Controlling blinking in multilayered quantum dots

Ruimin Wang, Yanpeng Zhang, Chenli Gan, Javed Muhammad, and Min Xiao

Key Laboratory for Physical Electronics, Devices of the Ministry of Education and School of Science, Xi’an Jiaotong University, Xi’an 710049, People’s Republic of China
Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701, USA

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The fluorescence intermittency of multilayered quantum dots (QDs) is experimentally investigated. The measured blinking statistical probabilities for QDs of different shell structures and at different excitation powers are compared with the diffusion controlled electron transfer model. The results show that the power law statistics for the “on” and “off” events depend strongly on the structure and thicknesses of the shells. Strongly suppressed blinking behavior is observed in the CdSe/CdS/ZnCdS/ZnS QDs. © 2010 American Institute of Physics. [doi:10.1063/1.3396985]

In recent years, colloidal semiconductor quantum dots (QDs) have attracted considerable attention because of their potential applications. One problem which greatly affects certain applications of QDs is the fluorescence intermittency (or blinking) phenomenon. It is generally believed that photoluminescence (PL) blinking is caused by extra charges in the nanocrystal that greatly enhance nonradiative decay rates. One way proposed to slow down the nonradiative Auger recombination is physical separation of the carriers into different spatial domains. Nearly nonblinking QDs were produced by growing a thick CdS shell onto the CdSe core. On the other hand, the nonradiative Auger recombination is strongly affected by the potential change in the confinement regime. Recently, nonblinking CdZnSe/ZnS QDs have been realized by growing gradually changing core/shell interfaces.

The CdSe/CdS QDs have high crystallinity but the fluorescence quantum yield (QY) is sensitive to surface effects due to the lower band offset of CdS. The CdSe/ZnS QDs have appreciable electronic passivation and chemical stability. However, large lattice mismatch can affect the QY and blinking behavior. In order to combine the advantages of both CdS and ZnS shell materials, the multilayered CdSe/CdS/ZnS QDs have been synthesized. The studies show that the multilayered QDs have high crystallinity, high QY, and improved photochemical stability. However, the blinking behaviors of such multilayered QDs are not very clear.

This experiment consists of five samples (labeled as samples A–E) of multilayered QDs. Starting with a CdSe core (sample A), adding a shell with 2 monolayers (MLs) CdS, 2 MLs ternary CdZnS, and 3 or 5 MLs ZnS to produce the 2, 4, 7, and 9 layered samples [samples B–E, respectively, see Fig. 1(a)]. The multilayered shells were synthesized by a modified successive ion layer adsorption and reaction method. Samples for PL intermittency measurements were prepared by spin coating dilute solutions of the QDs in hexane onto quartz coverslips. The QD density on the substrate was controlled by changing the concentration of the QDs in the solution before spin coating.

The measurements were performed by using a standard far-field confocal microscopic technique. The 488 nm line of an argon-ion laser was used as the excitation source. A high magnification microscope objective (150×, NA=0.55) was used to excite the sample and collect the fluorescence which was then sent to the spectrometer and detected by photomultiplier tube. The sample was placed on a quartz crystal coverslip mounted on a piezocontrolled XYZ translation stage. The entrance aperture to the spectrometer was reduced from 2 to 0.5 mm, ensuring that only one dot was being analyzed at a time [as shown in Figs. 1(b) and 1(c)]. Figures 1(d) and 1(e) depict the PL intensity trajectory of sample E over a 60 s period with a 10 ms integration time at an excitation intensity of 508 W/cm².

According to the diffusion controlled electron transfer (DCET) model, when time $t$ is larger than the critical time constant $t_{c,i}$, but shorter than the effective diffusion time constant $t_{r}$, the on- and off-probability distribution functions can be written as

$$P(t)=ct^{-m} \exp(-\Gamma_i t),$$

where $\Gamma_i=E_{A,i}/2k_B T_r$ and $i$ is “on” or “off.” $E_{A,on}=(\lambda+\Delta G_i^0)^2/4\lambda$ and $E_{A,off}=(\lambda-\Delta G_i^0)^2/4\lambda$ are the activation energies for electron transfer in the “on” and “off” states, re-

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*Electronic mail: ypzhang@mail.xjtu.edu.cn.
*Electronic mail: mxiao@uark.edu.

[FIG. 1. (Color online) (a) Examples of multilayered QDs. A: CdSe core; B: Sample A+2 ML CdS; C: Sample B+2 ML CdZnS; D: Sample C+3 ML ZnS; E: Sample D+2 ML ZnS. [(b) and (c)] PL images of single CdSe/CdS/ZnCdS/ZnS QDs with a fully opened entrance slit of the spectrometer and with a narrower slit for measuring the blinking of an individual QD. [(d) and (e)] Fluorescence trajectory segments (d) and the corresponding photon-count histograms (e) for sample E over a 60 s period with a 10 ms integration time at an excitation intensity of 508 W/cm².]
respectively. Issac et al. have shown that the exponent for the power law is correlated with dielectric properties. In CdSe/CdS QDs, a clear increase in $m_{\text{off}}$ with a decrease in $m_{\text{on}}$ has been reported. Figure 2(a) presents the “on”-time probability distributions for samples A to E at 300 K and at excitation intensity of 182 W/cm². Different probability distributions can be seen with growing multilayered shells. We determine the power-law exponent $m_{\text{on}}$ and the diffusion parameter $\Gamma_{\text{on}}$ by fitting our experimental data with Eq. (1).

Figure 2(b) shows the “off”-time probability distributions under the same conditions. Compared with the “on”-time events, there are no observable bending tails for the “off”-time, so the “off”-time distributions are fitted with a simple power-law function of $P_{\text{off}}(t)=ct^{-m_{\text{off}}}$. There are big differences in the “off”-time probability distributions for different samples.

Figure 3(a) gives the variation in the power-law exponent $m_{\text{on}}$ with respect to the number of shells excited at 182 W/cm². One can see that the CdSe core has the maximal power-law exponent of $m_{\text{on}}=1.35$. With the growths of 2 MLs CdS and then 2 MLs Zn$_{1-x}$Cd$_x$S shell layer, $m_{\text{on}}$ decreases continuously. When another 3 MLs of ZnS were grown onto the CdSe/CdS/ZnCdS core-shell QD, $m_{\text{on}}$ increases. However, as the thickness of the ZnS shell increases to 5 MLs, $m_{\text{on}}$ further decreases. The smaller value of $m_{\text{on}}$ corresponds to an increased probability of having long “on” times. $m_{\text{off}}$ shows just the opposite behavior from the trend of $m_{\text{on}}$. Sample E has a very large value of $m_{\text{off}}$, which indicates that the blinking behavior is suppressed in such multilayered QDs.

In CdSe/ZnS, there is an abrupt potential barrier which can increase the nonradiative rate [see Fig. 4(a)]. In the CdSe/CdS/ZnCdS QDs, the confinement potential presents a series of staircase variation steps. Because of the low band offset for each shell, the electronic wave function can distribute over the shells, where the hole wave function decreases rapidly due to the higher effective mass. In such case, electron confinement and the overlap between the electron and hole wave functions are reduced. Thus, the rate of Auger recombination is slowed down. When 3 MLs of ZnS were coated onto the CdSe/CdS/ZnCdS, the Zn-atoms might diffuse into the Cd-rich regions and form a high composition Zn$_{1-x}$Cd$_x$S region, thus increasing the band-offset of the shell and hence the effective confinement. In this situation, $m_{\text{on}}$ increases. With increasing ZnS shell thickness, the tunneling rate of an electron to surface traps will exponentially decrease and therefore, blinking can be further suppressed. It is reasonable to consider that a gradually changing confinement potential [the dashed line in Fig. 4(a)] can be obtained through modulating the compositions and thicknesses of alloy shells, which is similar to the non-blinking alloyed core QDs.

Figure 4(b) presents the fluorescence spectrum of sample E. Figure 4(c) shows the PL peak positions for samples A–E. It can be seen that the PL peaks shift to red with growing CdS and Zn$_{1-x}$Cd$_x$S shell. This is due to the extension of the electronic wave function into the shell region, which increases the effective size of QDs. A blueshift in PL peaks is observed when ZnS was coated onto the CdSe/CdS/ZnCdS. As discussed above, this is attributed to an increase of the quantum confinement. Similar results were reported by Xie et al.

In CdSe/CdS/ZnCdS/ZnS QDs, blinking behavior has a clear dependence on the ZnS shell thickness. This is inconsistent with the results reported in CdSe/ZnS QDs (Ref. 11) which blinking behaviors are independent of the ZnS thickness. We believe that the ZnCdS alloy shell plays an important role. Because of the large lattice mismatch between CdSe and ZnS, hole trapping at the core-shell interface provides a secondary nonradiative decay mechanism. For CdSe/CdS/ZnCdS/ZnS QDs, ZnCdS is used as a buffer layer. The TEM image of such QD (Ref. 6) reveals a high crystallinity with continuous lattice fringes throughout the entire particle. We believe that the electron tunneling to surface traps is the key mechanism for fluorescence intermittency in

FIG. 2. The log-log plots of the time dependence of $P_{\text{on}}(t)$ and $P_{\text{off}}(t)$ from experimental data of samples A to E at 300 K and at excitation intensity of 182 W/cm². The data (square points) are fitted to $P_{\text{on}}(t)=ct^{-m_{\text{on}}}$ in (a) and $P_{\text{off}}(t)=ct^{-m_{\text{off}}}$ in (b), respectively.

FIG. 4. (a) The potential energy functions of multilayered QDs. (b) The fluorescence spectrum of sample E with a 10 ms integration time at 300 K and at excitation intensity of 350 W/cm². (c) Variation in the PL peak position with respect to the number of shell MLs.
our samples. Increasing shell thickness may decrease the tunneling rate, so blinking is suppressed with a thicker ZnS layer.

However, the emission of multilayered QDs cannot be described simply by switching between the “on” and “off” states. The PL intensities have a continuous set of intermediate levels. PL intensity fluctuations indicate that there are different nonradiative decay channels. For multilayered CdSe/CdS/ZnCdS/ZnS QDs, there are several interfaces (such as CdSe/CdS, CdS/ZnCdS, and ZnCdS/ZnS). Electron or hole acceptor sites on different interfaces may result in a set of charge transfer states. Different from the deeply trapped surface states, the charges in the charge transfer states are in shallow traps and thus easy to reverse transfer.12 The existence of charge transfer states will change the population of the exciton state and reduce the PL intensity. In addition to the interface charge transfer states, there are deeply trapped surface charges on the outermost ZnS shell surface which can generate an internal local electric field. The local electric field also affects the PL intensity through shifting relative energy levels of the exciton and charge transfer states.

Figure 3(c) presents variations in the fit parameter \(\Gamma_{on}\) with respect to the excitation power. The power-law exponent \(n_{on}\) is kept constant for the same sample to determine \(\Gamma_{on}\). It can be seen that the value of \(\Gamma_{on}\) increases with the excitation power and the shell thickness. According to the DCET model, \(\Gamma_{i}\) is proportional to \(1/\tau_{i}\) and \(1/\tau_{i} = W/\tau_{f}, (W + \gamma_{0})\), where \(\gamma_{0}\) is the fluorescence decay rate and \(W\) is the pumping rate with \(W = 1/\tau_{f}\). The absorption cross section of QDs is given by \(\sigma_{abs}^{i} = (\omega/nc)^{2}f(\omega)^{2}2\pi n_{1}(4/3)\pi r^{3}\). \(n\) and \(n_{1}\) are the refractive indices of the medium and particles, respectively. \(r\) is the radius of particles. \(f(\omega)^{2}\) is the local-field factor. The shell structure can significantly affect the local-field factor. For a QD with a CdSe core-shell structure, \(f(\omega)\) can be written as \(f(\omega) = 3\varepsilon/(2\varepsilon + \varepsilon_{eff})\). \(\varepsilon\) is the dielectric constant of the medium and \(\varepsilon_{eff}\) is the effective dielectric constant of QDs. For the multilayered QDs with a CdSe core and three shells of CdS, CdZnS, and ZnS, \(\varepsilon_{eff}\) is a function of dielectric constants (\(\varepsilon_{1}, \varepsilon_{2}, \varepsilon_{3}\), and \(\varepsilon_{d}\)) and radii (\(a, b, c\), and \(d\)) of all layers. So \(\Gamma_{on}\) and \(\tau_{i}\) are sensitive to the light intensity and the structure of QDs. At higher light intensities or for QDs with a large effective radius, the effective diffusion rate \(1/\tau_{i}\) and the bending factor \(\Gamma_{on}\) increase. In addition, \(\Gamma_{on}\) is related to the excitation wavelength. When excited above the band gap the electron can more readily tunnel to surface traps.15

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