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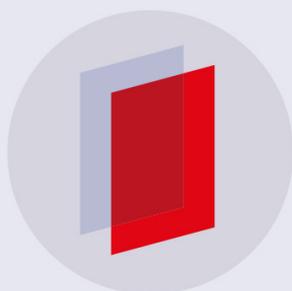
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Emission properties of colloidal quantum dots on polyelectrolyte multilayers

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Abstract

We present steady state and time-resolved photoluminescence (PL) characteristics of differently charged CdTe quantum dots (QDs) adsorbed onto a polyelectrolyte (PE) multilayer. The PE multilayer is built up using a layer-by-layer assembly technique. We find that the diffusion of the QDs into the PE multilayer is an important factor in the case of 3-mercaptopropyl, 2-propanediol stabilized QDs (neutral surface charge), resulting in a ~31-fold enhancement in PL intensity accompanied by a blue shift in the PL spectra and an increase in decay lifetime from 3.74 ns to a maximum of 11.65 ns. These modified emission properties are attributed to the enhanced surface related emission resulting from the interaction of the QD's surface with the PE. We find that diffusion does not occur for thioglycolic acid (TGA) stabilized QDs (negative surface charge) or 2-mercaptoethylamine stabilized QDs (positive surface charge), indicating localization of the QDs on top of the PE multilayer. However, the PL lifetime of the TGA stabilized QDs decreases from 9.58 to 5.78 ns with increasing PE multilayer thickness. This provides evidence for increased intrinsic exciton recombination relative to surface related emission, which results in an overall reduction in the average lifetime. Our studies indicate the importance of the QD surface charge in determining the interaction with the PE multilayers and the subsequent modification of the QD emission properties.

1. Introduction

Recently, novel/hybrid materials based on luminescent quantum dots (QDs) have become of enormous fundamental and technological interest [1–3]. For future applications of colloidal QDs, in thin films and three-dimensional device structures, the ease with which QDs can be incorporated into various polymer environments will be of crucial importance. Consequently, it is essential to understand how the radiative and non-radiative processes will be affected upon incorporation of the QDs into a polymer matrix. Recent investigations have reported modified optical properties [4], charge and energy transfer [5, 6] in hybrid polymer-QD systems.

Large surface to volume ratio is a key feature of semiconductor nanocrystal quantum dots. The surface

properties can be modified by the addition or removal of organic ligands/inorganic materials without altering the intrinsic electronic properties during the chemical synthesis [7–9]. The modified surface ensures solubility and stability. One can even alter the charge on the surface by changing the short chain thiol stabilizers ([7] and references therein). Efforts have been made to quantify the QD surface charge [10] and here we address the importance of the surface charge in determining the optical emission properties of the QDs once they are incorporated into a polyelectrolyte (PE) multilayer structure using a layer-by-layer (LBL) assembly technique.

The LBL assembly technique allows for the fabrication of ultra-thin films with monolayer control. The thin film structures are built up through sequential adsorption of monolayers of positively and negatively charged species [11, 12]. LBL can

be used to deposit monolayers of QDs, proteins, dyes, DNA, viruses and other nanoscale species [12]. This technique has received much attention due to its simplicity, and the possibility to localize layers of QDs at well defined positions within a multilayer structure. There are also many potential areas of application such as light emitting diodes, biosensors and biomedical devices [13–15].

However, very little is known about the significance of the role played by the QD surface charge in the optical emission properties when adsorbed onto a PE layer. Up to now, it has been thought that the QDs form a closely packed monolayer, which remains localized on or within the top PE layer after deposition [16, 17]. It was not expected that there would be any significant diffusion through the PE multilayer structure. Here we will clearly show that significant diffusion of the QDs into the PE matrix occurs and that the process is highly dependent on the QD surface charge. Furthermore, the changes induced in the optical emission properties depend on the surface charge. Three species of CdTe QDs, all emitting at ~ 540 – 560 nm, were investigated. They have been stabilized with thioglycolic acid (TGA), 2-mercaptoethylamine (MEM) and 3-mercapto-1,2-propanediol (MPD), which produce negative, positive and effectively neutral (slightly negative) surface charges respectively. We present and discuss the steady state and dynamic photoluminescence (PL) properties of a monolayer of CdTe QDs deposited on PE multilayers of varying thickness.

2. Experimental details

2.1. Sample preparation

Water-soluble CdTe QDs were synthesized, using TGA, MEM and MPD as short-chain thiol stabilizers, which impart negative, positive and neutral charges (slightly negative) respectively, on the QD surfaces. These CdTe QDs have peak PL emission between ~ 540 and 560 nm. The quantum yields are $\sim 20\%$ for TGA, $\sim 8\%$ for MEM and $\sim 8\%$ for MPD stabilized QDs. Further details of the growth conditions can be found elsewhere [7]. We have used the LBL technique to deposit multilayers of PE and a monolayer of QDs. Prior to deposition of the PE multilayer, the quartz substrates are thoroughly cleaned/ultrasonicated with NaOH and methanol. This renders the substrate hydrophilic in nature and facilitates the growth of the PE layers. The poly(diallyldimethylammonium chloride) (PDDA) solution is prepared by taking $150 \mu\text{l}$ (20 wt% in water) in 5 ml water. The poly(sodium 4-styrenesulfonate) (PSS) solution is prepared with a concentration of 0.412 mg ml^{-1} in water. Both are obtained from Sigma-Aldrich. For each 5 ml of PDDA and PSS solutions, 1 ml of 3 M NaCl is added. A PE bilayer is self-assembled by sequentially dipping a quartz substrate into an aqueous solution of the positively charged PDDA for 20 min, followed by 20 min in the negatively charged PSS. In between each dip the sample is rinsed with Millipore water to remove any loose molecules not ionically bonded to the surface. By repeating these dipping procedures, multilayer films are assembled to the required thickness. The thickness is approximately 1.4 nm for a single PDDA/PSS bilayer and 11.7 nm for a film composed of nine PDDA/PSS bilayers [18]. In this work we prepared films comprised of 5, 8, 10, 14,

and 18 PE bilayers. Finally, a monolayer of CdTe QDs is deposited by dipping the PE multilayer in an aqueous QD solution (concentration of 10^{-8} M) for 20 min. For the TGA (negative surface charge) and MPD (neutral/slightly negative charge) stabilized CdTe QDs, the final PE layer of the multilayer structure is a positively charged PDDA layer whereas for the MEM stabilized (positive surface charge) QDs the final PE layer is a negatively charged PSS layer. Following deposition of the QD monolayer, the samples are vacuum dried for 10 min. Octa(3-aminopropyl)octasilsesquioxane octahydrochloride ($\text{T}_8\text{NH}_3\text{Cl}$) is prepared according to the reported procedure [19] and was used to pack the PE multilayers and hence stop the diffusion of the QDs into the PE film.

2.2. Characterization of samples

Room temperature photoluminescence (PL) spectra were recorded using a Perkin-Elmer fluorescence spectrometer. The excitation wavelength of 400 nm is provided by a xenon lamp. The time resolved PL decays were measured using a PicoQuant Microtime200 time-resolved confocal microscope system, equipped with an Olympus IX71 inverted microscope. The samples were excited by 480 nm picosecond pulses, generated by a PicoQuant LDH-480 laser head, which is controlled by a PDL-800 B driver. The system has an overall time resolution of ~ 150 ps. The typical scanning area was $80 \mu\text{m} \times 80 \mu\text{m}$ with 150×150 lines. Lifetime maps are calculated on a pixel-by-pixel basis by fitting the lifetime of each pixel to the logarithm of the intensity. The PL decays are deconvoluted by nonlinear least-squares analysis using FluoFit, PicoQuant. The system time response is negligible compared with typical lifetimes of the QDs.

3. Results and discussion

3.1. Photoluminescence spectra

The PL spectra, presented in figure 1, are recorded from a monolayer of MPD stabilized CdTe QDs adsorbed on a quartz substrate coated with PDDA, as well as on PE thin films consisting of 5, 8, 10, 14, and 18 PE bilayers. As the PE film thickness is increased, the PL intensity of the QDs increases. The CdTe QDs deposited on the 18 bilayer PE film show a ~ 31 -fold enhancement in PL intensity compared to the emission from a monolayer of QDs deposited directly onto a PDDA coated quartz substrate. It is also evident that the CdTe QD PL peak is blue shifted to ~ 535 nm compared to a PL peak wavelength of ~ 546 nm for QDs on the PDDA coated quartz substrate.

In contrast, as shown in figure 2, for similar structures with a monolayer of TGA stabilized QDs, the PL intensity remains constant as a function of the number of PE bilayers. It can be noted that the PL intensity for the 5, 10, 14, 18 bilayer films is higher than that observed for the monolayer of QDs on PDDA coated quartz substrate. This is attributed to non-uniformity of the PDDA layer deposited on the quartz substrate. As the subsequent PE layers are deposited the uniformity of the top PDDA layer is expected to improve, and therefore a greater number of QDs will adsorb onto the topmost PDDA layer. This results in an initial increase of the QD PL intensity. It is also

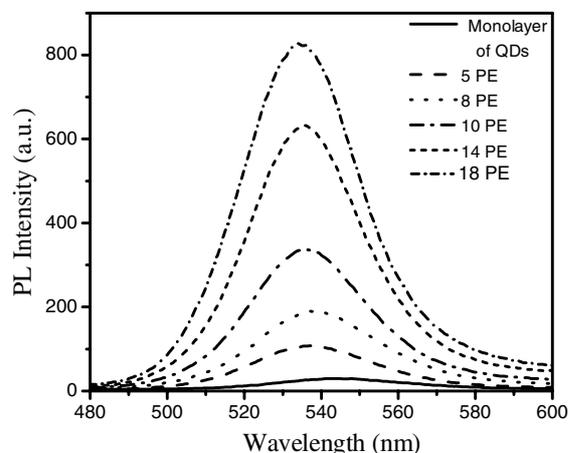


Figure 1. Photoluminescence spectra ($\lambda_{\text{ex}} = 400$ nm) of a monolayer of MPD stabilized CdTe QDs on a PDDA coated quartz substrate and on 5, 8, 10, 14, 18 polyelectrolyte bilayers. One bilayer consists of PDDA/PSS and the topmost layer before adsorption of the QDs is PDDA.

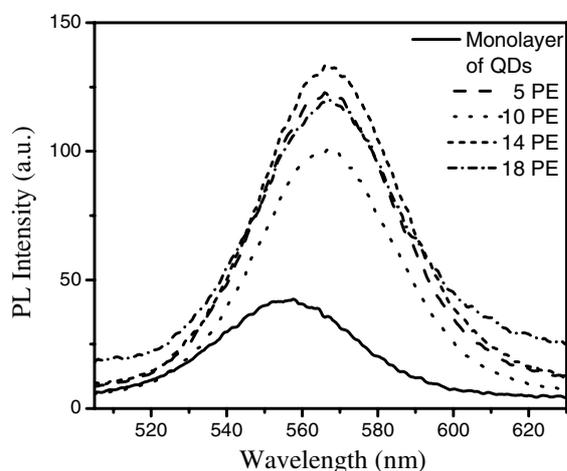


Figure 2. Photoluminescence spectra ($\lambda_{\text{ex}} = 400$ nm) of a monolayer of TGA stabilized CdTe QDs on PDDA coated quartz substrate and on 5, 10, 14 and 18 polyelectrolyte bilayers.

accompanied by a ~ 10 nm red shift in the PL peak position, which is due to resonant energy transfer from smaller to bigger QDs as the distance between the dots decreases, when a more uniform monolayer is formed [20]. The PL spectra of MEM stabilized QDs (positive surface charge) are also found to be independent of the PE multilayer thickness (not shown).

In the first instance, it can be expected that QDs adsorbed on a PE multilayer through the electrostatic interaction in the layer-by-layer assembly process, will remain relatively localized on or within the top PE layer [16, 17]. Therefore, modification of the QD optical emission could arise due to the interaction between the QDs and the top PE layer, and would be expected to be independent of the PE multilayer thickness, as observed for the TGA and MEM stabilized QDs. In contrast, the MPD stabilized QDs show a strong dependence on the PE film thickness and exhibit a much larger enhancement of their PL intensity. This PE film thickness dependence is evidence of diffusion of the MPD stabilized

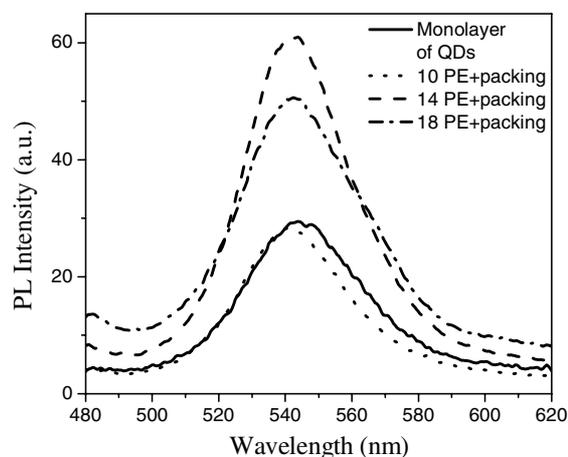


Figure 3. Photoluminescence spectra ($\lambda_{\text{ex}} = 400$ nm) of a monolayer of MPD stabilized CdTe QDs on a PDDA coated quartz substrate and with T_8NH_3Cl packed 10, 14, 18 polyelectrolyte bilayers.

QDs into the PE matrix. This is confirmed by packing the PE multilayer with octa(3-aminopropyl)octasilsesquioxane octahydrochloride (T_8NH_3Cl) before adsorbing the top QD monolayer. The T_8NH_3Cl crystals are sufficiently small to penetrate into the PE matrix [21]. The packing of the PE multilayer is achieved by dipping in a solution of 0.02 M concentration of T_8NH_3Cl nanocrystals, which are positively charged. As can be seen in figure 3, the large PL enhancement and the PE film thickness dependence of the PL intensity of the MPD stabilized QDs has been removed.

This is clear evidence that diffusion into the PE bilayers plays a key role for the case of MPD stabilized QDs. As a consequence, there are two factors which result in the large enhancement of CdTe QD PL intensity. Firstly, the diffusion of the QDs into the PE multilayer increases the number of QDs contributing to the PL signal. Secondly, as a large number of QDs are now incorporated into the PE multilayer, there is increased interaction between the QDs and the PE. This does not occur in the case of the TGA or MEM stabilized QDs. The difference is attributed to the larger surface charge of the TGA and MEM stabilized QDs, which provides a sufficiently strong electrostatic interaction to ensure firstly a strong attraction to the topmost oppositely charged PE layer and secondly a strong electrostatic repulsion to the second PE layer in the multilayer film, which is of the same charge as the QDs. The combination of the two effects prevents diffusion of the more highly charged QDs through the PE matrix. It seems the much weaker negative surface charge of the MPD stabilized QDs (effectively neutral) is insufficient to form a localized monolayer.

The increased interaction between the MPD stabilized QDs and the PE also contributes to the increased PL intensity and is further evidenced by the blue shift of ~ 10 nm (~ 40 meV) of the PL peak wavelength. The same shift, accompanied by an increase in the PL intensity, has been observed following the addition of PDDA and PSS to a solution of MPD stabilized QDs. To understand these results we must take into account the role of QD surface states in determining the PL properties. CdTe QDs emitting in the region ~ 540 – 560 nm have a diameter of approximately ~ 2.5 nm [22] and are primarily composed of surface atoms.

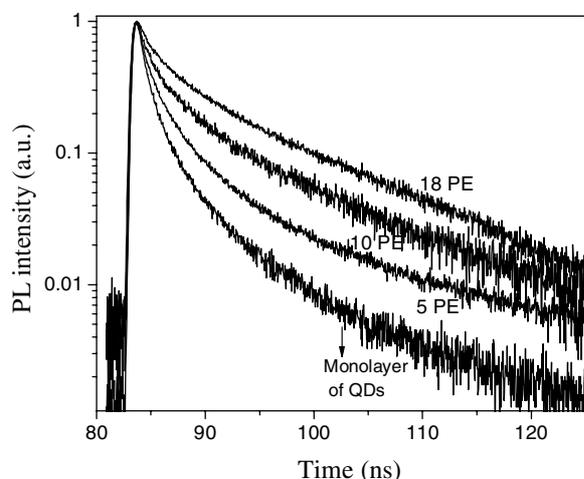


Figure 4. Luminescence decay curves ($\lambda_{\text{ex}} = 480 \text{ nm}$) of a monolayer of MPD stabilized CdTe QDs on a PDDA coated quartz substrate and on 5, 10, 18 polyelectrolyte bilayers.

Previous theoretical and experimental studies have clearly shown the dominance of surface interactions for semiconductor QDs of this size ($\sim 1\text{--}2 \text{ nm}$) [23, 24] and their importance in emission processes [25, 26]. In the case of MPD stabilized QDs we have observed strong band-to-band (1s–1s) absorption at $\sim 500 \text{ nm}$ in solution. The corresponding PL peak is observed at 538 nm . Emission occurs either via band-to-band recombination in the nanocrystal core or via radiative surface states. The large Stoke shift of 38 nm is an indication that the latter mechanism is dominant, with recombination occurring via localized surface trap states of the QDs. After diffusion of the QDs into the PE matrix some of the polymer chains binding to either Cd or Te surface atoms can modify surface state energies and/or passivate surface state defects. A 31-fold PL intensity enhancement from negatively charged mercaptocarboxylic acid-stabilized CdSe nanoparticles in a solution containing PDDA has also been reported and was primarily attributed to reduction of non-radiative recombination after surface defect passivation by the PDDA [27].

3.2. Time-resolved photoluminescence study

To gain further insight into the mechanism of modification of the QD optical emission, time-resolved PL was performed on both MPD and TGA stabilized QDs. Figure 4 shows the decay dynamics of MPD stabilized QDs on the PDDA coated quartz substrate as well as on PE multilayers comprised of 5, 10, and 18 bilayers. An average lifetime of 3.74 ns is measured for a monolayer of QDs deposited on PDDA coated quartz and it increases to 11.65 ns for the 18 PE bilayer structure. All average lifetimes are quoted with an uncertainty of $\pm 0.09 \text{ ns}$.

Colloidal QD recombination dynamics are highly sensitive to the surrounding medium. There are a few possible factors, which can contribute to the strong modification and multilayer thickness dependence of the MPD stabilized QD relaxation dynamics. Firstly, alteration of the radiative (k_r) or nonradiative (k_{nr}) components after surface modification will modify the decay rates since $\tau = \frac{1}{k_r + k_{nr}}$ [28, 29]. Secondly, the

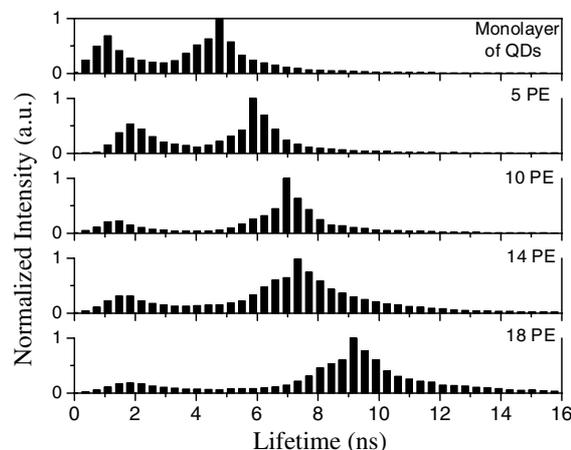


Figure 5. Lifetime histogram of monolayer of MPD stabilized CdTe QDs on a PDDA coated quartz substrate and on 5, 10, 14, 18 polyelectrolyte bilayers.

variation in the local dielectric environment can also influence exciton relaxation processes [30, 31].

A deeper understanding is obtained by performing a lifetime distribution analysis. The histogram of lifetime distribution is shown in figure 5 for MPD stabilized QDs on a PDDA coated quartz substrate as well as on 5, 10, 14 and 18 PE bilayers. The appearance of a multi-exponential behaviour is typical for QD emission [29, 32]. Firstly, it can be seen that the amplitude of the longer lifetime component increases relative to the shorter lifetime component signal. Secondly, the long lifetime component is shifted to higher lifetime values as the number of PE bilayers increases. This longer timescale component is very sensitive to the number of bilayers and is the dominant factor in the increase of the overall average lifetime of the PL decay.

This data suggests that the increased PL intensity observed in the steady state measurements may have a contribution arising from improved surface quality apart from the obvious increase due to the higher concentration of QDs contributing to the emission, as a consequence of their diffusion into the PE film. There is some evidence that longer lifetime components are associated with improved surface quality and are the most significant contribution in high quantum yield QDs [29]. This suggests that the increased interaction of the MPD-stabilized CdTe QDs with the PE chains suppresses the non-radiative recombination through reduction of the concentration of surface defects and/or less efficient carrier trapping at surface defects. Most likely, the dominant interaction is between the slightly negatively charged QDs and the positively charged PDDA polyelectrolyte. This can also result in a change in the polarity of the immediate QD surroundings. The emission can respond to the charges/polarity of the surrounding medium, which is generally expected for a system involving charged or charge separated states [30, 31]. As the PE multilayer thickness increases the contribution from the QDs within the multilayer becomes larger with respect to that coming from the QDs on the top surface of the PE layer.

Figure 6 shows the decay dynamics of a monolayer of TGA stabilized QDs on PDDA coated quartz as well as on PE films comprised of 5, 10, and 18 bilayers. The decreasing

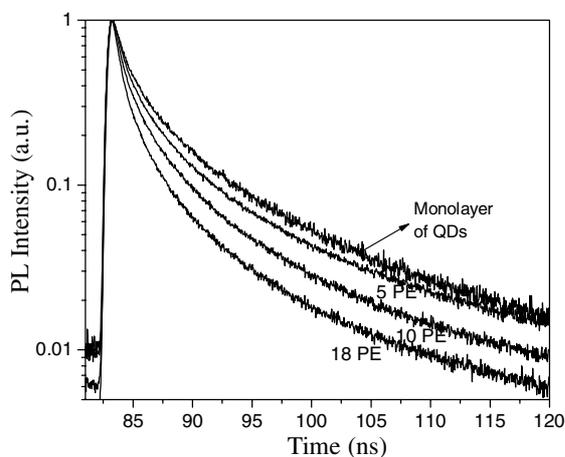


Figure 6. Luminescence decay curves ($\lambda_{\text{ex}} = 480$ nm) of a monolayer of TGA stabilized CdTe QDs on PDDA coated quartz and on 5, 10, 18 polyelectrolyte bilayers.

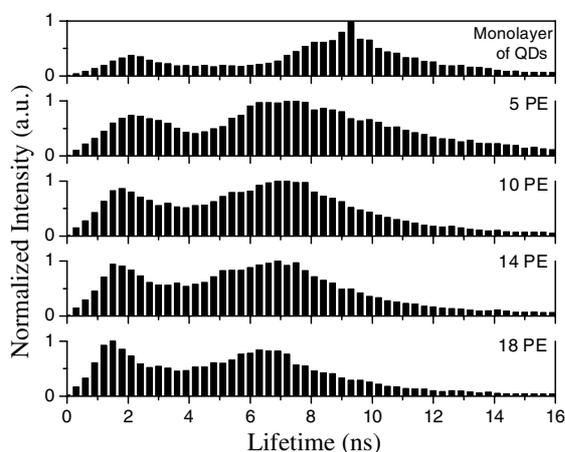


Figure 7. Lifetime histograms for a monolayer of TGA stabilized CdTe QDs on a PDDA coated quartz substrate and on 5, 10, 14, 18 polyelectrolyte bilayers.

lifetime is strongly dependent on the thickness of the PE layers. The average lifetime decreases from 9.58 ns for a monolayer of CdTe QDs on the PDDA coated quartz substrate to 5.78 ns for the QDs on the 18 PE bilayers. The lifetime histograms for the TGA stabilized QDs are shown in figure 7. It can be clearly seen that the ratio of the amplitude of the long lifetime to short lifetime component decreases as the number of PE bilayers increases. Furthermore, the long lifetime becomes shorter. Both of these factors lead to a decrease in the average lifetime.

A comparison of lifetime distributions of MPD and TGA stabilized QDs on the PDDA coated quartz substrate reveals that the PL decay dynamics are different in both cases. The short lifetime component peak position is nearly the same, as would be expected for the intrinsic lifetime due to recombination of the excited core population. However, there is a significant variation in the long timescale component peak position and intensity distribution. The intensity of the long lifetime component for TGA stabilized QDs is considerably higher than that of the short lifetime component, which infers

that there is a greater contribution to the emission from radiative surface state recombination in comparison to the MPD stabilized QDs. This is in agreement with the quantum yield estimates of 20% for TGA stabilized QDs compared with 8% for MPD stabilized QDs. The effect of the interaction with the PE multilayers on the short and the long lifetime components of the TGA stabilized QDs is quite different to that for MPD stabilized QDs. This is due to two main factors: firstly the variation in quantum yields and secondly the significant diffusion of MPD stabilized QDs into PE matrix.

In the absence of diffusion and with a constant PL intensity as a function of PE film thickness, it can be assumed that the number of TGA stabilized QDs is approximately the same for each structure. Therefore, it must be concluded that the modification of the PL lifetimes is entirely due to the influence of the increasing PE film thickness. One option to be considered is a change in the electric field induced at the top surface of the PE multilayer as a function of the number of bilayers. Such an effect could influence the decay dynamics. However, it has been previously shown that there is no variation in total electric field with increasing PE bilayers [33]. Interface effects between the QDs and the quartz substrate could result in a modified exciton relaxation in the PE/TGA stabilized QDs system [34]; however, this requires further investigation.

4. Conclusions

The universality and simplicity of the LBL technique enabled a comprehensive study of the interaction of differently charged QDs with polyelectrolytes and an improved understanding of the photophysics and nanoengineering of the assembled structures. We have addressed the importance of the surface charge of the QDs in determining their emission properties in LBL structures comprised of alternating layers of PDDA and PSS polyelectrolytes. The relatively weak surface charge of the MPD stabilized QDs allows for significant diffusion into the PE matrix to occur. Consequently, the QD surface passivation, through interaction with the PE layers, produces enhancement of the surface related emission, resulting in an increased quantum yield. The observed diffusion of the MPD stabilized QDs shows that QDs can also be easily incorporated into PE multilayers to form composite materials which will be used as building blocks for the bottom-up assembly of nanostructured functional materials. The tunability of the QD PL intensity and lifetime as a function of PE multilayer thickness for diffused or localized QDs is of potential interest for various applications from photon sources to biological labelling.

Acknowledgments

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