Observation of Spatial Fluctuations of the Local Density of States in Random Photonic Media

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We experimentally study spatial fluctuations of the local density of states (LDOS) inside three-dimensional random photonic media. The LDOS is probed at many positions inside random photonic media by measuring emission rates of a large number of individual fluorescent nanospheres. The emission rates are observed to fluctuate spatially, and the variance of the fluctuations increases with the scattering strength. The measured variance of the emission rates agrees well with a model that takes into account the effect of the nearest scatterer only.

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It is well known that the spontaneous emission rate of an excited quantum emitter is not only a property of the emitter itself, but also depends on its surroundings on the nanoscale [1,2]. Control of the emission rate of quantum emitters has been demonstrated with a wide range of systems, such as reflecting interfaces [3], microcavities [4], photonic crystals [5–7], and plasmonic nanoantennae [8]. The effect of the surroundings of the emitter is described by the local density of states (LDOS) that counts the number of optical modes available for emission at the position of the emitter [2,6].

In random photonic media that are promising systems to observe Anderson localization of light [9], it is an open question how spontaneous emission rates are affected by the surroundings. It has theoretically been predicted that the LDOS exhibits spatial fluctuations [10–14]. These LDOS fluctuations are determined by light scattering near the emitter and the variance of these fluctuations is of the order of the scattering strength $(1/k\ell)$, where k is the wave number of light in the medium and ℓ is the transport mean free path. In an infinite random medium the LDOS fluctuations are essentially equivalent to the C_0 intensity correlation function [11]. C_0 is an infinite-range correlation function for waves in random media [15]. The calculated variance of the LDOS was found to be highly sensitive to the level of scattering and absorption at the local scale [13], as well as to the dipole orientation [14]. No experimental observation of the LDOS fluctuations inside random photonic media has been reported so far.

Here we present an experimental study of fluctuations of the LDOS inside random photonic media. We use single nanoscale emitters as internal probes of the LDOS. Time-resolved fluorescence is recorded for many emitters inside random media with scattering strengths $1/k\ell$ up to 0.12. The distribution of the spontaneous emission lifetimes is used to test theoretical predictions from several different models.

The experimental setup shown in Fig. 1(a) is designed to optically probe a single emitter located deep inside a random medium, and to measure its time-resolved emission. The emitters are optically excited at a wavelength $\lambda = 543$ nm using a mode-locked supercontinuum fiber laser with a pulse duration of ∼5 ps and a repetition rate of 20 MHz. Excitation was performed through a microscope objective with numerical aperture (NA) of 0.63. The emis-
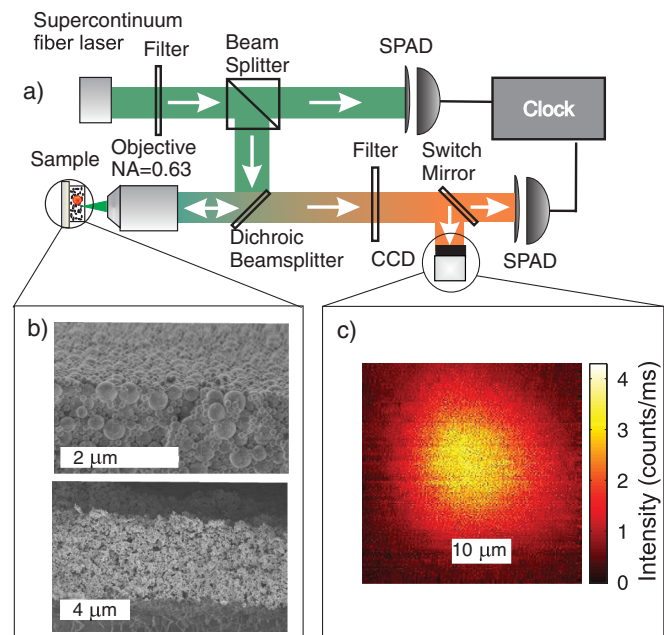

FIG. 1 (color). (a) Time-correlated single-photon counting setup with mode-locked supercontinuum fiber laser, CCD camera, and single-photon avalanche photodiode (SPAD). (b) Scanning electron micrographs (SEMs) of random photonic media made of polystyrene (PS) (top) and zinc oxide (ZnO) (bottom). (c) Fluorescence image of a single fluorescent nanosphere with a diameter of 22 nm embedded in a 7.4(5) μm-thick slab of PS random photonic medium at a depth $d = 3.3$ μm.

sion was collected near $\lambda = 620$ nm using a dichroic beam splitter (Semrock FF593-Di02-25 × 36), a cutoff filter (Schott RG610), and a 14-nm band pass filter (Semrock FF01–620/14–25). The location of a single nanoscale emitter is identified using a CCD camera and its time-resolved emission is measured by a single-photon avalanche photodiode with a time resolution of 50 ps.

We studied two types of random photonic media: slabs made from polystyrene (PS) and zinc oxide (ZnO) with thicknesses between $L = 4.0$ and 16.5 μm, see Fig. 1(b). To probe the emission rates and thus the LDOS, we doped the samples with fluorescent polystyrene nanospheres with a diameter of 22(2) nm, an emission peak at 612 nm, and a quantum efficiency of 96(4)% (Duke Scientific red fluorescent nanospheres). The fluorescent nanospheres are much smaller than the wavelength of light and contain about 30 dye molecules, which all sense the LDOS at essentially the same position. Since the orientation of the molecules is random and the LDOS is orientation dependent [14,16], dye molecules inside one fluorescent nanosphere emit at different rates. The fluorescent nanospheres show no photoblinking and are unaffected by the chemical environment since the dye molecules are protected from ambient oxygen and rigidly held in a polymer matrix. To fabricate PS random photonic media, a polydisperse suspension of spheres (Duke Scientific) doped with fluorescent nanospheres was deposited on a microscope cover slide, spread uniformly and allowed to dry, following a previous photonic crystal fabrication method [17]. We prevented crystallization by preparing a polydisperse mixture of different spheres. To fabricate ZnO random photonic media, a suspension of pigment (Aldrich ZnO 99%, <1 μm) doped with fluorescent nanospheres was sprayed on a cover slide [18]. The random photonic media have a low areal density of fluorescent nanospheres ranging from 0.03 to 0.12 μm^{-2}. As nonscattering reference samples with $1/k\ell = 0$, we prepared fluorescent nanospheres in transparent polyvinyl alcohol polymer layers that were spincoated on cover slides and covered by poly(methyl methacrylate) index matching layers [19]. The transport mean free paths for PS and ZnO random photonic media were determined by total transmission to be $\ell = 1.7(3)$ μm and $\ell = 0.82(12)$ μm at $\lambda = 620$ nm, yielding scattering strengths $(1/k\ell)$ of 0.06 and 0.12, respectively [18–20]. For time-resolved fluorescence, we measured a total of 96 single fluorescent nanospheres, namely, 12 nanospheres in each of four PS and four ZnO samples. We also collected data from 12 single fluorescent nanospheres in the reference polymer layer.

A fluorescence image of the diffuse spot of light due to a single fluorescent nanosphere deep inside a PS random photonic medium is shown in Fig. 1(c). The background fluorescence of the host is negligible compared to the emission of the nanosphere. We determined the depth of the nanosphere by modeling the spot of fluorescent light

with diffusion theory [18,21]. We conservatively estimate a depth accuracy of one mean free path. In the particular case of Fig. 2, we obtain $d = 3.3 \pm 1.7$ μm. For our measurements, we selected only single fluorescent nanospheres that were isolated from other fluorescent nanospheres and situated at a depth of approximately half the sample thickness [19].

In Fig. 2(a), we show the time-resolved fluorescence from two fluorescent nanospheres embedded in a PS random photonic medium at the same depth. The two nanospheres at different positions yield two different decay curves demonstrating the spatial fluctuation of the LDOS. In Fig. 2(b), the decay curve of a single fluorescent nanosphere in a nonscattering polymer layer is seen to be exponential. The time-dependent fluorescence of 12 single fluorescent nanospheres inside a polymer layer all show exponential decay with the same time constant of 0.26 ns^{-1} to within only 1%. We conclude that nonexponential decay of a single fluorescent nanosphere is a characteristic of the LDOS fluctuations in random photonic media, and we attribute the nonexponential decay to the strong dependence of emission rate on dipole orientation [14].

We quantitatively analyze the nonexponential time-resolved fluorescence curves with a distribution of emission rates using the method that successfully describes time-resolved emission in ordered photonic media [7]. By choosing a lognormal distribution of emission rates we ensure that only physical positive rates occur while adjusting only one extra parameter as compared to the single-exponential model. The parameters of the distribu-
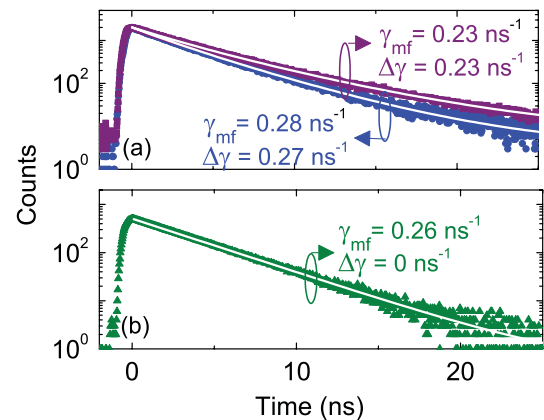

FIG. 2 (color). (a) Time-resolved fluorescence from a single fluorescent nanosphere embedded in PS random photonic medium with a thickness of 7.4(5) μm. The slow (purple) and the fast (blue) decay curves were measured on two different single fluorescent nanospheres at the same depth $d = 3.3$ μm. The white lines through the data are lognormal fits. The most-frequent decay rate γ_{mf} and the width of the distribution $\Delta\gamma$ are shown. (b) Time-resolved fluorescence of a single fluorescent nanosphere in a reference polymer sample (green) decays exponentially with a rate of 0.26 ns^{-1}.

tion are the most-frequent emission rate γ_{mf}, which is the peak of the distribution, and $\Delta\gamma$, which is its $1/e$ width. The mean emission rate γ_μ is equal to $\gamma_\mu = \gamma_{\mathrm{mf}}\exp(3/4[\sinh^{-1}(\Delta\gamma/2\gamma_{\mathrm{mf}})]^2)$ [7]. From the analysis of the emission curves of single probes inside PS samples in Fig. 2, the slowest emission curve is described by $\gamma_\mu = 0.28$ ns^{-1} while the fastest one has $\gamma_\mu = 0.33$ ns^{-1}.

Figures 3(a) and 3(b) show histograms of emission rates for ZnO and PS random photonic media, respectively, and Fig. 3(c) for a nonscattering reference medium. As a measure of the width of the distributions we show twice the square root of the variance $2\sigma = 2\sqrt{\mathrm{Var}(\gamma_\mu)}$. For all our samples, we verified that both the mean and the variance of the emission rate are independent of sample thickness. The distribution of emission rates is very narrow in the reference samples, showing that the fluorescent spheres have negligible intrinsic fluctuations. Interestingly, in moderately scattering PS samples ($1/k\ell = 0.06$) the width of distribution $2\sigma = 0.05(1)$ ns^{-1} is much larger than in the reference samples. In strongly scattering ZnO samples ($1/k\ell = 0.12$), the distribution is twice as broad, $2\sigma = 0.10(2)$ ns^{-1}. We note in passing that the maximum of the distribution also shifts, probably due to a change in effective refractive index [22]. The increase of the width tracks the increase of the scattering strength, in qualitative agreement with the theoretical prediction that LDOS fluctuations increase with the scattering strength [10,11].

The main result of our work shown in Fig. 4 is the measurement of the relative variance of the emission rate $\sigma^2/\langle\gamma_\mu\rangle^2$ versus scattering strength ($1/k\ell$). For nonscattering samples ($1/k\ell = 0$) the relative variance vanishes ($(\sigma^2/\langle\gamma_\mu\rangle^2 < 10^{-4}$). For PS ($1/k\ell = 0.06$) and ZnO ($1/k\ell = 0.12$) samples, we find a relative variance of $0.007(2)$ and $0.020(4)$, respectively. The relative variance

clearly increases with the scattering strength. Strikingly, the LDOS fluctuations predicted from the pointlike scatterer model [11] are about a factor 20 too high compared to our measurements. We attribute this difference to the fact that scalar wave and point scatterer approximations were used in Ref. [11], whereas in experiments the scatterers have finite size and the light waves have vector character. The vector character of light could have a strong effect as shown theoretically in Ref. [14].

As the pointlike scatterer model does not provide an accurate description of the immediate surroundings of the emitter, we propose an alternative model to estimate the fluctuations of the emission rate, wherein only one scatterer closest to the fluorescent nanosphere is considered. This is reasonable since in a dried sample fluorescent nanospheres are always in contact with the surface of at least one scatterer. The calculation is done by adapting the analytical model for the LDOS near a spherical surface [23]. We calculate the emission rate of a dye molecule at all positions inside a fluorescent nanosphere in contact with the surface of a PS or ZnO spherical scatterer for all possible orientations of the molecule. The relative variance of the emission rate is obtained by averaging over the size distribution of the spherical scatterers [19]. The calculated values are $0.010(3)$ and $0.022(5)$ for PS and ZnO samples, respectively, in good agreement with the experimental data (Fig. 4) [24]. This result confirms the hypothesis that the nearest scatterer dominates LDOS fluctuations in random photonic media [10,11].

It has been predicted that in infinite random media LDOS fluctuations are equivalent to C_0 fluctuations of emission intensity [11]. To probe C_0, we have measured the relative variance of the emission intensity of 20 individual fluorescent nanospheres deep inside 16.5 μm-thick
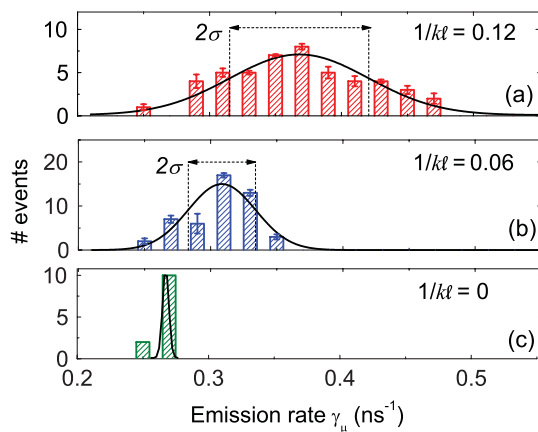

FIG. 3 (color).   Distribution of the emission rates for materials with different scattering strengths ($1/k\ell$). Histograms of the emission rates from fluorescent nanospheres embedded in three different materials: (a) ZnO, (b) PS, and (c) nonscattering polymer layer. Dotted lines: width of the distribution 2σ. Full lines: Gaussian fits to the histograms.
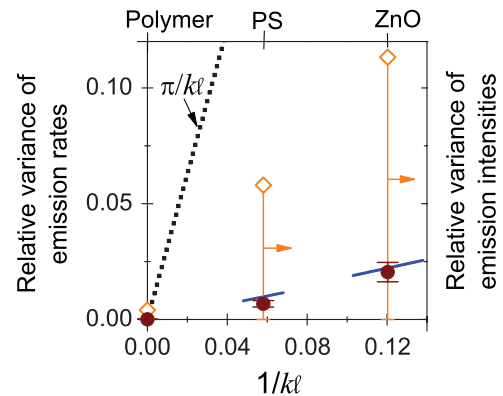

FIG. 4 (color).   Relative variance of the mean decay rate $\sigma^2/\langle\gamma_\mu\rangle^2$ versus scattering strength $1/k\ell$. The measured values are shown as filled circles with error bars indicating the statistical uncertainty for $N = 48$ measurements. Full lines: single-sphere-scatterer model for PS and ZnO scatterers. Dotted line: calculated LDOS variance for pointlike scatterers [11]. Empty diamonds: upper bound to C_0 determined from the fluctuations of the emitted intensity.

PS and 13.3 μm-thick ZnO random photonic media. We note that the variance of the intensity provides an upper bound to C_0 since it consists of both residual speckle variance and the desired C_0 contribution [19]. The intensity variance is therefore necessarily larger than C_0. The relative variance of emission intensity is shown in Fig. 4, it is indeed always higher than the relative variance of the emission rates. This observation means that our data are consistent with the hypothesis that the LDOS fluctuations and C_0 fluctuations are equivalent in our samples.

Recently, an interesting study has been made of emission rates of color centers in diamond nanocrystals at the surface of random media [25]. An interesting decrease of the average emission rate and random shifts of the individual emission rates were observed. In contrast to our work, the emitters have a broad distribution of intrinsic emission rates and the variance of the LDOS was not determined. It is exhilarating that fluctuations of the LDOS are not only observed deep inside random media, but also on the surface.

In conclusion, we observed fluctuations of the LDOS inside random photonic media through the spontaneous emission of individual fluorescent nanospheres embedded deep inside. The relative variance of LDOS fluctuations increases with scattering strength and agrees with a theoretical model. We suggest that C_0 may also be responsible for the broad distribution of emission rates observed in photonic crystals [7]. In view of the overestimation of fluctuations by the pointlike scatterer model, we anticipate that our observations will stimulate new studies of the LDOS in random and partly ordered photonic media.

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