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Probing the hot spot properties of semicontinuous gold films through the fluorescence polarization of CdSe/CdS colloidal nanocrystals

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Abstract. The coupling between thick-shell CdSe/CdS colloidal nanocrystals with the hot spots of a semicontinuous gold film is characterized by measuring simultaneously the photoluminescence decay rate and the linear polarization ratio. The absence of correlations between the two quantities is demonstrated. In contrast with the results obtained with continuous gold films, polarization ratios higher than 80% are achieved for the smallest nanocrystals. This ratio decreases quickly when the nanocrystals size is increased. © *The Authors. Published by SPIE under a Creative Commons Attribution 3.0 Unported License. Distribution or reproduction of this work in whole or in part requires full attribution of the original publication, including its DOI.* [DOI: [10.1117/1.JNP.11.046005](https://doi.org/10.1117/1.JNP.11.046005)]

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1 Introduction

Elaboration of nanostructures to tailor the coupling between light and matter is a major area of research in the field of nanophotonics. The control of the electromagnetic environment can be achieved through periodic dielectric or metallic materials. Metamaterials¹ and many optical cavities such as photonic crystals² have been engineered over the past few years. They cover a wide range of applications, including quantum information processing,³ solar cells for photovoltaic,⁴ or efficient analytical sensing in chemistry and molecular biology.⁵

An alternative strategy consists in using random structures without long-range spatial correlations in their geometry. Applications that need broadband operation can take advantage of the absence of a spatial periodicity. A two-dimensional (2-D) random pattern of holes can provide promising thin films to enhance the efficiency of solar cells.^{6,7} In the field of quantum optics, the spontaneous emission rate and the emission intensity can be increased following the Purcell approach.⁸ The local density of states (LDOS) can be tuned in order to operate over a wide range of wavelengths.⁹

Disorder can also lead to strong light localization. In random 2-D dielectric media, single or multiple scattering enables to adjust the transport mean free path of light¹⁰ and large increase and strong spatial fluctuations of the LDOS can generate a large distribution of Purcell factors.^{11,12} In a disordered photonic crystal waveguide, Sapienza et al. measured an increase of the emission rate of a single quantum dot coupled to Anderson-localized modes.¹³ Strong coupling was also theoretically predicted.¹⁴ In the case of semicontinuous metallic films, disorder is at the root of well-known localization and enhancement of the electromagnetic field in small nanometer-scale

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areas, also referred as “hot spots.” The coupling of colloidal nanocrystals (NCs) directly deposited on the film results in very high Purcell factors that can reach values up to 60.⁸

Parallel to the control of a single emitter fluorescence and in contrast to ensemble methods, the study of the coupling of a single fluorophore with a nanophotonic structure provides robust informations on the specific properties of the structure itself. As a consequence, the increase of the photoluminescence (PL) decay rate of nanosources has been extensively used to get insight in the LDOS. In addition to scanning near-field optical microscopy experiments,¹⁵ Krachmalnicoff et al. showed that the hot spots of a semicontinuous gold film correspond to large LDOS fluctuations that reach their maximum value at the percolation threshold when the film structure is characterized by fractal clusters.¹⁶

Amplitudes and fluctuations of the electric field can be analyzed by this approach but nothing can be deduced about the orientation of the field of the plasmon mode. Nevertheless, the fluorescence polarization is determined by the electric field of the plasmon mode so the specific optical properties of a plasmonic structure can be investigated through polarization measurements of nanoemitter fluorescence.^{17–20} Generally speaking, other techniques such as optical dark-field spectroscopy based on polarization measurements were also recently developed to investigate plasmonic structures.²¹

In this paper, the hot spots of a semicontinuous gold film at the percolation threshold are studied through the polarization properties encoded in the fluorescence of thick shell CdSe/CdS colloidal NCs spin-coated on the metallic film. Taking a flat gold film as a reference and measuring simultaneously the PL decay rate and the linear polarization ratio, we bring out specific properties of the electromagnetic field distribution at the surface of the random gold film. First, we show that the optical mode structure cannot be evidenced through the measurement of the PL decay rate alone since the PL decay rate and the polarization ratio are not correlated. Second, for the NCs with the smallest diameter (12 nm), polarization ratio as high as 80% are measured, that could be determined by the local topography of the gold structure. At longer distance from the gold nanostructure (for NCs with a large diameter of 30 nm), these optical modes are no more detected individually since the polarization ratio decreases strongly. Our results show that the structure of electromagnetic field varies considerably on these random gold films, even at the near-field scale.

2 Experimental Results

2.1 Samples

The random gold nanostructures are prepared by thermal evaporation under ultrahigh vacuum conditions (10^{-9} Torr), just below the percolation threshold (the metallic surface coverage is equal to 60%). Continuous gold films (thickness = 25 nm, roughness rms of 1 nm) are elaborated by the same method. Plasmon resonances for the random gold film appear from 550 nm to far-infrared due to the large distribution of sizes and shapes of metal clusters. The morphology and the absorption spectra of the disordered samples are shown in Fig. 1. Using spectrophotometric and AFM measurements, we checked that these characteristics are the same for the several gold films that were used in the following experiments.

The NCs are CdSe/CdS core shell NCs synthesized following the method described in Ref. 22. Their fluorescence corresponds to the one of two incoherent dipoles perpendicular to the NC *c*-axis. The emission of these NCs is within the plasmon resonances of the gold film (Fig. 1). Previous experiments have shown that the emission of the NCs is not quenched when they are directly deposited on the gold film, the shell acting as a spacer.²³ Three sizes of CdSe/CdS NCs are used to probe the properties of near-field modes at different heights. The first NCs (type 1) have a total diameter of 12 nm. Their wavelength emission is around 630 nm with a full-width at half-maximum of 30 nm [a typical spectrum of a single NC deposited on a glass coverslip and a semicontinuous film is shown in Figs. 2(a) and 2(b)]. The type 2 NCs exhibit a total diameter of 22 nm and their emission is around 660 nm. The third kind of NCs (type 3) presents a mean diameter of 30 nm and a wavelength also centered at 660 nm. The CdS surface of the NCs is surrounded by organic ligands that are mainly hexadecylamines and oleates. Their

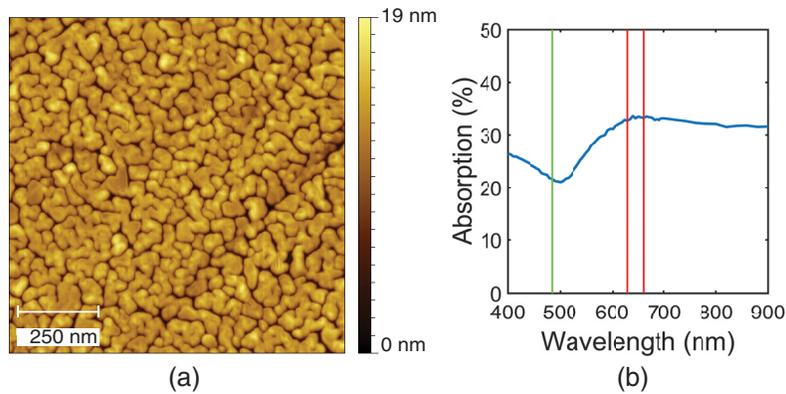


Fig. 1 (a) AFM topographic image (AFM) of a semicontinuous gold film. (b) Absorbance of the semicontinuous gold film. The red lines show the center wavelength of the three types of NCs, while the green line represents the laser wavelength.

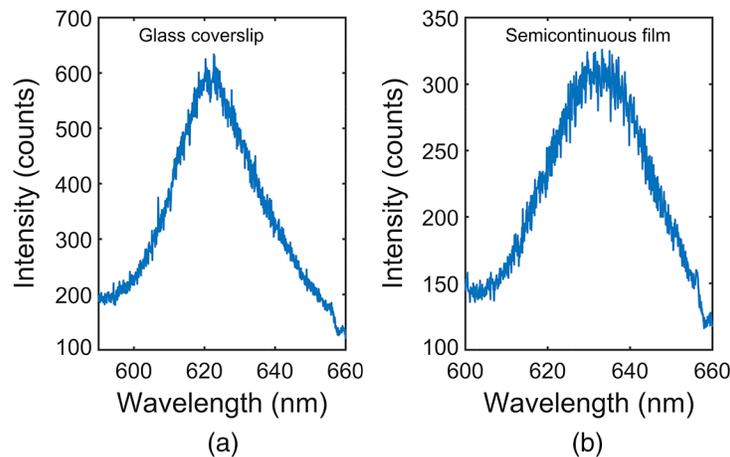


Fig. 2 Fluorescence spectrum of a single NC deposited on (a) a glass coverslip and (b) a semicontinuous gold film.

length is about 2 nm. Since the difference between the emission wavelengths of the different types of NC is of the order of the emission and plasmon linewidths and since the absorption of the semicontinuous film is nearly constant between 600 and 700 nm (Fig. 1), we consider that the coupling between the NCs and the gold structures does not depend on the type of NCs.

2.2 Experimental Setup

The NCs are spin coated on the films and their fluorescence is individually analyzed with a confocal microscope and a standard Hanbury Brown and Twiss setup based on two avalanche photodiodes (MPD, time resolution of 50 ps). The optical excitation is provided by a laser diode ($\lambda = 485$ nm and pulse duration ~ 100 ps, Picoquant LDH D-C). The excitation is far from resonance that means that the laser polarization has no influence on the NCs emission and the following polarization measurements. In order to create only one (e-h) pair, a low power excitation is used. A rotating polarizer is placed on one arm of the Hanbury Brown and Twiss in order to analyze the polarization of the emission. By normalizing the measured intensity on this arm by the intensity detected on the other arm, the polarization can be determined precisely even if the sample slightly drifts and the collected intensity fluctuates. The fluorescence intensity is recorded during the rotation of the polarizer and the polarization ratio is defined as

$$R = \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}}, \quad (1)$$

where I_{\max} is the fluorescence intensity detected along the maximum pass axis of the polarizer and I_{\min} along the minimum pass axis. The starting position of the rotating polarizer is the same for each measurement that enables to also determine the variation of the maximum pass axis direction θ (see Fig. 3) for the several NCs studied. The setup captures the absolute time of arrival of the photons and then the fluorescence intensity, the PL decay, and the polarization for one NC are determined from the same set of data.

Before studying the coupling between the emitters and the gold films, we characterized their PL decay rate at their single emitter level when they are spin-coated on a glass coverslip. In agreement with previous results,⁸ the mean exciton lifetime is around 60 ns (see Fig. 4 for the typical PL decay we obtained for an NC deposited on a glass coverslip or a random gold film) and does not change significantly for the three different samples. This value will be taken as a reference in the following.

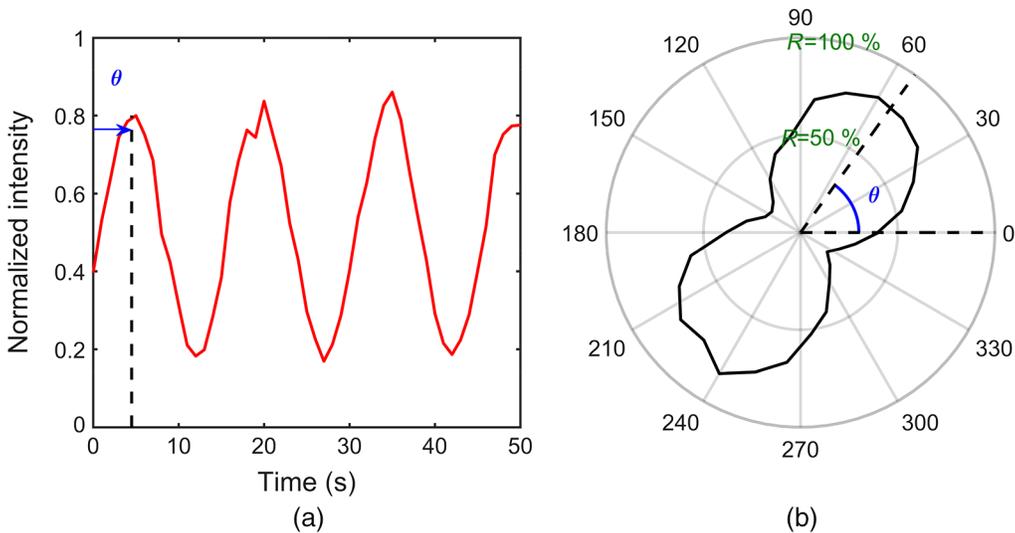


Fig. 3 (a) PL decay of a single NC deposited on glass. The red line is a biexponential fit (lifetime of 14 and 78 ns). (b) PL decay of a single NC deposited on a random gold film. The red line is a biexponential fit (lifetime of 0.36 and 2.4 ns).

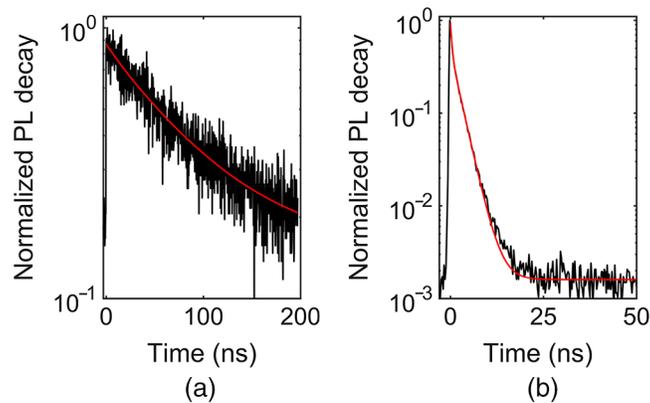


Fig. 4 Measurement of the maximum pass axis direction θ . (a) Intensity detected after the polarizer normalized to the intensity measured on the other arm of the HBT setup. The starting position of the rotating polarizer is the same for each NC. θ ranges between -90 deg and 90 deg. If a minimum is first reached while scanning the polarizer direction, the angle is then negative. (b) Polar plot corresponding to (a).

We first considered the small NCs (NC₁ type) deposited on a flat gold film [red ■ of Fig. 5(a)]. The Purcell factors (defined as the ratio between the PL decay rate measured on the gold structures and on glass) are between 4 and 15 [Fig. 5(a)]. This dispersion on flat gold can be explained on one side by the different orientations of the NCs but also by the shell size dispersion of the NCs itself. Concerning the polarization ratio, it ranges between 10% and about 30%. This result is compared to calculations for various NCs orientations.²⁴ The NC is then modeled with two incoherent dipoles perpendicular to the *c*-axis. The NC emits at 630 nm and is placed 10 nm above the surface with 25 nm gold thickness. The calculation predicts a linear polarization ratio ranging from 0% to 25%, in agreement with the experimental results.

In comparison with a flat gold film, drastic lifetime reductions observed on disordered films are induced by strong spatial localizations and enhancements of the field [green ◆ of Fig. 5(a)]. The disorder induces a strong modification of the optical modes. Discussions on the nature of these modes are wide.^{25–27} It has been shown that these surfaces could support localized and delocalized modes with an increase of localized modes close to the percolation threshold.¹⁶

Because the LDOS and the spontaneous emission of the emitter are linked, this modification can be probed by the measurement of the decay rates on the surface. The CdSe/CdS NCs are characterized by two incoherent dipoles and their orientation is randomly spread over the surface. The decay rate is then proportional to the partial local LDOS

$$\Gamma = \frac{\pi\omega^2}{\hbar\epsilon_0} |\vec{p}|^2 \rho_p(\vec{r}, \omega),$$

where \vec{p} is the transition dipole between two electronic states and $\rho_p(\vec{r}, \omega)$ is the partial LDOS. Depending on their orientation, NCs are more or less coupled to plasmon modes. The lifetime dispersion is then not only due to fluctuations of the LDOS but also to different orientations of the NCs. Purcell factors ranging from less to 10 to nearly 40 are observed on random gold accounting for strong localized modes on the surface, in agreement with previous results.⁸ The polarization analysis of the NCs fluorescence reveals a large distribution of polarization degrees on random gold structures. From 20%, it can exceed 80% with a standard deviation of 17%.

The polarization is a signature of the complexity of the modes on these kinds of samples due to the complex geometry and the existence of strongly polarized modes is striking. This could be explained by highly localized modes induced by a simple geometry corresponding to a dimer configuration. Polarization emission of molecules in a metallic dimer has been shown to be linear and its depolarization has been observed when introducing a third metallic particle.²⁸ Of course this model is too simple to explain all the electromagnetic modes on random surfaces but

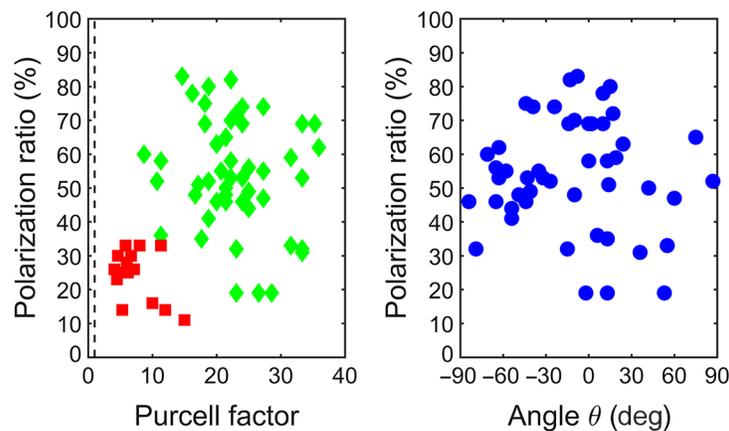


Fig. 5 (a) Polarization ratio as a function of the Purcell factor for individual NCs (type 1, diameter of 12 nm) deposited on a flat gold film (red ■) or a semicontinuous film (green ◆). (b) Polarization ratio as a function of polarization angle for the NC coupled to the semicontinuous film. The dashed line corresponds to a Purcell factor of 1.

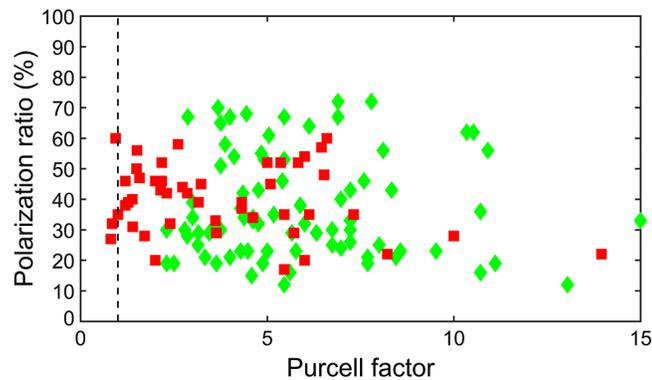


Fig. 6 Polarization ratio as a function of the Purcell factor for two kinds of individual NCs (type 2, diameter of 22 nm, green \blacklozenge , and type 3, 30 nm diameter, red \blacksquare). The dashed line corresponds to a Purcell factor of 1.

the polarized emission of some modes can be compared to a dimer mode emission, which can also exist on the complex structure.

No link between Purcell factors and the polarization degrees of the emission is observed. Even if the enhancement of the decay rate depends on the NC orientation, the 2D dipole structure and the large number of NCs studied suggest that the mode polarization and the mode localization are uncorrelated. The plot of the polarization ratio versus the polarization angle in Fig. 5(b) also illustrates the randomness of the coupling between the NCs and the semicontinuous gold film.

Bigger NCs (samples 2 and 3 with mean diameter 22 and 30 nm, respectively) have been used to probe the modes for a higher distance away from the surface. As expected, lifetime reductions are lower on both samples due to the higher distance to the surface (see Fig. 6). The Purcell factor is lower than 15 for the two samples and is clearly lower for the biggest NCs (red \blacksquare). The PL decay rate of some of these NCs is very few accelerated. This decrease accounts for the very fast decay of the electromagnetic modes with the distance to the surface. The statistics of the polarization ratio is also modified by the increase of the NCs diameter. The maximum is 72% for the 22 nm diameter NCs and 60% for the 30 nm diameter ones. Moreover the standard deviation also decreases from 17% to 11%. These results confirm the drop of the coupling with the distance between the film and the emitter. They also demonstrate that the hot spot structure is confined in the near field of the film at the scale of few nanometers.

These results confirm the decrease of the coupling with the distance between the film and the emitter. When the NC is close to the surface, the fluorescence carries the feature of the plasmonic mode. When the distance to the sample increases, the fluorescence tends to the emission of the NC dipole. This behavior has been observed for a molecule close to a gold nanorod where the plasmonic mode feature gets lost for distances to the nanorod larger than 20 nm.²⁹ This evolution is very fast and the plasmonic feature is quickly lost. Here is the interest of the NCs: the distance to the surface can be varied with their size and very short distances, allowing the ability to probe the plasmonic modes. Our analysis demonstrates that the hot spot structure is confined in the near field of the film at the scale of few nanometers.

3 Conclusion

In conclusion, the PL of thick-shell NCs directly coupled to random gold films has been investigated in detail. An original approach connecting polarization and lifetime measurements provides new insights concerning the hot spots observed in these plasmonic structures. Interestingly, in contrast with the lifetime reduction that depends on the orientation of the NC, the polarization ratio is only determined by the position of the NC. The modifications of the statistics of the polarization with the diameter of the NCs show that the near-field distribution is defined at the scale of some nanometers. From a general point of view, our approach could be extended to other plasmonic structures.

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