Spontaneous Emission of Europium Ions Embedded in Dielectric Nanospheres

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We measure fluorescence lifetimes of emitters embedded in isolated single dielectric nanospheres. By varying the diameters of the spheres from 100 nm to 2 μm and by modifying their dielectric surrounding, we demonstrate a systematic change of paradigm in the spontaneous emission rate, as we cross the border from the superwavelength regime of Mie resonances to the nanoscopic realm of Rayleigh scattering. Our data show inhibition of the spontaneous emission up to 3 times and are in excellent agreement with the results of analytical calculations.

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Spontaneous emission can be described by the interaction of an atomic dipole with the electromagnetic vacuum field [1]. It is therefore possible to modify the decay rate of an atomic excited state by placing it in a confined geometry where the vacuum fluctuations are altered due to reflections from boundaries [2]. Drexhage demonstrated this in 1970 by examining a flat mirror very close to a thin fluorescent layer [3] while many other groups have modified the radiative decay rate of emitters by putting them between two flat reflectors [4], between mirrors of high-finesse optical cavities [5], and in whispering gallery mode resonators [6]. In addition to superwavelength geometries, one might also expect that the presence of nanometer scale material could lead to the scattering of the vacuum field and therefore modification of the spontaneous emission rate. Indeed, several theoretical reports have predicted this phenomenon for an atom in the near field of nanoscopic spheroids, sharp tips, and substrates with lateral nanostructures [7], as well as for atoms inside subwavelength spheres [8,9]. Experimentally, a few reports have indicated that the fluorescence lifetime of chromium ions in ruby microcrystals [10], of color centers in diamond nanocrystals [11], and of emitters in ensembles of colloidal particles [12,13] differ from their bulk values. However, quantitative and conclusive investigations have been lacking. In this Letter we present a systematic demonstration that the spontaneous emission rate of ions placed in dielectric spheres is substantially reduced as one crosses the border from the superwavelength regime of Mie resonances to the nanoscopic realm of Rayleigh scattering.

The spontaneous emission rate of an electric dipole located at an arbitrary location in a sphere of a given diameter has been calculated analytically by Chew [8]. Figure 1 summarizes the results whereby we have normalized the emission rate to that in an infinitely large bulk dielectric and have averaged over different dipole orientations. We note that the strong oscillations for emitters near the surfaces of the larger spheres are due to the coupling to the whispering gallery modes [14] while the modulations at the center are caused by interference in the radial modes. As we go from the superwavelength to the subwavelength size regime, however, the oscillations disappear, and the spontaneous emission rate approaches a limiting value below the bulk rate, independently of a dipole's orientation and position.

In our experiment we have set out to measure the decay rate of the fluorescence signal from single dielectric spheres of various diameters $2R$ uniformly doped with emitters. We use polystyrene colloids doped with a europium chelate (TTA) at 5% weight concentration, commercially available (Duke Scientific). By spin casting a dilute solution of the colloids onto a microscope cover glass, we prepare samples with sparsely spaced spheres, as shown by a scanning electron microscope (SEM) image in Fig. 2(a). Note that although often one encounters isolated spheres, it also happens frequently that particles aggregate in the deposition process. Therefore, in order to identify the object under study, it is important to perform the measurements with a high spatial resolution. As shown in Fig. 2(b), we accomplish this by combining atomic force microscopy (AFM) and scanning confocal

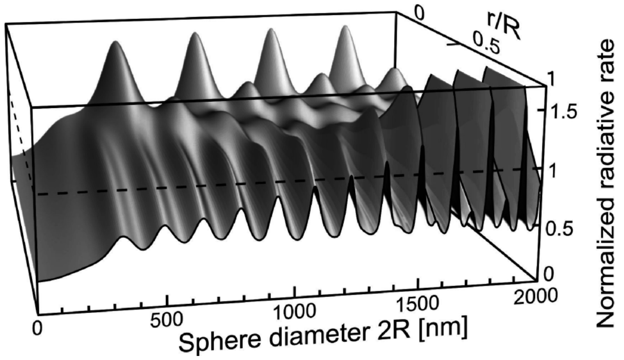

FIG. 1. Calculated radiative decay rate for a dipole emitting at $\lambda = 615$ nm inside a dielectric sphere ($n = 1.59$) placed in vacuum. The rates have been averaged over different dipole orientations and normalized to the radiative decay rate in the bulk. The horizontal axes display the diameter $2R$ of the sphere and the emitter position in it. Note that some of the sharp resonances have been truncated.

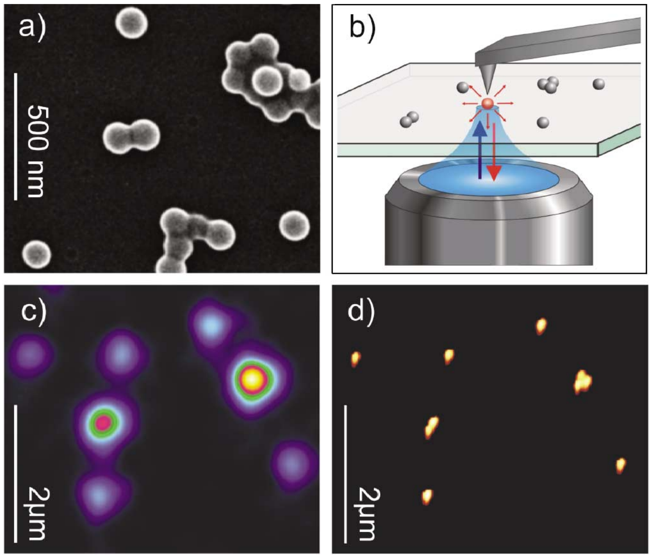

FIG. 2 (color). (a) A scanning electron microscope (SEM) image of the colloids on a glass substrate. (b) The schematic arrangement of the AFM and confocal microscope with a scanning stage. The tip is withdrawn by a few μm when the optical image is recorded. (c) A typical fluorescence confocal image of a sample containing 100 nm colloids. (d) The AFM image of the same part of the sample resolves aggregates not identified in (c). Note that the slightly extended shape of the spots in (d) is due to the convolution with an imperfect tip.

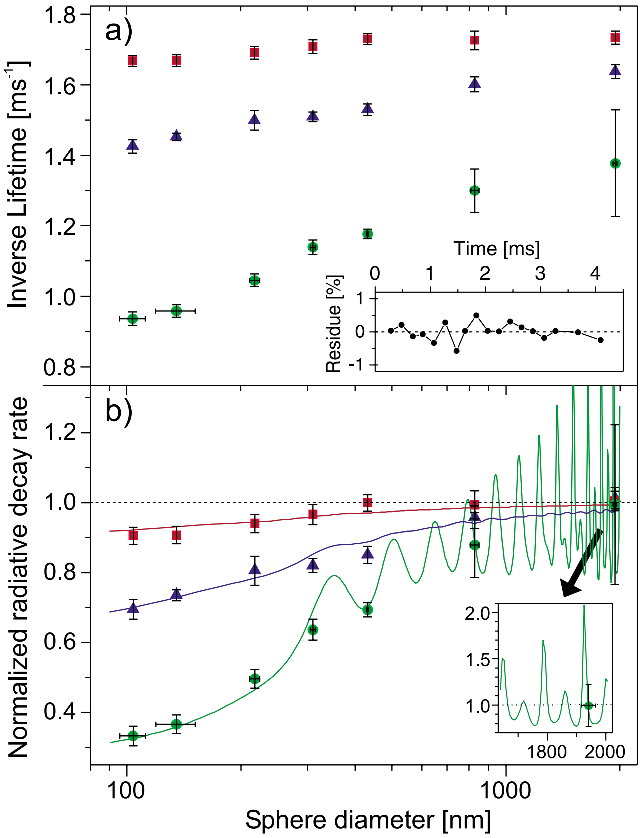

FIG. 3 (color). (a) Experimental raw data for the fluorescence decay rates as a function of the sphere diameter. Colors represent different surrounding media (green: air; blue: water; red: immersion oil). The inset shows the difference between the fluorescence decay signal of a single 100 nm sphere and a normalized single exponential fit function. (b) The radiative decay rates extracted from the data in (a) are normalized to the bulk rate and fitted by the theoretical curves. For larger particles in air the theoretical curve has been truncated. The inset nicely reveals that a slight spread in the diameter results in a large variation of the rates due to Mie resonances for larger spheres.

microscopy. A microscope objective (NA = 1.2) is used to focus the light at $\lambda = 364$ nm from an argon-ion laser onto the sample and to collect the resulting fluorescence. Upon absorption of the excitation light by the chelate the energy is transferred to the $^5D_0$ level of europium which then emits via the transition $^5D_0 \rightarrow {}^7F_2$ in a fairly narrow bandwidth of about 10 nm at $\lambda = 615$ nm. Since the decay to other ^7F sublevels is negligible, the fluorescence can be considered to be monochromatic, simplifying the comparison with the theory. Figure 2(c) shows a typical fluorescence confocal image. Figure 2(d) displays the corresponding AFM image of the same area, demonstrating that at the limit where the optical resolution is not sufficiently high, AFM measurements can be used to correlate the fluorescence signal with the constellation of the colloidal particles. Once an isolated sphere has been identified in a raster scan, it is targeted by the excitation laser beam that is modulated by a mechanical chopper with a rise/fall time of 1 μsec and its fluorescence decay signal is recorded.

The inset in Fig. 3(a) shows the residue obtained when subtracting the experimentally measured fluorescence decay signal from a single exponential fit function normalized to one. We note that although emitters at different locations in the sphere contribute to the decay signal, their fluorescence lifetimes are similar enough that the overall outcome can be still well approximated by a single exponential function. The residue shown is smaller than about 0.01 and is typical for all measurements reported here. The green circles in Fig. 3(a) represent the raw decay rates obtained for spheres of seven different diameters in the range of 100 to 2000 nm. Each point displays the average of the values recorded for tens of isolated spheres with the vertical bars representing the spreads (standard deviation) of these measurements. The horizontal values and error bars in Fig. 3 display the average diameters and their standard deviations for spheres of each size category, as determined by high resolution scanning electron microscopy [15].

In order to compare our experimental findings with theory [8], we have computed effective emission rates by fitting single exponentials to the sum of decay curves corresponding to dipoles at different positions and orientations, assuming a uniform distribution in a given sphere [see green curve in Fig. 3(b)]. This assumption is very robust for the essence of our study, namely, the behavior of spheres with diameters smaller or comparable with the size of the laser focus. However, for the larger spheres one expects that the exact position of the focus as well as the size of the collection angle favor emitters at certain locations. We have examined this issue theoretically [16,17] and have verified that for the spheres of diameters 800 and 2000 nm the deviations obtained for the values of the effective fluorescence lifetime remain around 1%–10%. Because we cannot determine and define the laser intensity distribution at the nanometer scale, we only plot the results from a uniform distribution, but we note that this effect might have contributed to the large error bars obtained for the sphere of diameters 800 and 2000 nm.

The blue and red solid lines show that if one surrounds the polystyrene spheres by water ($n = 1.33$) or oil ($n = 1.52$), the reduction of the contrast in the refractive index leads to a weaker dependence of the emission rate on the sphere diameter. In our experiment we have taken advantage of this effect to perform control experiments. We have added drops of water and immersion oil ($n = 1.52$) to the sample from above and have recorded the fluorescence lifetimes from the very same spheres that were measured in the dry state. The raw results shown by triangles and squares in Fig. 3(a) verify the expected tendency, but do not converge to the same value for larger spheres. In order to understand this discrepancy, one has to remember that in the condensed phase the immediate vicinity of emitters to the host molecules often introduces nonradiative decay channels. The total fluorescence decay rate is then written as $\Gamma = \Gamma_r + \Gamma_{nr}$ whereby Γ_r and Γ_{nr} denote the radiative and nonradiative contributions, respectively. To this end, we suspected that due to the leakage of the immersion liquid into the polymer spheres the nonradiative decay rates might have been changed in different surroundings. In order to confirm this hypothesis we coated a sample containing spheres of 2 μm diameter with a 3 nm layer of chromium to prevent the penetration of the liquid into the polymer. We then repeated the experiments with and without immersion liquids and verified that although the decay rates were higher due to quenching by the metal layer, they did not change as water or oil was added.

At this point we are ready to compare the experimental data with the theoretical predictions in a quantitative manner. In our analysis we have let the decay rates in Fig. 3(a) to be the sum of a nonradiative contribution that depends on the surrounding medium and a radiative part of interest. All radiative components were normalized to the bulk radiative rate Γ_r^{bulk} and then fitted to the corresponding theoretical values, allowing us to deduce $(\Gamma_r^{\mathrm{bulk}})^{-1} = 1.50$ msec, $(\Gamma_{nr}^{\mathrm{air}})^{-1} = 1.40$ msec, $(\Gamma_{nr}^{\mathrm{water}})^{-1} = 1.04$ msec, and $(\Gamma_{nr}^{\mathrm{oil}})^{-1} = 0.94$ msec as the only fit parameters. The obtained spontaneous emission rates normalized to the bulk rate are displayed by the symbols in Fig. 3(b). The excellent agreement of the data with the theory for a wide range of sphere diameters as well as indices of refraction for the surrounding media clearly demonstrates how the spontaneous emission rate is modified in nanoscopic spheres.

Let us now remark on additional observations, systematic checks and thoughts regarding our results. First, we point out that as indicated in the inset of Fig. 3(b), a slight spread in the size of the colloids or location of the laser focus become translated to large variations of the decay rates due to the sharp slopes of the Mie resonances in spheres of diameters 800 and 2000 nm. This is not the case for nanospheres of diameter 100 or 140 nm where the size dependence has flattened. On the other hand, the emission rates from such small particles are particularly sensitive to aggregation, which is almost inevitable in ensemble studies [13]. Indeed, by performing measurements on several touching triplets and doublets of 100 nm spheres, we have shown that $(\Gamma_r^{\mathrm{trip}})^{-1} = (0.93 \pm 0.01)$ msec $< (\Gamma_r^{\mathrm{doub}})^{-1} = (0.97 \pm 0.02)$ msec $< (\Gamma_r^{\mathrm{sing}})^{-1} = (1.06 \pm 0.02)$ msec. We are currently performing numerical calculations for decay rates of emitters in dielectrica of arbitrary shapes, and our preliminary results confirm that the spontaneous emission rate can be tuned to different values also by changing the shape of the subwavelength particles [17].

Next, we address the role of the substrate on our measurements. Since the presence of a dielectric surface is known to modify the emission rate of an atom [18], one might expect that the glass plate holding the spheres could also affect the lifetimes of the ions in them. First, we note that the vicinity of a dipole to the substrate is expected to increase its decay rate, whereas we observe a clear decrease of the radiative rates for smaller spheres. Furthermore, the data in Fig. 3 show that even if we add an immersion oil that perfectly matches the refractive index of the substrate, there exists a clear trend towards lower emission rates for subwavelength spheres. Since the data for particles under oil were fitted simultaneously with the data for immersion in water and air, we believe that the effect of the substrate is also negligible in these experiments. This is not very surprising because the influence of a dielectric surface on an emitter becomes significant only at separations less than about $\lambda/2\pi$ [18] so that most emitters that contribute to our signal in various runs are not affected very strongly by the substrate.

As a last point of discussion, we comment on the behavior of the spontaneous emission rate if one were to remove the dielectric molecules one by one until the emitter were left naked in vacuum. Chew's calculations predict that $\lim_{R\to 0} \Gamma_r = [9/(n^2 + 2)^2](\Gamma_r^{\mathrm{bulk}}/n)$, independently of the position of the emitter in the nanosphere [8]. In order to gain insight into this result, let us consider Fermi's golden rule $\Gamma_r = \frac{2\pi}{\hbar^2} |\langle e|\mathbf{E}.\mathbf{D}|g\rangle|^2 \rho(\omega)$ to obtain the spontaneous emission rate Γ_r, whereby $\mathbf{E}$ is the fluctuating vacuum field at the location of the atom, $\mathbf{D}$

is the transition dipole operator, and ρ is the density of photon states [19]. In a bulk dielectric of refractive index n, ρ and $\mathbf{E}$ are modified such that the spontaneous emission rate is n times faster than in vacuum [20]. Therefore, $\Gamma_r^{\rm bulk}$ becomes weaker by a factor of $\frac{1}{n}$ if the dielectric medium is shrunk. In addition, as the sphere size diminishes much below the wavelength, we approach an electrostatic limit where the vacuum field $\mathbf{E}$ inside the sphere is smaller than that outside by a factor of $3/(n^2 + 2)$ [21]. These two effects result in the decay rate inside an infinitesimally small sphere to be $9/[(n^2 + 2)^2 n]$ times lower than in bulk, explaining Chew's results.

Intuitively, however, one would expect $\Gamma_r^{\rm bulk} \longrightarrow \Gamma_r^{\rm vac}$ as $R \longrightarrow 0$. Here we have to take into account the local field corrections inside a dielectric. It turns out that if we consider a model where the emitters are simply superimposed on a homogeneous dielectric background, this correction results in an additional factor of $(n^2 + 2)^2/9$ in the spontaneous emission rate [22–24]. Therefore, if we include the local field corrections, we do indeed recover $\Gamma_r^{\rm vac}$ for spheres of vanishingly small diameters. Nevertheless, it must be emphasized that the model of a homogeneous dielectric is not suitable for very small clusters made of only a few molecules because in this extreme case macroscopic concepts such as the refractive index and the local field corrections are no longer applicable in their common forms [25].

In conclusion, we have presented a quantitative and systematic study of the reduction of the spontaneous emission rate by up to 3 times in nanoscopic spheres. The dependence of the emission rate on the dimensions and morphology of the dielectric environment plays an important role in the optics of quantum dots and single photon sources based on nanoemitters [11]. We plan to extend our studies to investigate nanoscopic dielectrics of various shapes and extensions.

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