

Relaxation time mapping of single quantum dots and substrate background fluorescence

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We experimentally investigated the role of background signal in time resolved photoluminescence experiments with single quantum dots on substrates. We show that the background fluorescence signal from thin gold films fabricated by electron-beam evaporation and from Al₂O₃ layers fabricated by atomic layer deposition have to be taken into consideration in experiments on the single photon level. Though all investigated components can be distinguished by their photoluminescence decay rates, the presence of the background signal prevents the observation of photon anti-bunching from single quantum dots. Moreover, a single quantum dot acts as a hot-spot enabling the plasmon supported fluorescence enhancement of gold.

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1. Introduction. With the rapid development of nanotechnology it has become possible to engineer and study hybrid quantum-classical systems at the nanometer scale. Of particular interest is the research field of plasmonic hybrid systems consisting of a quantum emitter, e.g. a quantum dot (QD), dye molecule or nitrogen-vacancy center, coupled to a plasmonic nanostructure supporting surface plasmon-polaritons [1–3]. For example, coupling to a plasmonic nanoantenna changes the radiative properties of a quantum system by enhancement of spontaneous emission rate [4, 5] and improvement of its directionality [6–8]. Moreover, in the strong coupling regime, when the distance between a nanoantenna and a single quantum emitter is merely several angstroms, quantum effects in the nanoantennas become relevant [9, 10]. The strong coupling regime is of great interest for fundamental science and its realization promises benefits for signal processing applications at the single-photon level [11].

Obviously, the conduction of experiments in the strong coupling regime on the single photon level requires a critical evaluation of experimental conditions. Nowadays, time resolved photoluminescence (PL) measurements are broadly used as a powerful method for

the investigation of the interaction between quantum emitters and nanoantennas. With this technique a relaxation rate enhancement is routinely observed for quantum emitters in the vicinity of the nanoantennas [6]. At the same time an appropriate processing of the experimental data and their correct interpretation is the main problem. The first step in such complex experiments is supposed to be done on unstructured substrates in order to provide a reference. In spite of the many published experimental papers devoted to the topic of optical nanoantennas (see for example references in Ref. [12]), scant attention is paid to the accurate differentiation between effects caused by the structured and unstructured components such as substrates, for example. Additionally, only a few authors address possible pitfalls in such experiments associated with background fluorescence of the used materials [13].

In this contribution we present our experimental results on time resolved fluorescence measurements of single CdSe/ZnS quantum dots spin-coated on substrates to be used in single nanoantenna experiments. We targeted on a system consisting of a nanoantenna fabricated using focused ion beam lithography applied to an electron-beam evaporated thin gold film. The main goal of the performed test was twofold: first, to quantify the luminescence from the substrates in order to extract

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this luminescence from the following tests with single QDs; and second, investigate relaxation enhancement due to the substrates using the developed methodology. As quenching of quantum dots placed directly on a metallic surface can occur [14], we investigated whether an isolating layer made of Al_2O_3 can be used in such systems. As the dimension of the system is a critical parameter for the experiments in the strong coupling regime we worked with CdSe/ZnS QDs with outer diameter of about 5 nm. Additionally, we experimentally verified, whether the observation of photon anti-bunching from QDs in correlation measurements can be applied in the systems under investigation for the identification of a single quantum dot [15]. Obviously, if the background fluorescence signal is strong enough and spectrally overlaps the observation of photon anti-bunching fails.

A. Sample preparation. In our experiments we investigated CdSe/ZnS core shell QDs (maximum emission wavelength around $\lambda = 620$ nm) commercially available from PlasmaChem GmbH [16]. The core diameter of these QDs was about 4.4 nm [17], the ZnS shell thickness varies between 0.5 and 0.7 nm.

Time resolved photoluminescence experiments on CdSe/ZnS QDs were conducted on the following substrates: commercially available borosilicate glass, glass covered with a 15 nm Au layer, and glass covered with a 15 nm Au and 5 nm thin Al_2O_3 layer further referred to as Au/ Al_2O_3 layer stack. The substrates were prepared as follows. The cover slips were coated with 3 nm titanium as adhesive layer and 15 nm gold by an electron beam evaporator with a rate of 0.1 nm/s for titanium and 1 nm/s for gold. After this step some samples were coated with a thin Al_2O_3 layer produced by atomic layer deposition (ALD). For this process trimethylaluminium and water were used as reactants at a process temperature of 200 °C. The size of the gold grains was estimated to be about 20 nm.

For the photoluminescence experiments CdSe/ZnS QDs were spin-coated on cleaned substrates. Spinning was performed in two steps: 1) 15 s with 500 r.p.m. and 2) 30 s with 2000 r.p.m. speed. Substrates were cleaned first with acetone for 5 min, then in methanol for 5 minutes, rinsed with deionized distilled water and blown with pure nitrogen. QDs were suspended in toluol with different concentrations from 10^{-7} to 10^{-8} ppm. In order to ensure the suspension of QDs in clusters the suspensions were ultrasonicated for 10 min before spin-coating on substrates.

B. Measurement technique and data processing. The PL measurements were performed with a commercial PicoQuant MicroTime 200 time-resolved confocal fluorescence microscope. For the excitation a picosecond

diode laser (FWHM about 70 ps) with 5 MHz repetition rate and a wavelength of 530 nm was used. The excitation and collection of the optical signal was performed with a water immersion 60 \times objective with NA = 0.6. The power in the center of the excitation beam was estimated to be 0.35 kW/cm². Detection of the optical signal was performed with single photon avalanche diodes. Data acquisition was based on the Time-Correlated Single Photon Counting (TCSPC) method [18]. The wavelength of the excitation laser was filtered out by a long pass filter with transmission only for wavelengths higher than 540 nm. The time resolution of the measurements is defined by the instrument response function (IRF) of the MicroTime 200 and is about 80 ps. Photon anti-bunching tests for the verification of single QDs were performed by Hanbury Brown-Twiss setup [19] incorporated into the MicroTime 200.

The data processing was performed using the resolution fitting method, while the IRF was measured using the reflection from a gold mirror. The number of exponents used to fit the experimental data depends on the number of physically different luminescence sources, which is a priori unknown. Thus, the number of the exponents was selected to provide the optimal fit of the original curves.

2. Experimental results. First, in the case of the borosilicate glass no detectable signal has been observed.

Second, we conducted time-resolved PL measurements on a pure gold layer and an Au/ Al_2O_3 layer stack without QDs (see Fig. 1a). For the pure gold sample, fitting of the measured PL decay curves was performed using single exponential model that gave the relaxation time $\tau_{\text{Au}} = 0.08 \pm 0.01$ ns. At the pump intensity level of 0.35 kW/cm² the origin of this relaxation curve could be both pump signal replica or a luminescence with a relaxation time less or comparable with the IRF. In the case of the Au/ Al_2O_3 layer stack a two exponential fitting function was used, which resulted in two decay times $\tau_{1,\text{Au}} = 0.08 \pm 0.01$ ns and $\tau_{2,\text{Al}_2\text{O}_3} = 3 \pm 0.2$ ns. The first time is identified, as in the case of pure gold, as a pump replica plus and possible fast luminescence from gold, while the second time is attributed to the luminescence of the Al_2O_3 layer.

Third, a series of experiments were performed with QDs on substrates. Positions of single QDs were first tested by means of confocal scanning of the optical signal in a scanning area of 80 \times 80 μm^2 . At concentrations of 10^{-7} ppm and below we observed well separated single QDs. In Figs. 2a and 3a a scan of the PL signal for a single CdSe/ZnS QD on a pure borosilicate glass and a typical time trace are shown, respectively. It is notice-

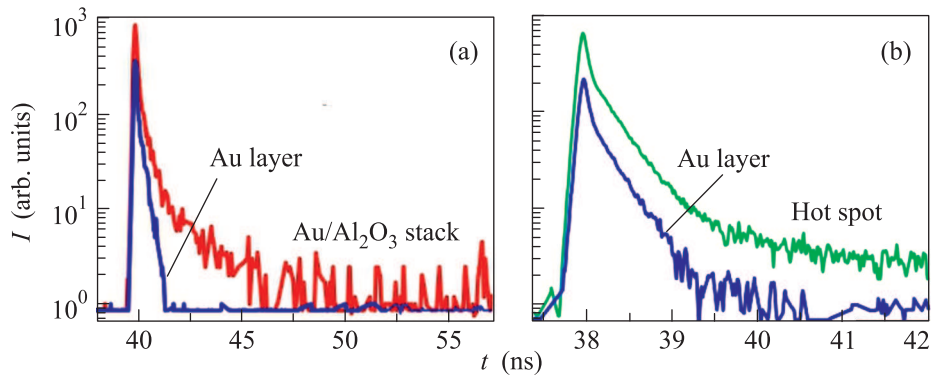


Fig. 1. (a) – Time-resolved photoluminescence for a gold layer and Au/Al₂O₃ layer stack. (b) – PL decay dynamic measured from a hot spot on a gold layer formed by a bleached QD; PL decay dynamics from a gold substrate without a hot spot

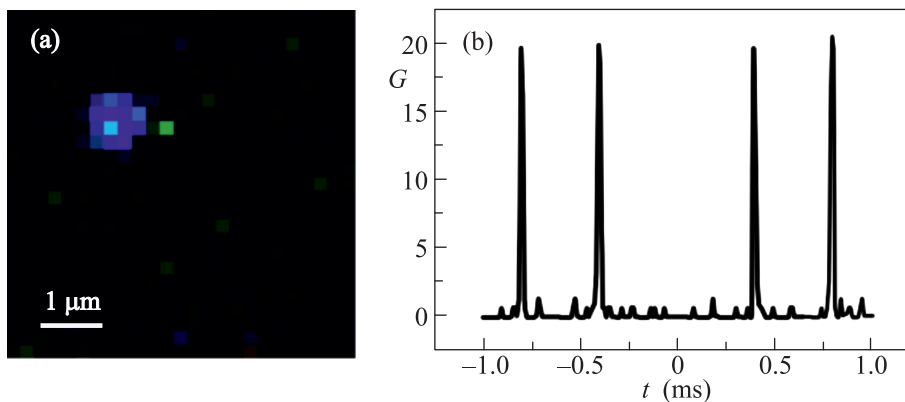


Fig. 2. Results for a single CdSe/ZnS QD on a pure borosilicate glass. (a) – Scan of PL signal. (b) – Correlation function $G(t)$

able that CdSe/ZnS QDs were bleached after about 30 s of illumination. Thus, the full time for the data acquisition was limited by the bleaching time of QDs. A single exponential fit allowed for a perfect approximation of a measured decay histogram (see Fig. 3b). The life time for a single CdSe/ZnS QD on a pure borosilicate glass was estimated to be $\tau_{\text{QD}} = 3.8 \pm 0.3$ ns. By performing a photon anti-bunching measurement we verified the presence of a single QD in the measured volume. An example of photon anti-bunching measured with a single CdSe/ZnS QD on a pure borosilicate glass is shown in Fig. 2b.

A typical time trace measured on a single CdSe/ZnS QD on a pure gold layer is shown in Fig. 3c. Bleaching of a CdSe/ZnS QD occurs after several seconds of illumination and the PL signal goes to the level of the background PL signal from gold. The PL signal is very unstable and has typical spikes on the time scale of 0.5 s. Due to the background signal the photon anti-bunching observation failed and we could not verify presence of a single QD. Fitting of a measured PL decay curve

(see Fig. 3d) with a double-exponential model gives two components: one with a short life time τ_{Au} of about 0.08 ± 0.01 ns corresponding to the gold layer as previously mentioned and a longer one with $\tau_{\text{QD}} = 2.3 \pm 0.3$ ns corresponding to the fluorescence of QDs.

The time trace measurements for CdSe/ZnS QDs on the Au/Al₂O₃ layer stack show more stable PL behaviour (see Fig. 3e). Again, we observe bleaching of CdSe/ZnS QDs on the time scale of 10 s without blinking. The best fit of the experimental decay histogram (see Fig. 3f) was achieved with a three exponential model. The retrieved life times correspond to gold layer $\tau_{\text{Au}} = 0.08 \pm 0.01$ ns, Al₂O₃ layer $\tau_{\text{Al}_2\text{O}_3} = 3 \pm 0.2$ ns, and QDs on Au/Al₂O₃ layer stack $\tau_{\text{QD}} = 1 \pm 0.2$ ns.

3. Discussion. First of all we would like to discuss the origin of the background PL signal measured from the gold and Al₂O₃ layers (see Fig. 1a). Fluorescence from bulk gold in the visible spectral range was observed already in 1969 by Mooradian [20]. The gold fluorescence is associated with a radiative recombination of photo-excited holes from the *d*-band with electrons from

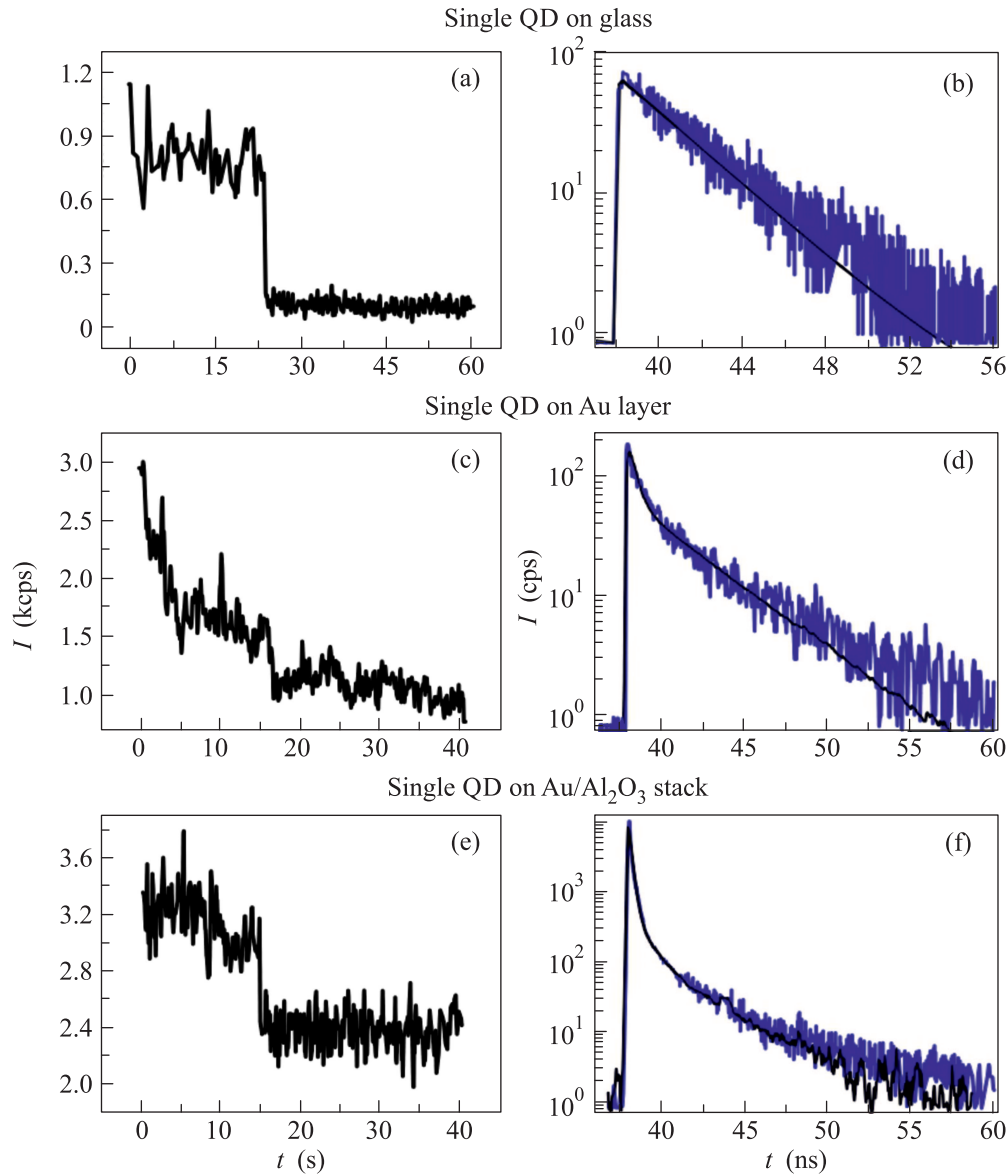


Fig. 3. (Color online) Results for a single CdSe/ZnS QD on different substrates: a pure borosilicate glass (a, b); on a gold layer (c, d), and on a Au/Al₂O₃ layer stack (e, f). (a, c, e) – Typical time trace measured on corresponding substrates. (b, d, f) – PL decay dynamic (blue curves – measured histograms, black curves – fitting functions)

Table 1. Measured life times (ns) retrieved from time resolved measurements on pure substrates and substrates with CdSe/ZnS QDs

	Borosilicate glass	Gold	Au/Al ₂ O ₃ layer stack
Pure substrates	No PL signal	$\tau_{\text{Au}} = 0.08 \pm 0.01$ ns	$\tau_{\text{Au}} = 0.08 \pm 0.01$ ns $\tau_{\text{Al}_2\text{O}_3} = 3 \pm 0.2$ ns
Substrates with QDs	$\tau_{\text{QD}} = 3.8 \pm 0.3$ ns	$\tau_{\text{Au}} = 0.08 \pm 0.01$ ns $\tau_{\text{QD}} = 2.3 \pm 0.3$ ns	$\tau_{\text{Au}} = 0.08 \pm 0.01$ ns $\tau_{\text{Al}_2\text{O}_3} = 3 \pm 0.2$ ns $\tau_{\text{Al}_2\text{O}_3} = 3 \pm 0.2$ ns

the conduction band. The fluorescence from bulk gold is extremely low and is characterized with a maximum efficiency of recombination processes of about 10^{-10} .

Investigations conducted on nanostructured gold particles [21, 22] and rough gold surfaces and films [23, 24] showed that the fluorescence increases in comparison

with the bulk by several orders of magnitude. The fluorescence increase is associated with enhancement of exciting and outcoming fields due to the coupling to the structural surface plasmon resonances [24]. In our thin films, plasmons can be related to the internal polycrystalline structure of the Au films determined by the islands-like growing process in the *e*-beam evaporation process [25]. The lifetime of *d*-holes was measured by Varnavski et al. [26] in emission time-resolved experiments on gold nanoparticles and was reported to be less than 50 fs. Though the decay time of the gold fluorescence is beyond the resolution of our experimental technique, which is 80 ps, we still can register the presence of fluorescence from the gold substrate. It is worth mentioning that the presence of a bleached (not emitting) QD causes the increase of the photoluminescence signal from the gold layer. The comparison of the fluorescence signal from a QD on a gold substrate after the QD was bleached with the fluorescence of pure gold (see Fig. 1b) shows that background fluorescence from gold increases more than 4 times. Here, the QD itself plays the role of a hot spot, which couples light to a surface plasmon and hence triggers the mechanism of the gold fluorescence enhancement. This means that even when using gold layers with a smooth surface in single QD experiments an enhancement of the background fluorescence signal due to the QD hot-spot is to be expected. It is worth to mention that it is hard to distinguish between the gold luminescence and pump replica photons in the performed tests based only on the time resolved PL measurements and comprehensive spectral measurements have to be performed for their separation.

In our experiments we also observed fluorescence from the Al₂O₃ layers. The intensity of the background signal from the Au/Al₂O₃ stack exceeded twice the respective intensity from the pure Au substrate. The typical PL decay time for this component was $\tau_{\text{Al}_2\text{O}_3} = 3 \pm 0.2$ ns. Noticeable the Al₂O₃ layers demonstrate reversible bleaching (not shown here).

Now we will summarize the luminescence decay times of CdSe/ZnS QDs on different substrates. The general tendency is an bleaching of CdSe/ZnS QDs on the time scale of 30 s on the glass substrates, on the time scale of 2–3 s on the pure gold layer, and on the time scale of 10 s on the Au/Al₂O₃ layer stack (see Figs. 3a, c, and d). The mechanisms of CdSe/ZnS QDs bleaching have been extensively investigated by van Sark et al. [27, 28]. It has been shown that the main mechanism of bleaching for thin shell CdSe/ZnS QDs at room temperature is the photoinduced oxidation of the CdSe crystallites due to the oxygen present in the atmosphere. In the experiments of Ref. Sark et al. [27] photobleach-

ing of CdSe/ZnS with a ZnS shell counting 4 monolayers on glass substrates in air atmosphere occurred after less than 60 s. The number of monolayers corresponding to the ZnS shell thickness of 0.6 nm of QDs used in our experiments can be estimated to be about 2 monolayers [29]. Accordingly, we can conclude that using appropriate host media for the prevention of QDs from photooxidation is essential for the design of single QD based hybrid systems with long-term functionality.

The almost non-blinking behavior of the CdSe/ZnS QDs in our experiments correlates with extremely short bleaching periods due to the photoinduced oxidation of their core. This means that the photooxidation mechanism drastically shortens the ionization period of nanocrystals. An additional contribution into the suppression of the blinking behavior of CdSe/ZnS QDs on gold substrates is provided by the rapid energy transfer between the QD and a surface [14, 30]. In our experiments we observed decreasing of the PL decay time from $\tau_{\text{QD}} = 3.8 \pm 0.3$ ns for CdSe/ZnS QD on a borosilicate substrate to $\tau_{\text{QD}} = 2.3 \pm 0.3$ ns for QDs on gold layers and to $\tau_{\text{QD}} = 1 \pm 0.2$ ns for QDs on Al₂O₃ layer stack. This tendency is commonly associated with decreasing of the non-radiative recombination rate due to the electromagnetic coupling of the QD to the surface plasmons [14, 31]. A single exponential decay dynamics for the QDs means that the relaxation happens only through a single channel for a single QD and the biexciton contribution [6] is excluded. The measured PL decay times for QDs on a glass, gold layer, and Au/Al₂O₃ layer stack substrates are summarized in Table 1.

4. Summary. We conducted time resolved PL investigations to identify the role of the background signal in the investigation of quantum dot – plasmonic hybrid systems. Targeting experiments on plasmonic systems strongly coupled to individual QDs we investigated thin shell CdSe/ZnS QDs on different substrates, including thin gold layers fabricated with the electron-beam evaporated process and gold substrates covered with an Al₂O₃ isolating spacer of 5 nm. We observed rapid bleaching of thin shell QDs in air, which implies the use of an appropriate host medium in order to realize a system with long-term functionality. In our experiments, the background luminescence intensity from both gold and Al₂O₃ was comparable with a PL signal from a single QD. This prevents the observation of photon anti-bunching from single QDs on gold substrates and Au/Al₂O₃ layer stack substrates. Moreover, a single QD acts as a hot-spot increasing the luminescence of the gold. Thus, observation of photon anti-bunching in strongly coupled hybrid systems becomes questionable. Nevertheless, the different signal sources in the in-

vestigated systems can be distinguished provided they exhibit different PL decay times.

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