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Radiative exciton recombination dynamics in QD-tagged polystyrene microspheres

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Abstract Fluorescent polystyrene microspheres are prepared by the incorporation of fluorescent CdSe/CdS core/shell semiconductor nanocrystals (quantum dots, QDs) using the emulsification/solvent evaporation method. The radiative exciton recombination dynamics is investigated by nanosecond time-resolved fluorescence spectroscopy at ambient conditions. The time constants of fast and slow fluorescence decay in QDs, dispersed in toluene, were 3.5 and 17.8 ns, respectively. For the QD-tagged microspheres, the time constants of fast and slow processes were ~2–3 and ~11–12 ns, respectively, and did not depend significantly on the QD-content of the microspheres. The fast decay component could be attributed to the recombination of delocalized exciton in the internal core states, and the slow component was attributed to the localized exciton in the surface states. It was found that the ratio of amplitudes of the fast and slow processes also changed after incorporation of QDs in microspheres. The observed differences in fluorescence decay between non-entrapped QDs and QD-tagged microspheres were probably due to energy transfer between the nanocrystals, which were in close proximity inside the microspheres. The obtained fluorescent QD-tagged microspheres are characterized by the other methods as well, which makes them of value for various applications as optical materials.

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Introduction

The semiconductor nanocrystals (known as colloidal quantum dots, QDs) are promising fluorescent materials, which are intensively studied as probes in biological imaging and diagnostics [1–3]. They possess excellent optical properties, such as tunable fluorescence wavelength by size, resistance to photobleaching, broad excitation spectra, narrow and symmetric emission spectra, which make them suitable for long-term bioimaging and analysis [4]. Polymer coating of QD-nanocrystals seems to be one of the most powerful tools toward diagnostics and sensorics [5]. The fluorescent QD-nanocrystals have been found rather suitable for fluorescent tagging of polymeric microspheres for immunoreactions and diagnosis [6, 7]. An increase in the multiplicity and sensitivity is expected due to the narrow emission spectra of QD-nanocrystals and their significantly low photobleaching rate. Some of the methods for loading QD-nanocrystals in polymeric microspheres are (i) swelling of the microspheres and diffusion of the nanocrystals inside, (ii) surface immobilization of nanocrystals onto the polymeric microspheres, (iii) incorporation of nanocrystals during the polymerization of microspheres, (iv) emulsification/solvent evaporation method. The first method by far is quite popular (a chloroform/alcohol mixture is usually used as the swelling agent) [6, 8, 9]. However, the microspheres, obtained by this method, display strong surface textures and the QD-nanocrystals are immobilized only close to the microsphere surface, which makes them to be easily

"washed out" in buffer- and protein-containing solutions [10]. This method has been improved using mesoporous microspheres instead, which significantly increases the quality of the obtained fluorescent particles [11]. In the second category of methods, water-soluble QD-nanocrystals (negatively charged) are used. Their entrapment in polymeric microspheres is performed via alternate layer-by-layer adsorption of nanocrystals and polyelectrolytes to form the microspheres [12, 13]. The QD-nanocrystals are strongly fixed on the microsphere surface so that antibodies can be covalently coupled to the outer surface of polyelectrolytes. This kind of nanocrystal entrapment is employed to demonstrate Fluorescence Resonance Energy Transfer (FRET) between the QD-nanocrystals and organic dye molecules [14]. The third method comprises a direct polymerization in the presence of QD-nanocrystals, being apparently the most straightforward technique [15–17]. A disadvantage of this method is that the as-obtained microspheres are polydisperse in size. The emulsification/solvent evaporation method is not popular for the entrapment of QD-nanocrystals in polymer microspheres, although it has been used for the incorporation of CdSe/ZnS nanocrystals in polyisoprene microparticles [18]. In this method, the nanocrystals and the polymer are dispersed in a certain amount of volatile organic solvent, which is then emulsified in aqueous surfactant solution. The slow evaporation of the polymer solvent results in QD-tagged microspheres, stabilized by surfactant. Various QD-tagged polymeric microspheres have been prepared also by other methods, based on electrostatic interaction [19, 20], electrospray [21], and microfluidic system [22].

On the other hand, previous investigations of radiative exciton recombination in QD-nanocrystals by time-resolved fluorescence measurements have demonstrated that the fluorescence decay follows a biexponential function [23–26]. The relatively longer fluorescence lifetime of QD-nanocrystals in comparison with organic fluorophores has been exploited to enhance fluorescence biological imaging contrast and sensitivity by time-gated detection [27]. Although there are many studies devoted to the preparation and characterization of various QD-tagged polymeric microspheres, there is lack of information about the exciton recombination dynamics in such systems. The present article is focused on the preparation of polystyrene microspheres, tagged with CdSe/CdS core/shell QD-nanocrystals, and investigation of their dynamic fluorescence properties by time-resolved measurements. Different QD-tagged microspheres are obtained by the emulsification/solvent evaporation method at various polystyrene/nanocrystals ratios and characterized by fluorescence and scanning electron microscopy. Time-resolved fluorescence studies are performed at time-to-amplitude conversion range of 200 ns and compared with that of non-entrapped QD-nanocrystals. The obtained results are interpreted using a theoretical biexponential model.

Experimental section

Materials and reagents

Polystyrene (PS, Mw ~190000) was from Sigma-Aldrich. Triton X-100 was purchased from Merck. Chloroform was of analytical reagent grade from Labscan Ltd (Ireland). Toluene and chloroform were purified by distillation. All the other chemicals and solvents were used as received without additional purification.

Preparation of QD-nanocrystals

The CdSe/CdS QD-nanocrystals were synthesized, characterized, and purified according to a previously reported method [28]. In brief, CdSe cores were prepared in liquid paraffin (15 mL) from cadmium stearate (0.39 mmol) and tributylphosphine selenide (0.125 mmol) precursors at 260 °C, then purified from the unreacted Se-precursor by washing with toluene and transferred in solution of cadmium stearate (0.39 mmol) in liquid paraffin (15 mL). Then, tributylphosphine sulfide (0.25 mmol) was added and the temperature was raised gradually from 100 to 250 °C to grow the CdS shell, as described previously [28]. The liquid paraffin was removed from the obtained QD-nanocrystals by washing with toluene and the excess of cadmium stearate was removed by triple extraction with methanol/chloroform. The nanocrystals from a single synthesis (50 mg) were dispersed in chloroform (7 mL) for the further use. The QD-nanocrystals may form aggregates upon standing, which are dispersed by gentle heating.

Preparation of QD-tagged polystyrene microspheres

QD-tagged polystyrene microspheres with different PS/QD ratios were prepared by the emulsification/solvent evaporation method as follows. Solutions of PS in toluene with different concentrations (2.2, 3.3, 6.8, and 13%) were prepared. Each PS/toluene solution (2 mL) was mixed with QD/chloroform dispersion (0.8 mL) to obtain different QD/PS mass ratios of 0.15, 0.1, 0.05, and 0.025, respectively (in order to obtain QD-tagged PS microspheres with mass content of QDs 13, 9, 4.6, and 2.5%, respectively). A portion (0.5 mL) of each mixture is slightly heated to disperse any aggregates of QDs and then added to aqueous solution of Triton X-100 (0.5%) under vigorous stirring (600 rpm). The obtained emulsions were stirred for 24 h to evaporate the volatile organic solvent. All the experiments are performed at constant stirring rate (since the emulsification is

expected to depend on the stirring rate). Any residual organic solvent was removed by rotary evaporation under reduced vacuum. Distilled water was added to the final dispersion to obtain a total volume of 10 mL.

Characterization of the QD-tagged microspheres

The microspheres in dried state were also visualized by scanning electron microscopes (SEM) Philips XL20 and JSM 5510 (JEOL). Size distribution of the particles has been evaluated from the SEM images by measuring the size of at least 500 particles. The absorbance spectra of CdSe/CdS nanocrystals in toluene (with the addition of few drops TBP) were recorded using Cary 5000 (Varian) UV/Vis/NIR spectrophotometer at room temperature. Fluorescence measurements were performed on QD/toluene solutions at 375 nm as the excitation wavelength, by means of a Fluorolog 3 spectrofluorometer (HORIBA Jobin-Yvon), equipped with double grating both excitation and emission monochromators. Fluorescence spectra of QD-tagged microspheres, dispersed in aqueous media, were measured similarly. For this purpose, an aliquot (0.2 mL) of the prepared microbead suspension was dispersed in distilled water (2 mL). For fluorescence microscopy, a small volume of the suspension of QD-tagged microspheres was diluted with distilled water, centrifuged and washed with distilled water to remove the excess of surfactant (Triton X-100), and then deposited by drop casting onto a properly cleaned microscope glass substrate and observed by means of epi-illumination microscopy system using mercury lamp for light source.

Time-resolved (TR) measurements of the fluorescence emission of CdSe/CdS nanocrystals (dispersed in toluene, as well as embedded in PS microspheres) were carried out by means of Time Correlated Single Photon Counting (TCSPC) technique, using a FluoroHub (HORIBA Jobin-Yvon), equipped with fast responding detector (TBX ps Photon Detection Module, HORIBA Jobin-Yvon) and specialized software for data acquisition and processing. The samples were excited at 375 nm using a picosecond laser diode (NanoLED 375L) emitting $\tau = 80$ ps pulses at a 1 MHz repetition rate. Time resolution of experimental system was $\sim$200 ps. The fluorescence decays at the wavelength of emission maximum were recorded at time-to-amplitude conversion range of 200 ns.

Results and discussion

The core/shell CdSe/CdS QD-nanocrystals, used in this research, are prepared by previously reported colloidal synthesis in hot liquid paraffin and their detailed preparation and characterization are described by us elsewhere [28]. The average size of the QD-nanocrystals used in the present study is $\sim$4 nm, the fluorescence quantum yield is $\sim$60%. The wavelength of the exciton absorbance maximum is 575 nm and the emission maximum appears at 594 nm (for QDs, dispersed in pure toluene). The full width at half maximum (FWHM) is 35 nm. The respective absorbance and fluorescence spectra of the QD-nanocrystals (dispersed in toluene), used in this study, are shown in Fig. 1. It has been previously shown that such nanocrystals are hydrophobic and not dispersible in aqueous medium due to stearate coating (stearate, attached on the nanocrystal surface, comes from the Cd(II) stearate precursor used for synthesis of QDs); however, they could be entrapped in hydrophobic polymers, such as poly(butyl methacrylate) [29]. The core/shell QD-nanocrystals possess superior optical properties than the core-only nanocrystals, such as increased fluorescence quantum yield and increased stability against photobleaching [2–4]. Such characteristics are of great importance for their applications as optical materials.

The as-obtained QD-tagged particles are spherical, as seen from the SEM image in Fig. 2a. The average particle size is about 3–4 μm. The average particle size of microspheres is slightly larger at higher concentration of the PS/toluene solution used for their preparation ($\sim$5 μm for particles, prepared with 13% PS solution). The increased average size and polydispersity at higher concentration of the PS solution is expected due to the increase in solution viscosity and has been previously observed for the preparation of QD-tagged polyisoprene microparticles by similar approach [18]. The size distribution seems to be rather broad (Fig. 2b), which is probably a result of the broad size distribution of the precursor emulsion. Therefore, uniform in size particles are expected to form by emulsification/

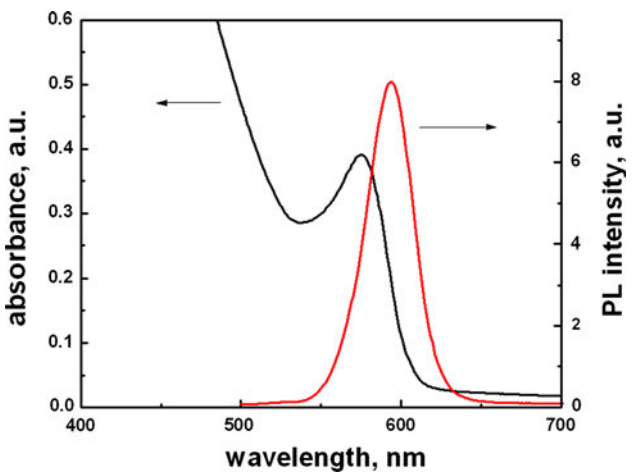

Fig. 1 Absorbance and fluorescence spectra of the CdSe/CdS QD-nanocrystals, used for the preparation of QD-tagged polystyrene microspheres

solvent evaporation starting from a monodisperse emulsion. The emulsification/solvent evaporation approach also allows easily controlled surface chemistry of the QD-tagged microspheres through the choice of surfactant (emulsifier) employed to form the emulsion. In preparation described here, Triton X-100 is used as emulsifier. It is a non-ionic surfactant, which has a hydrophilic polyethylene oxide group (on average it has 9.5 ethylene oxide units) and a 4-(1,1,3,3-tetramethylbutyl)-phenyl hydrophobic group. Triton X-100 is expected to remain in the aqueous phase due to its high solubility in water and is adsorbed on the polystyrene (hydrophobic) surface of the obtained QD-tagged microspheres.

Observation of the hybrid QD-tagged particles by fluorescence microscopy indicates that the fluorescent QD-nanocrystals are incorporated inside the PS particles, since the PS alone does not possess any fluorescence. Representative bright-field and fluorescent images are shown in Fig. 3. Figure 3a represents an image of the microspheres in white transmitted light, and Fig. 3b is the corresponding true color fluorescence image for the same sample and field of view. It shows that the location of the QD fluorescence corresponds to the location of the microparticles. The image in Fig. 3c is obtained in combined illumination with white light (transmitted) and UV-light (epi-illumination). As seen, the QD-nanocrystals are not uniformly spread inside the polymer, but form tiny aggregates in the core of the particles. Similarly, aggregation of QD-nanocrystals has been previously observed during their entrapment in poly(lactide-co-glycolide) [30] particles. The relative brightness of each QD-tagged microsphere, as expected, is highly non-uniform due to the polydispersity of particle size. Even at low content of QD-nanocrystals (2.5%), the fluorescence from the QD-tagged microspheres is clearly observable due to the high brightness of emission from the embedded nanocrystals.

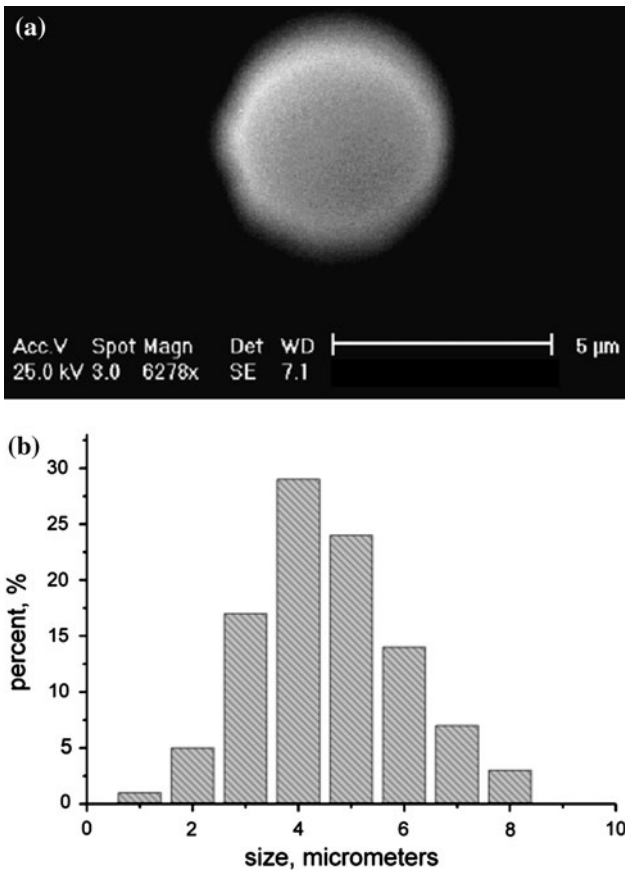

Fig. 2 **a** A representative SEM image of a single QD-tagged PS microsphere (the size *bar* is 5 µm). **b** Histogram of the size distribution of QD-tagged PS microspheres at QD/PS ratio 0.025

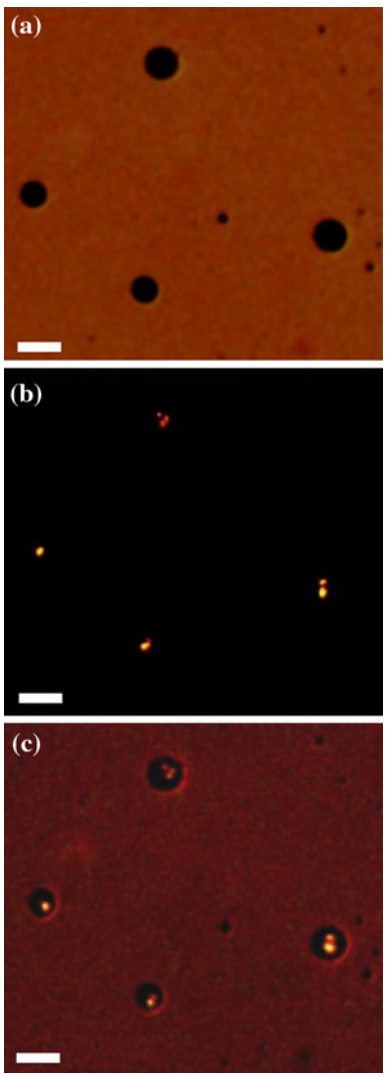

Fig. 3 Optical microscopic images of QD-tagged polystyrene microspheres in **a** bright-field, **b** true-color fluorescence, **c** combined bright-field and true-color fluorescence. Each image shows the same field of view at different operation modes. The size *bar* is 10 µm

The fluorescence spectrum of QD-nanocrystals after their incorporation in the PS microspheres is slightly red-shifted (PL maximum at 597 nm) in comparison with the spectrum of the same nanocrystals in toluene dispersion (Fig. 4). The fluorescence spectra are not considerably affected by the different concentrations of PS. The different QD/PS ratio does not affect the position of the emission maximum. Interestingly, similar red-shifts of the fluorescence spectra have been previously observed after incorporation of CdTe/CdSe nanocrystals in poly(lactide-co-glycolide) particles [31], as well as after polymer modification of CdSe/ZnS nanocrystals [32, 33].

The TCSPC experiments allow measuring directly the fluorescence decay curves (i.e., fluorescence intensity as a function of time; decay time is defined as the time after fluorescence signal reaches the given maximum intensity and decay begins) after exciting of the sample with a short laser pulse of UV-light (Fig. 5). Fitting the experimental data with a proper function, in particular a biexponential function (Eq. 1) one can make a quantitative estimate about a particular mechanism of relaxation [23–26].

$$A(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_\infty \quad (1)$$

where A_1, A_2, and A_∞ are the respective amplitudes of the signal, while τ_1 and τ_2 are the time constants (fluorescence lifetimes) of fast and slow relaxation, respectively. In order to obtain correct values for the fluorescence lifetimes, the profile of instrument response function (excitation pulse) has to be measured in addition to the fluorescence decay. This is because the UV-source (laser) pulse has a finite temporal width (<1 ns), which distorts initially the intrinsic fluorescence response from the sample. The data analysis is then performed using the model function (Eq. 1), by fitting of the data using a sort of least square method for minimizing

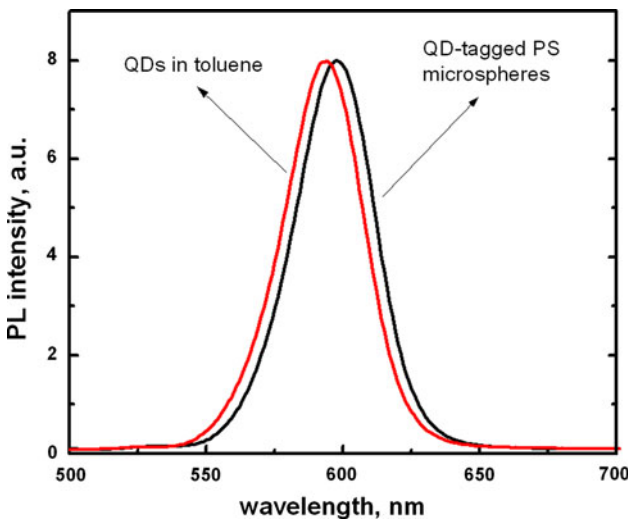

Fig. 4 Normalized integrated fluorescence spectra of QD-nanocrystals dispersed in toluene and embedded in PS microspheres

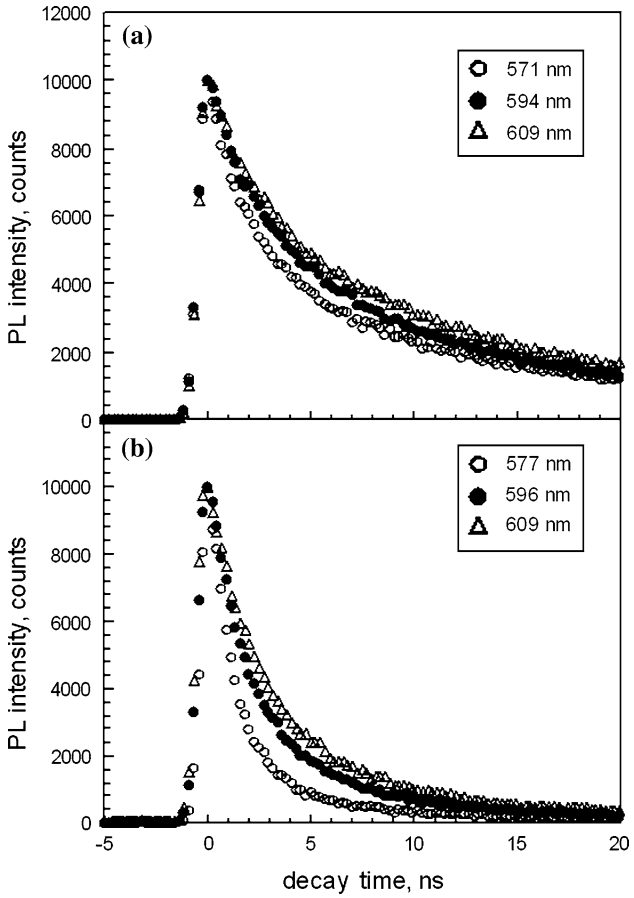

Fig. 5 Fluorescence decay of CdSe/CdS nanocrystals at different detection wavelengths: **a** dispersed in toluene, and **b** incorporated in PS microspheres (QD-content 13%)

the differences between the experimental points and the biexponential function. Such a biexponential function has been widely used for description of the fluorescence decay of QD-nanocrystals [23–26]. The fast decay lifetime component (few nanoseconds) can be attributed to the recombination of delocalized exciton in the internal core states, and the slow lifetime (few tens of nanoseconds) is attributed to the localized exciton in the surface states [24] and varies with different surface modifications [33]. Therefore, it is expected that the longer lifetime would be sensitive to surface modification of QD-nanocrystals. Indeed, previous investigations have confirmed that the shorter lifetime is relatively insensitive to surface modification, but the longer one alters dramatically with the different surface modification [33]. All the investigated samples in our experiments exhibit biexponential decay behavior. Representative fluorescence decay profiles of QD-nanocrystals dispersed in toluene, as well as embedded in PS microspheres (at QD/PS ratio 0.15; QD-content 13%) are shown in Fig. 5. The obtained fitting parameters (with respective standard errors) of the biexponential function from all the experiments are

summarized in Table 1 (data are for detection wavelengths 594 and 596 nm for QD-nanocrystals in toluene and embedded in PS microbeads, respectively).

The time constants τ_1 and τ_2 for QD-nanocrystals dispersed in toluene, are 3.45 and 17.8 ns, respectively (Table 1). These values noticeably decrease upon incorporation of the nanocrystals in PS microspheres; τ_1 and τ_2 for QD-tagged particles are ~2–3 and ~10–12 ns, respectively. As seen, both exciton recombination processes accelerate after entrapment of the QDs in PS. The observed differences in fluorescence decay between non-entrapped QDs and QD-tagged microspheres were probably due to the different environment around the nanocrystals and their aggregation inside the microspheres. The values of the shorter lifetime component τ_1 slightly decrease with increasing the QD-content of tagged microspheres. The τ_2 component does not exhibit any characteristic dependence on the QD-content. The decrease of fluorescence lifetime of nanocrystals in microspheres can be attributed to the reduced distance between nanocrystals in microspheres (also, the observed partial aggregation inside the microspheres—see Fig. 3), which enhances the exciton recombination. Also, aggregation of QDs inside the microspheres is observed in all the samples (aggregation state does not depend on the QD-content of microspheres), which together with the similar chemical environment inside the microspheres could be the reasons for the observed similar exciton recombination dynamics that is relatively independent on the QD-content of the microspheres. The larger lifetime values in non-entrapped nanocrystals can be attributed to long-lived excitons as a result of the relatively longer average distance between the nanocrystals in dispersion. The amplitude values of the shorter (A_1) and the longer-lifetime (A_2) components are also changed after entrapment of the nanocrystals inside the microspheres, which is another indication for changed exciton recombination dynamics. The ratio of the A_1 and A_2 amplitudes depends on the relative role of core-state recombination and surface-related emission. The ratio A_1/A_2 for QD-nanocrystals dispersed in toluene is 1.528, which indicates prevalence of the faster core-state exciton recombination. The A_1/A_2 ratio for QD-tagged microspheres is around threefold to fourfold higher (see the data in Table 1). These results indicate decreased role of the surface-related radiative recombination in QD-tagged microspheres.

The observed changes in the fluorescence behavior of QD-nanocrystals after their incorporation in microspheres could be attributed to energy transfer between the nanocrystals, which depends on the proximity of nanocrystals. Both the observed red shift of the fluorescence spectrum (although a rather small shift of few nanometers) and the decreased fluorescence lifetime of the incorporated nanocrystals are indicative for energy transfer. It is known that close-packed QD-nanocrystals (in 3D or 2D arrays) have fluorescence spectra shifted to longer wavelengths in comparison with the spectra of dispersed nanocrystals, which is indicative of interactions between nanocrystals in the solid state [34–39]. It has been shown that the fluorescence red shift of close-packed QD-nanocrystals relative to that of nanocrystals dispersed in solution is consistent with long-range resonance transfer of electronic excitations from the small to the large nanocrystals in an inhomogeneous sample [34, 35]. Previous investigations of the fluorescence properties of QD-monolayers have shown shortening of the fluorescence decay with increasing concentration of nanocrystals [36, 37]. The fluorescence decay curves depend on the emission wavelength as seen from the data in Figs. 5 and 6. The decay curves recorded at the shorter wavelength, corresponding to the smaller in size QD-nanocrystals, show a faster decrease in emission intensity than the respective decay curves recorded at longer wavelengths. This is due to energy transfer from smaller QD-nanocrystals to the larger ones. The wavelength dependence of the fluorescence decay curves provides clear evidence for such energy transfer, which has been previously observed for close-packed CdSe [34] and CdTe [39] nanocrystals.

Table 1 Fitting parameters from the biexponential decay analysis of QDs in toluene and QD-tagged PS microspheres with various QD-content (given in %)

Sample	τ_1 (ns)	τ_2 (ns)	A_1/A_2	A_∞	R^2
QDs in toluene	3.45 ± 0.03	17.8 ± 0.1	1.528	50 ± 2	0.9989
2.5% QDs	2.84 ± 0.02	10.7 ± 0.2	4.780	25 ± 1	0.9994
4.5% QDs	2.78 ± 0.02	12.8 ± 0.3	6.657	56 ± 1	0.9989
9.0% QDs	2.68 ± 0.02	11.4 ± 0.2	4.700	32 ± 1	0.9991
13.0% QDs	2.07 ± 0.01	10.0 ± 0.2	5.446	48 ± 1	0.9988

The correlation coefficient (R^2) from the fit is also given

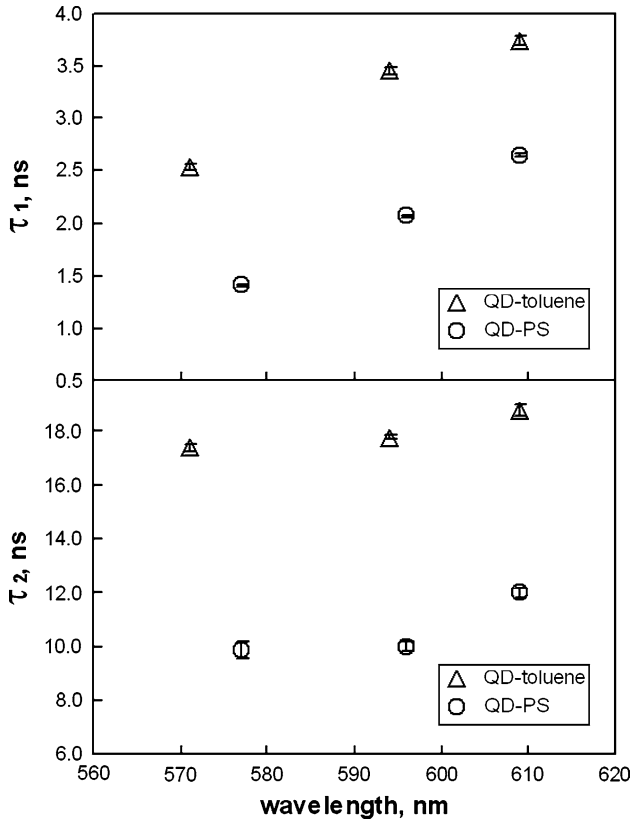

Fig. 6 Dependence of the fluorescence lifetimes (τ_1 and τ_2) of CdSe/CdS nanocrystals (dispersed in toluene and embedded in microspheres) on the fluorescence detection wavelength. The QD-content in QD-tagged microspheres is 13%

Conclusions

In this article, we reported the preparation of polystyrene microspheres, tagged with CdSe/CdS QD-nanocrystals, by the emulsification/solvent evaporation method with different QD/polystyrene ratios. The QD-nanocrystals preserve their bright fluorescence in the embedded state, which is confirmed by both stationary spectral measurements and fluorescence optical microscopy. To understand the radiative exciton recombination dynamics in QD-tagged microspheres, we performed nanosecond time-resolved fluorescence measurements at ambient conditions and time-to-amplitude conversion of 200 ns. We found that a biexponential function describes well the fluorescence decay results, accounting for the fast (core-state recombination) and slow (surface-related recombination) processes of radiative relaxation in QD-nanocrystals. Both fluorescence lifetimes (for the fast and slow processes) for QD-tagged microspheres are sensibly smaller than those for free nanocrystals in toluene dispersion. The recombination dynamics does not significantly depend on the QD-content of microspheres. We found also that the decay amplitudes are changed after entrapment of the nanocrystals inside the microspheres, indicating decreased role of the slower surface-related radiative exciton recombination. These results indicate for energy transfer processes between nanocrystals in the entrapped state, which is manifested also by a small red shift of the emission maximum in time-integrated fluorescence spectra. The investigation of transient fluorescence of QD-tagged microspheres could be useful for understanding of the mechanisms of exciton recombination dynamics in QD-systems. These results could also be helpful for the future development of various fluorescence systems based on such materials.

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