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Suppression of grey state and optimization of the single photon emission of a colloidal semiconductor at room temperature

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The excitation energy dependency of single colloidal CdSe-CdS core-shell nanocrystals is investigated at ambient conditions. It was demonstrated that the photoluminescence blinking effect is totally suppressed by optically exciting nanocrystals with a laser wavelength located at a very low absorption spectrum range. The mechanism of this effect is theoretically attributed to excitation of only the core instead of both the core and the shell. The signal to noise ratio and the photon count are also significantly improved and better purity in terms of single photon generation is achieved.

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During the last decades, semiconductor nanocrystals (NCs) with core-shell structures, also called colloidal quantum dots,^{1,2} have been extensively studied. Their high quantum efficiency with high photostability at room temperature has attracted substantial research interest for a wide range of applications. They were first used in opto-electronic devices such as light emitting diodes,³ solar cells,⁴ and lasers.⁵ In biology, their surface can also be functionalized with a large number of chemical groups, which makes them excellent emitters for biological labeling⁶ and bio-analysis.⁷ At the single molecule level, semiconductor NCs are also potential and promising candidates for quantum information technology through single photon generation.^{8,9}

However, at the single level, semiconductor NCs exhibit a complex fluorescence intermittency also called the blinking effect. Solving this drawback is a necessary step for the implementation of single NCs into nanophotonic devices. Therefore, understanding the blinking mechanisms and finding a way to suppress them has been the focus of intensive studies.^{2,10,11} A variety of theoretical models have been proposed to explain the mechanism of NC photoluminescence blinking. The most common model is based on the transition from the neutral state to an ionized one, which is dark due to the very high efficiency of Auger recombinations.¹² Other models take into account the surface trapping states and defects in NCs.^{13,14}

A significant effort has been experimentally devoted to solve this problem including the synthesis of a surface charge compensator¹⁵ as well as the realization of a thick core-shell^{2,16} or a multi-core-shell structure.^{17,18} The crystalline growth of CdS shell NCs has been considered as the most useful method.^{16,19} For this specific structure, the photoluminescence blinking is strongly reduced and very long off periods are no longer observed. However, the photostability is not completed yet because the photoluminescence

still shows slight variations with grey periods corresponding to the emission from a grey state. The grey state results from the increase in the Auger lifetime as a consequence of electron delocalization in the whole core-shell structure.^{16,19}

In this letter, we demonstrate that optical excitation of the CdSe core alone enables to totally suppress the photoluminescence blinking of single CdSe-CdS core-shell NCs and make them an excellent single photon source at room temperature. Actually, most of the studies have been performed using a wavelength located in the absorption band of the core-shell NC, i.e., the excitation energy is well above the energy gap of both the core and shell. We therefore propose to excite only the CdSe core. In detail, we investigate the photoluminescence properties (blinking, photostability, emission rate, and single photon purity) of a single CdSe-CdS core-shell NC excited by two different laser wavelengths. The first and standard one having high photon energy are absorbed by both the core and the shell whereas the second laser, the newly proposed one, having low photon energy excites only the CdSe core.

The colloidal CdSe-CdS core-shell NCs were chemically synthesized by the isotropic and epitaxial growth of a CdS layer on a 2.5-nm-diameter CdSe core. The thickness of the CdS shell was tuned to reach 5 nm by controlling the sequential addition of cadmium and sulfur precursors as described by Mahler *et al.*² Figure 1(a) represents a transmission electron microscope (TEM) image of the colloidal NCs, confirming their quasi-spherical shape with an average diameter of 13 nm. The inset figure illustrates a structure model of the CdSe-CdS NCs with detailed parameters of the core and shell components. The NCs are diluted in a mixture of 90% hexane–10% octane with a nanomolar concentration.

The absorption spectrum shown in Fig. 1(b) was measured at ambient temperature using a Lambda 950 UV/VIS-Perkin Elmer spectrometer. An energy diagram model is proposed in Fig. 1(c) to explain the absorption mechanism of this core-shell structure. The band gaps of the wurtzite CdSe bulk crystal [$E_g(\text{CdSe})$] and CdS [$E_g(\text{CdS})$] are 1.74 eV and 2.42 eV, respectively. Due to quantum confinement, the

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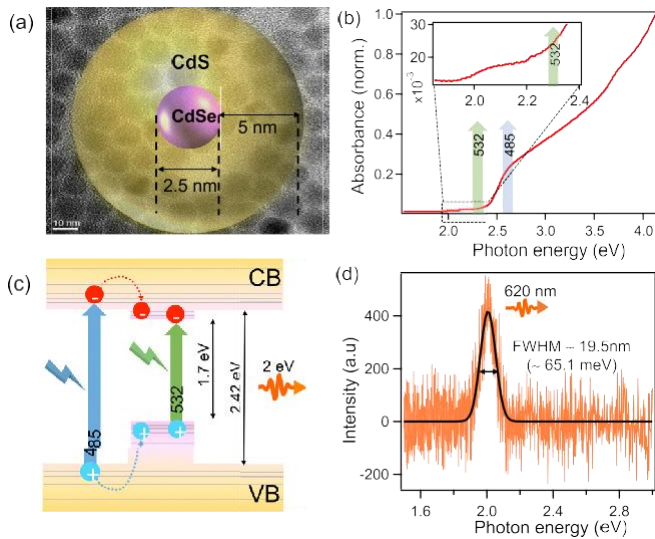


FIG. 1. (a) TEM image of colloidal CdSe-CdS NCs and illustration of the core-shell structure. (b) Measured UV-vis absorption spectrum of CdSe-CdS NCs in a hexane-octane solution. The two vertical lines indicate the excitation laser wavelength at 532 nm and 485 nm, corresponding to 2.34 eV and 2.56 eV photon energy, respectively. The zoom in the figure shows the first excitonic absorption peak of the colloidal semiconductor. (c) Schematic illustration of the energy diagram of the core-shell CdSe-CdS with 2 different mechanisms of the excitation. (d) The emission spectrum of a single NC with an emission peak at around 620 nm.

lowest excitonic transition inside the CdSe core is observed around 2.0 eV. The absorption gradually increases until 2.5 eV, as seen in the inset of Fig. 1(b). Above this value, excitons are also excited inside the CdS shell and the absorption cross section rises sharply.

In order to study the influence of the excitation wavelength on the single NC fluorescence at ambient conditions, the NCs are first spin-coated on a glass coverslip and then optically and individually characterized by a confocal microscope.²⁰ This confocal system was modified by using two continuous-wave lasers for excitation. The first one (“green” in the following) operates at 532 nm–wavelength, equivalent to a photon energy of 2.34 eV, which is higher than the CdSe band-edge transition but lower than the CdS one. The other laser emitting at 485 nm–wavelength (“blue” in the following), is equivalent to a photon energy of 2.56 eV, which is 140 meV above the CdS band gap. The two excitation energies are shown on the absorption spectrum [Fig. 1(b)] and on the schematic CdSe-CdS NCs energy band diagram [Fig. 1(c)]. When excited by any excitation wavelengths, electrons and holes relax rapidly to the band-edge states of the CdSe core. Finally, a radiative recombination takes place with an energy of 2 eV (620 nm) corresponding to the fluorescence spectrum shown in Fig. 1(d) with the full width at half maximum (FWHM) of about 20 nm. More precisely, the analysis of about 20 NCs shows that the FWHM is slightly larger (about 2 nm) when 485 nm excitation is used. This can first come from a higher spectral diffusion at low wavelength excitation, as observed by Emedocles and Bawendi.²¹ Moreover, by 485 nm excitation, the fluorescence of a single NC can switch between bright and grey states that are spectrally shifted by a few nm. In contrast, by 532 nm excitation, the bright state is mostly observed as shown in the following.

We then investigated the fluorescence flickering of a single NC by measuring the photon emission as a function of time. Figure 2 shows a comparison of the photoluminescence of the same single NC excited by either 485 nm (standard) or 532 nm (low absorption) laser sources. As usual, the fluorescence obtained by the blue laser switches between two states. Low emitting periods, considered as the grey state, with a random duration are observed in the fluorescence intensity trajectories at room temperature, as evidenced on the fluorescence image [Fig. 2(a)] and on fluorescence time dependence [Fig. 2(b)]. The histogram of the intensity (time bin of 1 ms) plotted in Fig. 2(c) also clearly shows two peaks corresponding to the two emitting states.

In strong contrast, for the same NC and the same fluorescence intensity (the excitation power was tuned to take into account the difference between the absorption cross sections at 532 nm and 485 nm), the switches between the grey and the bright states are completely suppressed under the excitation of the green laser. The fluorescence image shows a continuous and smooth intensity [Fig. 2(d)] and the fluorescence intensity is completely stable for a long duration, as shown in Fig. 2(e). The intensity histogram [Fig. 2(f)] also only shows a narrow peak which is quantitatively adjusted by a Poissonian distribution. Thus, by exciting with the green laser, the single NC no longer oscillates between the two states having different quantum efficiencies, resulting in a perfectly stable fluorescence emission.

Actually, the blinking properties of NCs are quite complex. Previous experiments reported the dependence on the wavelength of CdSe/ZnS NCs^{22,23} or nanorod²⁴ blinking. The statistics of the duration of “Off” periods is insensitive to the photon excitation energy but long “On” periods are less likely to occur for short wavelength excitation. As for CdSe/CdS NCs, the generation of excitons by photons with a high energy with respect to the band gap results in a reduction of the “On” period duration. However, in the case of

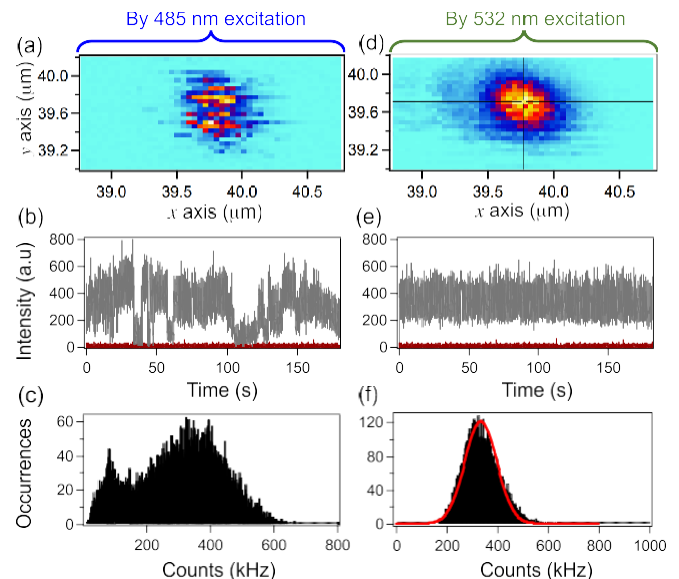


FIG. 2. Comparison of the fluorescence blinking effect of a single CdSe-CdS NC excited by two different laser wavelengths: 485 nm and 532 nm. (a) and (d) Fluorescence images obtained by a raster scan. (b) and (e) Fluorescence intensity versus excitation time. The red curves represent noises. (c) and (f) Corresponding intensities distributions.

CdSe/ZnS NCs, blinking can be only reduced by increasing the wavelength excitation while our data shows that blinking suppression can be achieved with excitation near resonance for CdSe/CdS NCs. The mechanism of this fluorescence stability is already mentioned and illustrated in Fig. 1(c). 532 nm excitation prevents the hole to access trap states since it is created and remains confined in the core. Concerning the electron, it is delocalized in the whole core-shell structure for the two excitation wavelengths. However, trapping of this carrier during relaxation to the minimum of the conduction band through mechanisms such as phonon-assisted ones is much less probable by the 532 nm excitation since less energy has to be dissipated.²² Ionization of the NC is then hindered when operating at 532 nm. The low one-photon absorption technique provides thus an efficient approach to improve the stability of the emission.

Furthermore, the emission characteristics of the NCs are also improved. In Fig. 3(a), we first plotted the count rate versus the pumping power where the emission rate increases from few hundred counts to million counts per second. Due to the larger absorption-cross section of CdSe-CdS NCs toward the higher energetic wavelengths, we obtained higher emission rates for the blue laser comparing to the green laser. However, increasing the pump power also facilitates the larger probability of photobleaching of the NCs. The first experimental data concerning the PL quenching of NCs are shown in Fig. 3(b). The NC can emit from just a few seconds to hours strongly depending on the excitation power. With the 532 nm laser, the emission duration of the single NCs significantly increases by approximately two orders of magnitude compared to the case by 485 nm excitation. This is due to the higher absorption cross section at 485 nm. More interestingly, Fig. 3(c) shows that, for a given count rate, i.e., for a given number of excitons generated by the optical excitation per unit of time, the emission duration is higher for the green laser. This result infers that the transitions excited by the 532 nm laser have less chance to create charge carriers in the NC, which is at the origin of the photobleaching effect. This result again shows a great advantage of using green laser as the excitation source for core-shell CdSe-CdS NCs, as compared to the blue standard one.

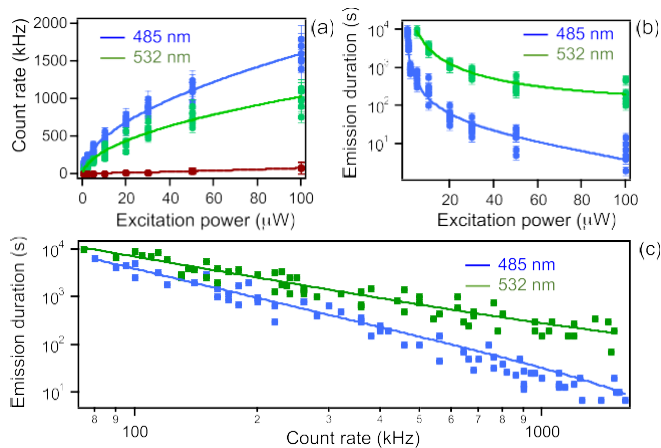


FIG. 3. (a) The dependence of the count rate of individual NCs upon the excitation power at the laser wavelength of 485 nm (blue) and 532 nm (green), and noise (red). (b) Fluorescence duration versus the excitation power of two excitation lasers. (c) Emission duration versus the photon counts.

Beyond the photostability and the photobleaching effect, the single photon generation characteristics also depend on the excitation wavelength. We then characterized the time statistics of the photons at a short time scale through the second-order intensity correlation function defined as

$$g^{(2)}(t; t+s) = \frac{\langle I(t)I(t+s) \rangle}{\langle I(t) \rangle \langle I(t+s) \rangle}; \quad (1)$$

where $I(t)$ is the fluorescence intensity, $\langle \rangle$ indicates ensemble averaging, and s is the time delay between two detection events. The single photon purity is commonly determined by the value of $g^{(2)}(0)$: an ideal single photon source corresponds to $g^{(2)}(0) = 0$, whereas, a coherent laser source gives $g^{(2)}(0) = 1$. This $g^{(2)}(0)$ parameter was experimentally determined by using a standard Hanbury Brown and Twiss experiment.

Figure 4(a) shows the evolution of $g^{(2)}(0)$ as a function of the count rates, obtained by different excitation powers. The experimental data is directly presented without background subtraction. Over 200 individual NCs were examined in this experiment. The emission rate increases from 2 kHz to over 1000 kHz as a function of the excitation power. The value of $g^{(2)}(0)$ increases from 0 to 1 as the contribution of multiexcitonic recombinations rises for high excitation intensity. The trend lines display the influence of the laser wavelength on single photon emission. For the same detected count rate, using the green laser provides the highest single photon purity, i.e., the lower $g^{(2)}(0)$ value. Considering the standard limit of $g^{(2)}(0) = 0.5$, the data of Fig. 4(a) shows that the NC remains as a single photon source for a count

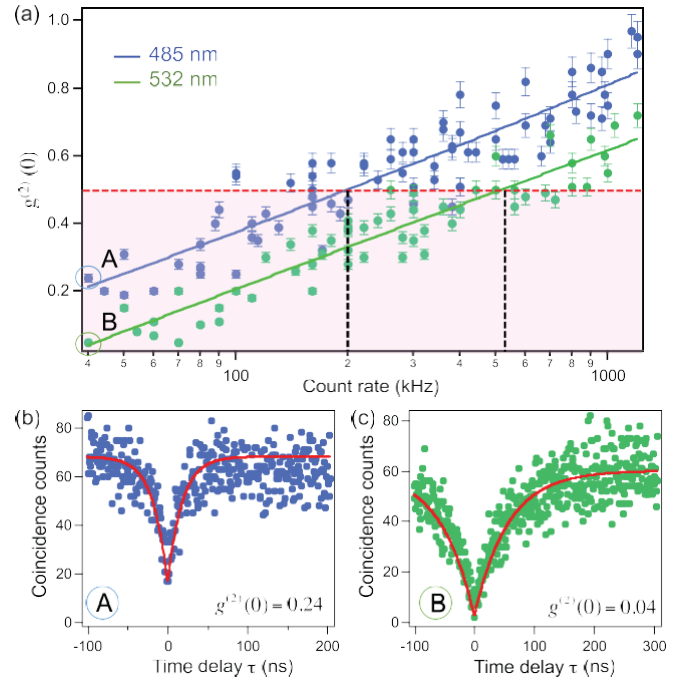


FIG. 4. (a) Variation of $g^{(2)}(0)$ as a function of the count rate, obtained by exciting the same individual NC with different laser wavelengths: 485 nm (blue) and 532 nm (green). Markers as experimental data and lines are fitted curves. The pink color area indicates the region where $g^{(2)}(0) < 0.5$ (the standard limit to consider that single photon generation is achieved). Second-order correlation $g^{(2)}(s)$ obtained by 485 nm laser (b) and by 532 nm laser (c), corresponding to points A and B shown in (a), respectively.

rate about three times higher when the green laser is used. Namely, the single photon source emits less than 200 thousands photons per second when excited by a 485 nm laser but can reach about 500 thousands photons per second when excited by a 532 nm laser.

In order to better understand the influence of the excitation wavelength on the single photon purity, let us consider the two data points A and B [Fig. 4(a)] for which a single NC is excited by the blue or the green laser and emits the same low count rate (about 4 kHz). Figures 4(b) and 4(c) show clearly the influence of the excitation energy on the antibunching property. We fitted the antibunching curves

using an exponential curve $1 - be^{-s_0 t}$.²⁵ For an atomic two-level system and well below the saturation limit, s_0 is mostly related to the lifetime of the excited level²⁵ (the lifetime is the asymptotic value reached at zero pumping). In our case, the fit provides the lifetime and $g^{(2)}(0)$ values. These two values express the contribution of the ionized and neutral states to the fluorescence dynamics at the nanosecond time scale.

For the blue laser, $s_0 = 18$ ns which is an intermediate value between the excitonic lifetime (typically 60 ns for these NCs) and the trion lifetime (typically 10 ns),¹¹ showing that the emission of both ionized and neutral states is collected. In contrast, for the green laser, the value of $s_0 = 56$ ns is close to the typical excitonic lifetime (the small correction is due to the non-zero pumping rate), which is another confirmation of the blinking suppression in this case. Concerning the amount of antibunching, we also observe a significant difference of $g^{(2)}(0)$, obtained by two excitation lasers, namely $g^{(2)}(0) = 0.24$ (point A) and $g^{(2)}(0) = 0.04$ (point B). By blue excitation, ionization is more likely to occur. Since multiexcitonic recombinations exhibit a higher relative quantum efficiency for the grey state,²⁶ the amount of antibunching then decreases for this wavelength excitation.

In conclusion, we demonstrated that tuning the wavelength of the optical excitation to a very low absorption range can be used to improve the fluorescence properties of single CdSe-CdS core-shell NCs at room temperature and under air condition. First, the creation of excitons in the core solely enables the suppression of the residual blinking effect observed in the emission of these colloidal nano-emitters. The photobleaching effect is also strongly reduced leading to a single photon emission of hours at room temperature. Thanks to the lack of ionization, the purity of the single photon source is clearly observed at a very high emission rate, namely 500 kHz. These results are of high importance since this approach is easy to implement. It could be extended to study the time coherence of the emission at low temperature.

In this case, resonant excitation, which is more challenging to implement practically, should be also considered.

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