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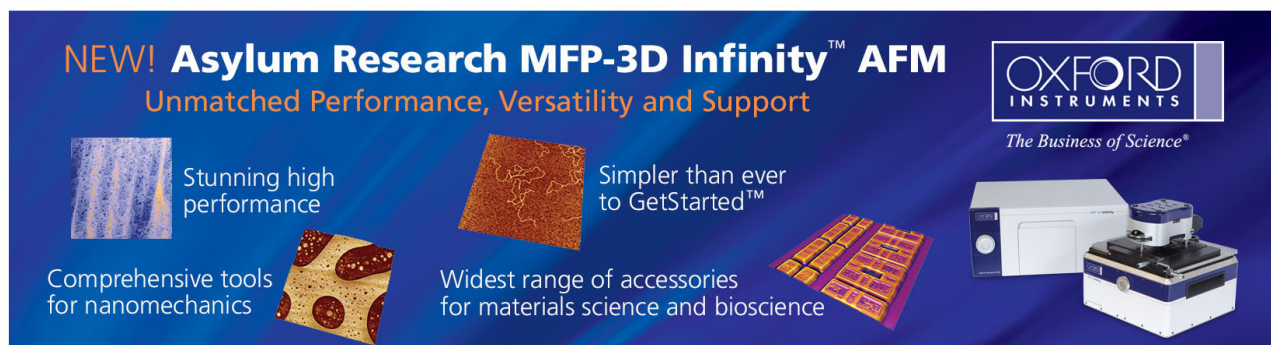
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Blinking suppression of colloidal CdSe/ZnS quantum dots by coupling to silver nanoprisms

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Fluorescence blinking of quantum dots (QDs) is a common but annoying behavior for practical applications as fluorescent markers or single photon sources. We demonstrate here, by coupling colloidal CdSe/ZnS QDs to silver nanoprisms, fluorescence blinking behavior can be suppressed. For most of coupled QDs, two emissive states with different fluorescence intensities and lifetime were observed. We suggest that energy transfer could play an important role in suppressing blinking behavior. © 2009 American Institute of Physics. [DOI: 10.1063/1.3154551]

Single-molecule detection (SMD) is a powerful tool to investigate temporal dynamics of biological molecules, for example, conformational dynamics of DNA, enzymatic dynamics, and protein folding/unfolding.¹⁻³ One of the key elements for the SMD technique is an appropriate single-molecule label. There are several requirements for these labels, including bright fluorescence at physiological temperatures, small sizes comparable to biological targets, good photostability, and nonblinking.⁴ However, for commonly used organic-dye molecules, fast photobleaching significantly degrades their practical use as single-molecule labels.⁵ Fortunately, in recent years, semiconductor colloidal quantum dots (QDs) were developed using low-cost bottom-up chemical methods.^{6,7} These QDs exhibit excellent fluorescence properties and meet most of the aforementioned requirements except for fluorescence blinking.⁸

Fluorescence blinking is a universal characteristic for single fluorophores.^{5,8,9} There are many interesting and puzzling phenomena behind the blinking behavior. However, this blinking behavior is an undesirable drawback for practical use in SMD. Therefore, better understanding of the physics involved in blinking and suppression of blinking is important.¹⁰ Actually, the blinking behavior in colloidal QDs has been investigated extensively.¹¹⁻¹³ Some characteristics were found, including a widespread time range from milliseconds to minutes and universal power-law on/off time distribution. One of the models called diffusion-controlled electron transfer was proposed by Tang and Marcus^{12,14} to explain these phenomena. Several of the model predictions appear to agree with the experimental observations. The off-state is often attributed to the formation of a charged QD, which a photoexcited electron is ejected out from the QD core into a trap state on the surface or surrounding matrix.^{15,16} In a charged QD (dark states), the exciton energy could be transferred to the excess hole in the core by efficient Auger-type relaxation.

Consequently, to suppress the blinking behavior of QDs, one simple idea is to block the electron transfer either by attaching organic ligands on the surface^{17,18} or by capping a thick layer.^{19,20} For the former case, the attached chemical ligands unfortunately are not very stable and could be removed.²¹ For the latter case, a multishell QD leads to an

increase in the size. Furthermore, due to large lattice mismatch between the CdSe core and the ZnS shell ($\sim 12\%$), CdS was chosen to form the thick shell because of a smaller lattice mismatch. However, this approach leads the formation of type-II band alignment. Such a structure could degrade the fluorescence performance due to less wave function overlap of electron and hole. In some other approaches, noble-metal materials were used to modify the blinking behavior.^{22,23}

In this work, we describe a simple method to suppress universal blinking behavior by introducing Ag nanoprisms. Upon coupling to Ag nanoprisms, fluorescence time traces change from binary blinking to nonblinking behavior with some intensity fluctuations. We suggest that energy transfer might play an important role in suppressing this blinking behavior.

Colloidal CdSe/ZnS QDs were purchased from Evident Technology (emission at ~ 600 nm). The Ag nanoprisms with an edge length of 47 nm were synthesized using the published method with minor modifications.^{24,25} Time-tagged, time-resolved (TTTR) measurements were performed during SMD. TTTR is based on time-correlated single-photon counting technique to record all time information for every detected photon, including relative time between excitation pulse and photon emission as well as the absolute time between the experimental start and photon emission.

Figure 1 shows the fluorescence time traces of representative single colloidal CdSe/ZnS QDs with and without coupling to silver nanoprisms. A typical binary blinking characteristic was observed for CdSe/ZnS QDs on glass. In

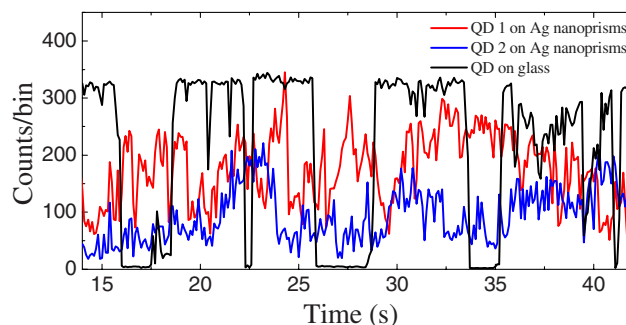


FIG. 1. (Color online) (a) Fluorescence time traces of single CdSe/ZnS QDs with and without coupling to Ag nanoprisms.

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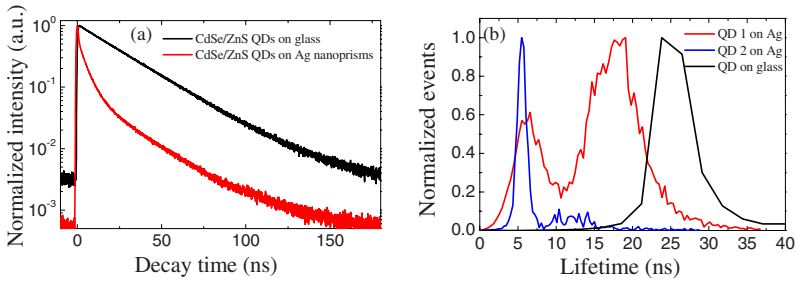


FIG. 2. (Color online) (a) Fluorescence decay profiles of single CdSe/ZnS QDs with and without coupling to Ag nanoprisms. (b) Fluorescence lifetime distribution of single CdSe/ZnS QDs with and without coupling to Ag nanoprisms.

contrast, a nonblinking trace with some intensity fluctuations was found for coupled CdSe/ZnS QDs on silver nanoprisms coated substrates. Obviously, the dark periods were absent for coupled QDs. More than 75% of individual QDs within the ensemble samples exhibit this nonblinking behavior. The most prominent interactions between QDs and metal nanostructures are energy transfer and plasmonic effects. These two effects are competing with each other and the overall results depend on the QD/metal separation. As shown in Fig. 1, we selectively display two cases for coupled QDs with different intensities for comparison. In spite of different fluorescence intensities, most fluorescence time traces display stochastic fluctuations but without obvious dark states. It is likely that each QD couples to nearby Ag nanoprisms differently because the distance to nanoprisms could vary from QDs to QDs.

In order to clarify the origins, we also performed TTTR measurements during the course of SMD. Figure 2(a) shows the fluorescence decay profiles of single CdSe/ZnS QDs with and without coupling to silver nanoprisms. The decay curve for QDs on glass exhibits single exponential profile with ~ 25 ns lifetime, in contrast, for coupled QDs, the decay is biexponential with one lifetime of ~ 5 and another lifetime of ~ 20 ns. Here, we also combined time-correlated single-photon counting technique and maximum likelihood estimation analysis to obtain fluorescence lifetime distributions. As shown in Fig. 2(b), most of the coupled QDs show two peaks centered at 10–20 ns and ~ 5 ns, respectively. The longer component varies from dots to dots, but the shorter component appears to remain at ~ 5 ns for most of QDs.

Figure 3(a) displays the fluorescence time trace for a selected coupled QD, which exhibits stochastic intensity

fluctuations without long-lived off states. In order to correlate the fluorescence intensity and the decay lifetime, fluorescence decay profiles were constructed by selecting a time-gated region, which involves either a high (yellow area) or a low (blue area) fluorescence intensity, as shown in Fig. 3(b). Clearly, these two time regions exhibit distinct lifetimes. Similarly, lifetime distributions were also recorded for overall high (pink area) and low (green area) intensity regimes, as shown in Fig. 3(c). In accordance with the time-gated results, there are two lifetime distribution profiles corresponding to the high and the low intensity regimes. These observations further support the existence of two distinctive states for single QDs coupled to silver nanoprisms.

Based on the present blinking models, the dark state is attributed to the formation of a charged QD. Therefore, to suppress blinking behavior, one could block electron transfer from a QD, or to make the charged QD emissive. Hohng and Ha¹⁷ and Fomenko and Nesbitt¹⁸ independently used similar methods to suppress single-QD blinking in solution by attaching specific surfactants to the surface. This surfactant can passivate the QD surface states, thus can reduce trapping of the photogenerated electron. Alternatively, Shimizu *et al.*²² incorporated colloidal QDs onto a rough gold substrate to obtain nonblinking QDs. In this case, the hopping between the neutral and the charged states are still present, but the original dark state becomes bright with an emitted photon energy shifted by ~ 20 meV. In addition, the fluorescence decay rates can be enhanced dramatically.

In contrast, in our case, no significant energy shift was observed (data not shown). Consequently, we attributed this nonblinking behavior to energy transfer from QD to silver nanoprisms. Previous reports have demonstrated that by introducing efficient relaxation channels (either energy transfer or defect states) to compete with Auger ionization, the transition to dark states can be reduced.^{23,26} With a coupling to silver nanoprisms, energy transfer from the excited QDs to silver nanoprisms could occur. Due to broad absorption band in silver nanoprisms caused by multiple plasmonic modes, QD emission can effectively couple to silver nanoprism and can cause efficient energy transfer process. In this case, the electron and hole could annihilate simultaneously and thus prevent the formation of the charge-separated dark states. Because near-field energy transfer process cannot be observed directly, the common way is to probe the far-field fluorescence properties. In general, fluorescence quenching and lifetime shortening are the main evidences for the occurrence of energy transfer. Indeed, in our experiments these two characteristics were found for most of coupled QDs.

In conclusion, we report a simple approach to suppress blinking by coupling to Ag nanoprisms. Fluorescence time traces shows a stochastic fluctuation without long-lived dark states. We suggest that energy transfer from QDs to silver

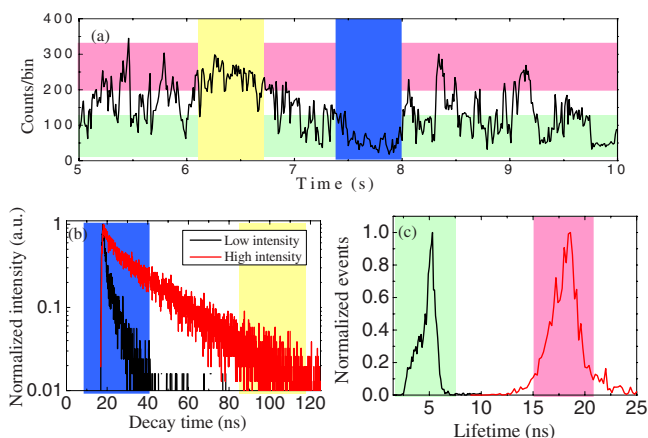


FIG. 3. (Color online) (a) Fluorescence time traces of selected single QDs coupled to Ag nanoprisms. (b) Fluorescence decay profiles for specific time gates of low and high fluorescence intensity. (c) Fluorescence lifetime distribution for high and low intensity sections.

nanoprisms is responsible for the suppression of blinking behavior.

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