Spectral diffusion of single semiconductor nanocrystals: the influence of the dielectric environment

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Abstract

We have explored the influence of different matrices on the emission line shape of individual homogeneously coated CdSe/CdS/ZnS nanocrystals. The results obtained corroborate previous observations of a correlation between blinking events and spectral diffusion but in addition we have found that the extent of spectral diffusion is almost independent of the dielectric environment of the NC. Additionally, we report the observation of a correlation between the line width and emission energy which is not expected to occur in the spherical - symmetric NCs employed in this work. The implications of these results are discussed.

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Chemically synthesized semiconductor nanocrystals (NCs) exhibit interesting optical properties when studied individually. For instance, the photoluminescence (PL) emission experiences continuous random shifts both in its peak position and line width, a process known as spectral diffusion [1]. Stark spectroscopy experiments carried on individual NCs [2] have revealed that the emission peak position can shift as the result of the application of an external electric field that modifies the NC energy-level spacing through the quantum-confined Stark effect (QCSE) [3]. Consequently, the observed spontaneous spectral diffusion is thought to occur due to fluctuating electric fields produced by accumulation and redistribution of charges placed either in the near-by environment of the NC or directly on its surface [2]. These fluctuations are believed to dominate the line width of the emission of single NCs due to an inherent averaging on the position of emission that takes place during the time required to measure a spectrum [1], explaining why the widths obtained are significantly larger than the reported homogeneous line width measured by spectral hole burning [4]. In addition to these observations, recent experiments have shown that there is a correlation between the extent of these spectral shifts and switch-on events in the photoluminescence blinking of single NCs [5]. Blinking in NCs has been explained in terms of an Auger recombination mechanism, whereby a charged NC is in a non-emissive state due to efficient energy transfer from exciton annihilation to the excess charge carrier present in the NC [6]. Evidence for this model is supported by the intermittent presence of charges on single NCs [7] and the sensitivity of blinking dynamics to the dielectric environment of the nanocrystal [8]. This increases the probability of observing longer off-times in matrices with high static dielectric constants as a result of better solvation of the charged NC.

Based on this experimental evidence and the observed correlation between blinking and spectral diffusion, it seems reasonable to question whether there is a relationship between the dielectric environment of the NCs and spectral diffusion. In this paper we address this issue by following the temporal evolution of the emission spectra of single NCs embedded in matrices with different dielectric constants. We show that the extent of spectral diffusion is not affected by the polarity of the external medium that surrounds the NCs, and we show that for spherically symmetric NCs, the position of the PL is correlated to its line width.

We studied the photoluminescence (PL) of single CdSe/CdS/ZnS core/shell NCs that were synthesized following the methods of van Embden et al. [9, 10] (core diameter 4.3 nm, overall shell thickness 2 nm, passivated with octadecylamine and tri-butyl phos-
phite, ensemble emission max. 2.019 eV). A representative TEM image shown in Fig. 1(d). The samples were highly diluted from chloroform dispersions and spin-coated on top of thin films of polymer matrices that were initially deposited on clean glass coverslips from 1% w/w solutions. For the preparation of these films, we employed poly(vinyl alcohol) (PVA), poly(N-vinylpyrrolidone) (PVP), poly (methylenethacrylate) (PMMA) and polystyrene (PS). PMMA and PS were dissolved in chloroform together with the NCs, PVP was dissolved in ethanol whereas PVA was dissolved in demineralized water. The PL of individual NCs was measured using a modified commercially available laser-scanning confocal microscope (Olympus Fluoview 500), using a 60x/1.4 numerical aperture objective in the epi-illumination configuration. The PL was excited with the 488 nm line of an argon ion laser at typical powers of 300 nW (excitation power measured in front of the microscope objective) and dispersed onto a 0.55 m imaging spectrograph with a resolution of 0.1 nm (Jobin Yvon, TRIAX 550). The spectra were acquired at room temperature with integration times of 3s using a liquid-nitrogen-cooled charge-coupled device camera.

In Figure 1(a) we show a series of consecutive PL spectra for a single NC in PMMA. Consistent with previous reports [1, 11, 12], we observe that both the peak position and the line width of the emission of an individual NC constantly change during the measurement time (Fig. 1(b)). The extent of these changes can have a net value of up to 10 meV for the peak position, with the direction of these shifts fluctuating randomly in time. This demonstrates that the spectral shifts are not due to an irreversible process, such as photoinduced chemical changes or permanent reorganizations at the surface of the NCs. Additionally, it can be seen in this figure that relatively big shifts in the PL peak position are always likely to follow a switch-on event, a result that confirms the existence of a correlation between blinking and spectral diffusion [5].

In order to assess the possible effects of the matrix on the observed SD, we compiled histograms of the energy differences between consecutive emission events for a set of NCs deposited in different polymer matrices; the results are shown in Figure 2. In agreement with the works in references [3, 11, 12], the histograms of Figure 2 can be described by Gaussians, the width of which serves as an indication of the extent of spectral diffusion. As can be seen in Table 1, the values obtained for the widths of these histograms do not differ significantly for the different matrices employed. This indicates that the extent of spectral diffusion during consecutive emission events cannot be linked to charge trapping and reorganization.
in the matrix, as such processes would be sensitive to dielectric stabilization [8]. As discussed in reference [5], there are shifts in emission energy that occur in conjunction with blinking events which are known to take place on broadly distributed time scales [13]. Given that the histograms of Figure 2 were compiled from sets of spectra acquired on a time scale of 3 seconds, the widths of these histograms also include time-averaged information of events in which the NC, according to the charging hypothesis, could have ejected a charge carrier into the matrix several times. On this basis, the results shown in Table I demonstrate that ionization of the NC is not the dominant mechanism responsible for the magnitude of the SD and that if charge reorganization is responsible for the spectral shifts, then it must take place either at the surface of the NCs or directly at the core-shell interface. We note additionally that for the case of PMMA, the obtained width of 3.7 meV is comparable to that reported by Neuhauser et al from similar experiments that were carried out at cryogenic temperatures [5]. The fact that the width of this diffusion histogram remains almost unchanged by an order of magnitude increase in temperature indicates that the mechanism responsible for the extent of spectral diffusion is not thermally activated [11, 12].

In Figure 3 the emission line width and peak position shift (defined as the difference between the peak emission energy and the highest emission energy recorded in a given time series) are plotted for single NCs deposited in the different matrices. This figure clearly shows a correlation between these two parameters for spherical core-shell NC: the emission line width increases as the spectra redshifts.

This type of correlation has recently been observed in CdSe NCs overcoated with an elongated CdS shell [11, 12]. For this system, it was postulated that a QCSE is produced by a surface charge that moves and oscillates along the shell. Due to the one-dimensional character of this shell, the strength of the electric field at the NC core depends on the location of this surface charge along the length of the shell. When the charge is located close to the core the electric field perturbing the exciton increases, the effect of which is twofold. Firstly, the emission peak position is redshifted and secondly a broadening of the emission profile is observed due to fluctuations in the peak position, which occur to a greater extent in the presence of higher field strengths [11, 12]. However a corollary of this hypothesis is that such correlations should not be observed for spherically symmetric NCs, since in this case the distance from the NC core to the excess charge is radially symmetric. The results presented in Figure 3 clearly demonstrate that fast oscillations and diffusion of a charge carrier along
the length of an elongated shell are not responsible for the broadening associated with the redshifted emission and that such correlations are intrinsic to the NCs, regardless of the symmetry of their capping shells. This have been supported not only by the data presented here but also by the fact that similar observations have been reported for CdS nanorods in the absence of an inorganic shell [14].

In summary, we have presented experimental data that shows that the extent of SD does not depend on the dielectric constant of the matrix surrounding the NCs. It is therefore possible to infer that the charge reorganization that leads to the QCSE responsible for the spectral shifts occurs either at the surface of the NCs or directly at the core-shell interface. We have also shown the existence of a correlation between the position of the emission and the line broadening for NCs of spherical shape. This suggests that the mechanism responsible for the correlated broadening and redshift in the PL is intrinsic to the NC core. However, the exact mechanism that gives rise to the correlation remains at present unknown.

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FIG. 1: Spectral diffusion of the emission of a single CdSe/CdS/ZnS (4.3 nm core diameter, ensemble emission max. 2.019 eV) NC measured at room temperature in PMMA. (a) Temporal evolution of the PL spectrum. (b) Peak position and line widths as obtained from Lorentzian fits to the data shown in (a). (c) Switch - on spectral shifts (d) TEM image of the sample used, scale = 10 nm. Excitation power = 300 nW, integration time 3s. Excitation wavelength 488nm

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FIG. 2: Histograms of the difference in emission energy ($E_{i+1}^{\text{max}} - E_i^{\text{max}}$) between consecutive emissive events compiled from the emission of single CdSe/CdS/ZnS NCs deposited in (a) PS, (b) PMMA, (c) PVP, (d) PVA. The lines are best fits to a Gaussian distribution.

TABLE I: Widths of Gaussian fits to the histograms shown in figure 2. The values in parentheses correspond to the uncertainties of the fit. The static dielectric constants, $\epsilon_0$, were obtained from ref. [8].

| Matrix | $\epsilon_0$ | Width (meV) |
|--------|--------------|-------------|
| PS     | 2.5          | 3.9 (0.1)   |
| PMMA   | 3.4          | 3.7 (0.1)   |
| PVP    | 4.8          | 2.9 (0.2)   |
| PVA    | 14           | 3.9 (0.1)   |
FIG. 3: Correlation between line width and peak position shift for the emission of single CdSe/CdS/ZnS NCs in (a) PS, (b) PMMA, (c) PVP and (d) PVA.