finally, we verified that the longer fluorescence decay was not the result of photon trapping in the scattering medium. To do this, we focused 10 ps pulses of laser light onto the interface between the cover glass and the scattering medium to mimic the spatial mode of the DNC emission. We then interrogated the temporal profile of the reflected light in a confocal detection arrangement with and without the scattering medium. This allowed us to rule out any pulse lengthening within the time resolution of 0.4 ns.

Our measurements provide the first report of the fluctuations of the spontaneous emission rate in a disordered scattering medium. Our experimental approach sets the ground for studying strong localization of light by monitoring and mapping the variations of the local density of states directly in the coordinate space. Such studies promise to connect the nanoscopic behavior of light scattering with conventional macroscopic ensemble measurements. An important advantage of this approach is that observation of the inhibition of the spontaneous emission rules out systematic effects of absorption since those would always lead to a reduction of the fluorescence lifetime.

The experiments reported here can be improved in several ways. First, particle composition and compactification of the scattering medium can be varied and characterized. Second, use of color centers with narrow emission spectrum in the near infrared could simplify the analysis of the density of states in comparison to the broad emission of NV centers. Another advantage of such emitters would be the availability of very strongly scattering media based on large-bandgap semiconductors. Furthermore, we plan to extend our work to the measurement of the fluorescence lifetime via a thin optical fiber that carries a single DNC attached to its end placed deep into a three-dimensional scattering medium.
Finally, we hope that theoretical progress in modeling the modification of radiative effects in strongly scattering media will allow quantitative comparisons with experimental data.

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