

Effect of visible and UV irradiation on the aggregation stability of CdTe quantum dots

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Abstract The possibility of controlling the aggregation stability of CdTe quantum dots (QDs) stabilized by thioglycolic acid (TGA) is important for implementation of quasi-resonant laser-induced self-assembly. This study examines the influence of irradiation by the UV as well as by the visible light on the photostimulated aggregation of QDs. Different photochemical mechanisms are identified, depending on whether light wavelength falls into an interband transition or the first excitation transition. Irradiation by visible light does not lead to changes in the absorption spectra but decreases luminescence intensity through the detachment of TGA and the formation of dangling bonds, leading to the creation of radiativeless relaxation centers. UV irradiation (in the 300–370 nm range), at an intensity of 0.4 W/cm², initially (during the first 75 min) leads to the degradation of the stabilizer and QDs' surface. After 75 min of combined UV and visible light irradiation, a gradual increase in spontaneous aggregation takes place, testifying excessive decrease in stabilizing potential barrier height. Hence, the laser-induced self-assembly of CdTe QDs is

recommended to be performed over a time period of between 80 and 100 min after the beginning of low-intensity UV irradiation under conditions equivalent to those applied in this study.

Keywords Nanotechnology · Quantum dots · Photostimulated aggregation · Photostability · Colloids · Laser-induced self-assembly

Introduction

Semiconductor nanocrystals with the characteristic size in the nanometer scale (quantum dots, QDs) exhibit unique optical properties due to the quantum confinement effect (Gaponenko 1998; Gaponik et al. 2010) and can be employed as components of solar cells, sensors, LEDs, et al. (Buhbut et al. 2011; Kamat 2013; Kim et al. 2012; Frecker et al. 2016). Among the fundamental problems hindering the broad application of QDs, one should emphasize the lack of inexpensive and reproducible techniques for forming structures composed of QDs. As a solution to the latter problem, several chemical methods were used to form nanostructures with a limited number of available configurations (Gong et al. 2012; Wang et al. 2013). Certain universality of available configurations can be achieved using an electro-dynamical approach of creating the nanostructures with the pre-defined geometry, as considered in Slabko et al. (2012, 2013, and 2014). This approach is based on laser-induced attraction of nanoparticles, enabling their self-assembly to be controlled by the laser

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frequency and polarization. Smart selection of the potential barrier is important for this method. First of all, this potential barrier must combat spontaneous aggregation; however, the shape and the height of this barrier are extremely important for the geometry of obtained nanostructures.

The paper (Tsipotan et al. 2016) featured the laser-induced self-assembly technique being experimentally demonstrated for the first time. The process chosen for the demonstration was the formation of CdTe QDs pairs. Formation of the pairs in that experiment required substantially higher laser pulse intensity than was predicted by the paper (Slabko et al. 2014), and possible reason for this mismatch might be higher aggregation-preventing barrier with respect to that used in the calculation. The possibility to control the QDs' aggregation stability and, therefore, the height of the aggregation-preventing potential barrier is important for laser-induced self-assembly controlled by frequency and polarization. One of the possible ways to control the barrier height is the preliminary illumination of the colloidal QDs' solutions by weak optical radiation in the period preceding the laser-induced self-assembly. The influence of weak optical irradiation on the aggregation of colloid solutions is well documented. e.g., the spectral dependence of the photostimulated aggregation rate of colloidal silver nanoparticles has been investigated in several papers (Karpov et al. 1997). The mechanisms leading to the decrease of the height of the barrier preventing spontaneous aggregation in the case of silver nanoparticles were discussed in Karpov et al. (2002) and, as a rule, they are related to electron photoemission. The latter leads to the accumulation of a positive charge by a particle's core and to an increase in the electric potential of its surface, which leads to the compression of the stabilizing layer which stabilizes the surface of the metallic particle, and to subsequent aggregation of nanoparticles. Similar studies concerning the control of aggregation stability of semiconductor QDs under the irradiation in various spectral ranges are absent.

At the same time, the photostability of QDs themselves, as well as the methods for improving it, is presently under extensive study. The photostability of thiol-coated CdSe QDs is investigated in Aldana et al. (2001). Irradiation by mercury lamp with a dominating 254-nm line in the presence of ambient oxygen leads to a decrease in both the luminescence intensity and optical density of the CdSe solution, ascribed either to the photocatalytic oxidation and degradation of the

stabilizing layer or to the photooxidation of QDs themselves. Recently, advanced sol-gel technology has been developed to produce highly photostable CdSe QDs (Majdabadi et al. 2015). Under durable 365-nm irradiation, the saturated drop in luminescence was less than 3%. The irradiation of CdSe QDs' solutions in a special buffer with a pH of 7.2 under 405-nm action at an intensity of 10 mW/cm² during an hour (Ibrahim et al. 2014) led to a tenfold increase in luminescence due to the improvement of the QDs' surface quality. However, further irradiation was reported to force the stabilizer's degradation followed by aggregation and luminescence quenching. Concerning the materials under study in this present paper, CdTe, synthesis, and surface passivation methods, as well as photostability and photoluminescence control of water-soluble CdTe QDs under different irradiation conditions are studied in Gaponik et al. (2002), Emin et al. (2010), and Tirado-Guizar et al. (2015). The phenomena observed for UV-irradiated CdTe QD solutions are generally similar to those of CdSe. Unfortunately, little attention was paid to the spectral content of irradiation used in these studies. The longest irradiation wavelength specified in the photostability studies cited above was 405 nm (Ibrahim et al. 2014), the corresponding photon energy being well above the energy of the first CdTe QDs' exciton transition. On the contrary, the action of the visible laser radiation (488 nm) onto CdTe solutions was studied in Ma et al. (2007), and a luminescence decrease was detected due to the stabilizer's photoinduced detachment.

In this paper, we study the photostability of CdTe QDs stabilized by thioglycolic acid (TGA), as well as the possibility of altering the aggregation stability of QDs' solutions by weak UV or visible light irradiation. Well-defined spectral content of acting radiation allows to investigate different photochemical and physical processes that may be different for visible and UV light.

Materials and methods

The QDs under study

The water-soluble CdTe QDs under study were produced by PlasmaChem GmbH (Berlin, Germany); they were pre-coated with TGA by the producer and exhibited strong luminescence peaking at 550 nm (Fig. 1). The molar concentration of QDs in the solution was

$C = 3 \cdot 10^{-6} \text{M}$. The morphological structure and local elemental composition were determined via high-resolution transmission electron microscope (HRTEM) JEOL JEM-2100 (LaB₆) equipped with energy-dispersive spectrometer Oxford Inca x-sight. The TEM CdTe QD image is shown in Fig. 2a. The CdTe QDs are featured by crystalline structure (see the inset with the HRTEM image in Fig. 2a) and nearly spherical in shape. The diameter of CdTe QD ranges between 2.5 and 5.0 nm, with the mean diameter equal to 3.2 nm (Fig. 2b).

Instrumentation and measurements

The colloid solutions were illuminated using a LOMO DRSh-250-3M high pressure mercury lamp. The spectrum of this lamp is plotted in Fig. 3a and contains a number of intense lines ranging between 275 and 600 nm. In two separate sets of experiments, either the UV or visible part of spectrum was selected using the appropriate filters; the corresponding spectra of filtered radiation were recorded using SOLAR TII MSDD1000 monochromator spectrometer equipped with Hamamatsu R928 PMT; these spectra are presented in Fig. 3b, c.

The radiation power over $1 \times 2 \text{ cm}^2$ aperture of the colloid solution was measured with a thermopile light sensor and was found to be $P = 0.067 \text{ W}$. This power was adjusted to be just the same for both UV and visible light irradiation by the variation of the distance between the light source and the cells with solutions; the intensity of the irradiating light being $I = 0.4 \text{ W/cm}^2$ both for UV and visible illumination. The distances mentioned above were approximately 30 and 50 cm, correspondingly.

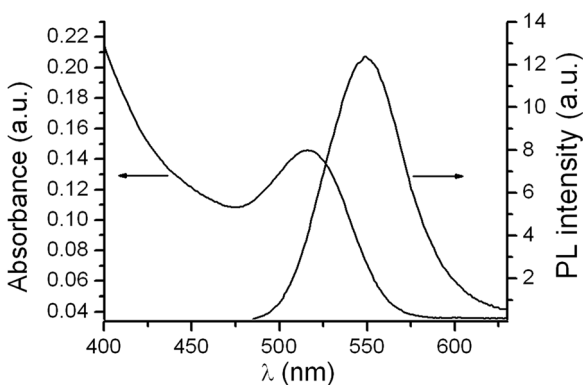


Fig. 1 Optical density of 0.9-cm thick CdTe solution (Perkin-Elmer Lambda 35, *left scale*) and luminescence spectra excited at 480 nm (HoribaJobinIvon Fluorolog3, *right scale*)

The QD solutions' irradiation was performed in quartz cells; the maximum sum irradiation time being 75 min. This maximum irradiation time was chosen from the analysis of preliminary studies' results that evidence the minor role of aggregation process at intensity used for irradiation period quoted above. The absorption and luminescence spectra were measured in the course of 2.5-min breaks after every 15 min of irradiation. Separate irradiation experiments were conducted on another set of solutions, no filters being used, while the intensity was adjusted to 0.4 W/cm^2 again. The maximum irradiation time was extended to 150 min in this set of

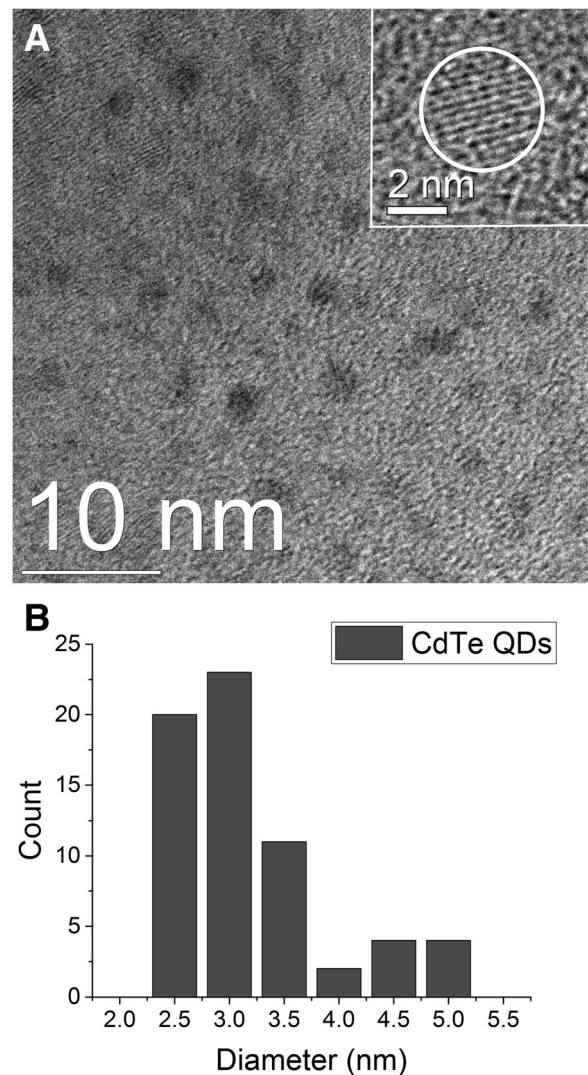


Fig. 2 **a** TEM image of CdTe QDs, the *inset*, HRTEM image of an individual CdTe QD, and **b** histogram of diameter distribution of CdTe QDs

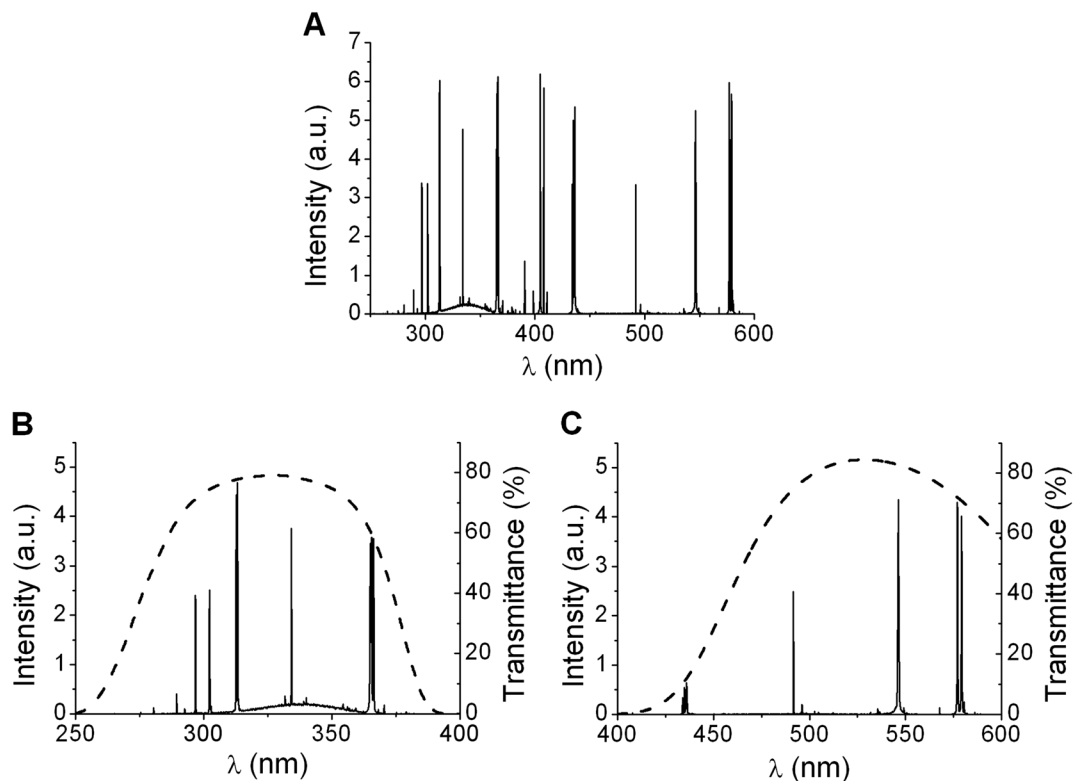


Fig. 3 Spectra of DRSh-250-3M lamp used for CdTe QDs' solution illumination. **a** Net spectrum. **b** UV part after filtering. **c** Visible part after filtering. *Dashed lines* are filters' transmittance curves

experiments in order to reveal the complete dynamics of the solutions' behavior, including the time period when aggregation becomes pronounced.

Results and discussion

The two different types of irradiation exploited in this study fall into absorption bands of different nature. UV radiation in the range of 300–370 nm forces interband transitions with the formation of electrons in the conduction band and holes in the valence band. Visible radiation falls into the exciton band and produces electrons and holes in a mutually bound state. As we mentioned above, the action of radiation onto the QDs' solutions can lead to the destruction of either the stabilizer molecules or the QDs' surfaces. Partial violation of the stabilizer layer leads to spontaneous aggregation due to either a Coulomb or van der Waals interaction. Degradation of the QDs' surface leads to a decrease in the size of initially dissolved QDs. Both processes lead to a decrease in the absorption coefficient and in luminescence intensity

within the spectral range of the first exciton transition, accompanied by changes in the absorption spectra at shorter wavelengths. Figure 4 depicts the spectra of solutions with an increasing irradiation dose by UV (Fig. 4a) and visible light (Fig. 4b). UV irradiation yields modification in absorption spectra as well as a considerable decrease in luminescence, while visible irradiation of the same intensity yields a less pronounced luminescence decrease and leaves absorption spectra practically untouched. More specifically, UV irradiation in the QDs' solution leads to a decrease in the maximum absorption coefficient of the exciton transition and to the simultaneous blue shift of this maximum position (Fig. 5 a, b). The UV-induced decrease of the absorption coefficient better fits the exponential law than the linear one. The visible light irradiation of QDs, according to Fig. 3c, acts mainly via an excitonic absorption band. This type of irradiation does not lead to any observable changes in absorption spectra (Fig. 5a, b).

The UV-induced luminescence decrease (19% after 75 min irradiation) follows the exponential law rather well (Fig. 6), and there is not any luminescence band

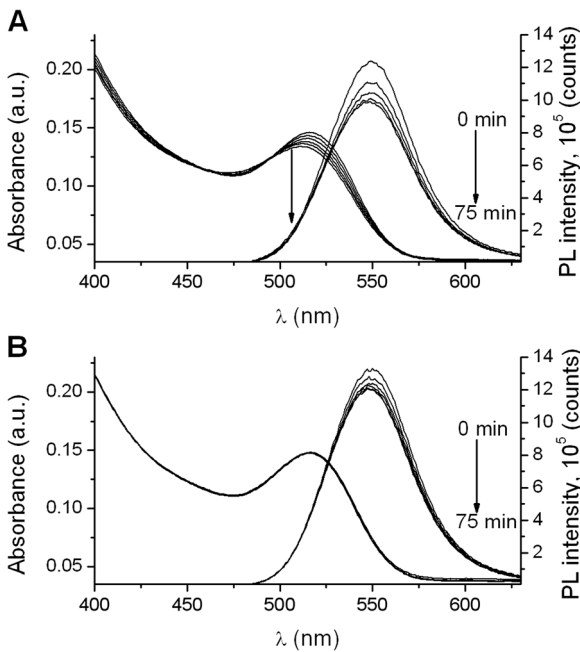


Fig. 4 Evolution of absorption and luminescence spectra in the course of irradiation **a** by the UV and **b** by the visible light

shift. At the same time, the visible-irradiation-induced luminescence drop is 10% after 75 min of visible

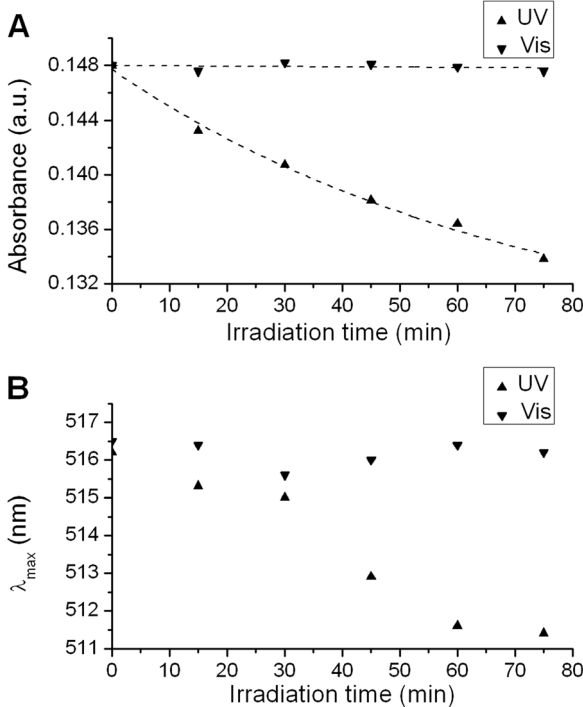


Fig. 5 Variation of **a** magnitude and **b** position of maximum excitonic absorbance of QDs' solutions on the irradiation time

irradiation (Fig. 6), smaller than in the case of UV irradiation, with no luminescence peak shift, similar to the case of UV irradiation.

This behavior of the CdTe solutions under UV irradiation is generally similar to that of CdSe QDs (Ibrahim et al. 2014). We can deduce from our experiment that the irradiation of TGA-capped CdTe QDs by radiation in the range of 300–370 nm leads to photocatalytic oxidation and degradation of the TGA layer. This process is accompanied by the simultaneous photooxidation of QDs and the resulting decrease in their average size. Due to the quantum confinement effect (Gaponenko 1998), the decrease in the QDs' size leads to the blue shift of the exciton absorption band, in agreement with our observation. Simultaneously, with the absorption modification, luminescence-quenching defects are produced, leading to decrease of the luminescence intensity. The detachment of both the TGA and QD constituents produces dangling bonds serving as luminescence quenchers. QDs with these defects exhibit low luminescence and do not contribute to its spectrum; the latter being formed by QDs which have not undergone any degradation.

After 60 min of UV irradiation, QDs' size stabilizes as evidenced by the stabilization of the exciton peak's position, probably due to equilibrium between atoms' detachment from QDs and atoms' attachment to QDs from the solution; meanwhile, the decrease in optical density continues due to the continual loss of the TGA-stabilizing effect and the onset of aggregation.

In contrast to UV light, the visible irradiation light falling into the exciton absorption band, as seen in Figs. 4b, 5, and 6, forces no noticeable changes in the absorption spectra; however, it decreases the

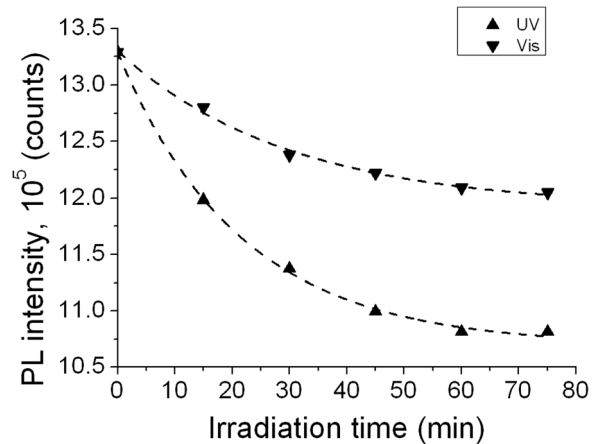


Fig. 6 Variation of peak luminescence intensity on the UV and visible radiation exposure time

luminescence intensity. A stable position of the exciton absorption peak means that the detachment of QDs' constituents and the subsequent decrease in the QDs' size does not take place under the conditions of visible irradiation. Hence, the formation of luminescence-quenching defects is to be ascribed to the detachment of TGA molecules from QDs under visible irradiation. It has recently been discovered that TGA molecules possess an absorption band below singlet-to-singlet transitions and this band protrudes to wavelengths of an order of 550 nm (Attar et al. 2011). TGA illumination at 400 nm was found to force the conversion of TGA into an α -thiol-substituted acyl radical (α -TAR, S-CH₂-CO \cdot). The decrease in CdTe QDs' luminescence under visible irradiation observed in our study can be explained by the TGA detachment due to such a mechanism. Earlier, the photodetachment of TGA under 532 nm laser irradiation at 8 W/cm² (20 times higher intensity than in our experiment) was verified by additional Raman study (Ma et al. 2007).

To investigate the longer-term dynamics of CdTe QDs' solutions, we exposed them to mercury lamp irradiation using no filters for the course of 150 min. The radiation intensity was set to be equal to the intensity used in previous experiments with separate UV and visible light irradiation, i. e., 0.4 W/cm². The evolution of absorption and luminescence spectra during this irradiation session is presented in Figs. S1 and S2 of Supporting Information. The temporal evolution of exciton absorption and luminescence magnitudes and the absorption and luminescence exciton peak position is depicted in Fig. 7.

After approximately 75 min of irradiation, the magnitudes decrease becomes faster; meanwhile, the positions of the bands turn from the blue shift to red shift after 100 min of irradiation. During the latter irradiation period, the formation of QDs' aggregates becomes easily visible to the naked eye; these aggregates are sparse and probably possess a fractal structure. Shifts in the absorption of particles within aggregates, including fractal ones, due to electrodynamic interaction between particles, are well documented. This shift strongly depends on a particle's environment, resulting in the inhomogeneous broadening of the absorption band and the redshift of its maximum accompanied by an absorption magnitude decrease. More particularly, the electrodynamic interaction of metallic particles leads to the splitting of particles' plasmon resonance absorption line into two components shifted to the blue and to the red with

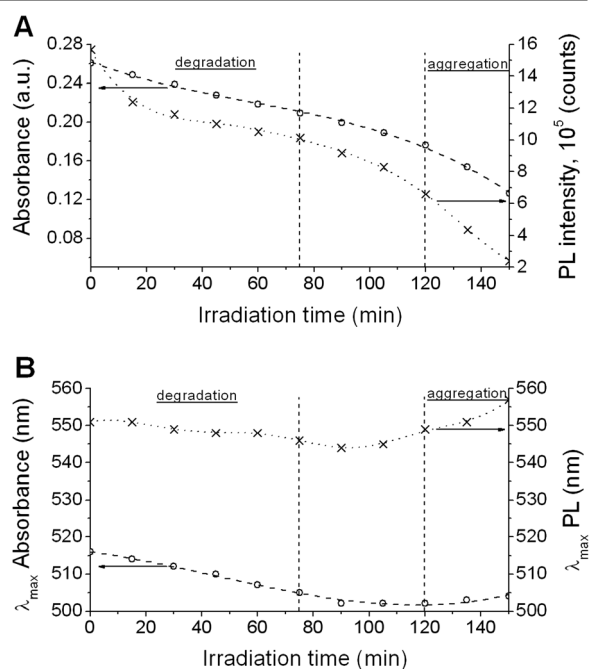


Fig. 7 Dependences of **a** magnitudes and **b** positions of absorption and luminescence peaks on the UV + visible irradiation time

respect to the position of the isolated particle resonance (see, e.g., Karpov et al. 2000). The extent of the spectral shift depends on interparticle distance, and upon the formation of a fractal aggregate, the interaction of a separate particle with the neighbors, with the account for the averaging over the distances and mutual orientations within an ensemble, results in the observable inhomogeneous broadening of the absorption bands in the red and in the blue. For semiconductor QDs, the blue splitting component is masked by the interband transition. The redshift of CdTe QDs' maximum luminescence observed in our study after 100 min of irradiation is evidently due to the influence of electrodynamic interaction within aggregates. One may expect creation of additional radiativeless relaxation mechanisms in aggregates as well. In any case, the luminescence of CdTe QDs continues to drop during the aggregation stage. On the whole, the case of illumination-induced phenomena with semiconductor QDs is considerably more complicated than the case of metal nanoparticles; the latter being governed by a single mechanism, namely photoelectron emission. The individual optical properties of metal nanoparticles, especially their absorption spectra, remain untouched by irradiation and the inhomogeneous broadening of the absorption band is due to the electrodynamic interaction of the particles within

the fractal cluster. The stabilizer's strong influence on the QDs' optical properties leads to a fundamentally different nature of QDs' light-induced aggregation. Photochemical interactions lead to the destruction of the stabilizer and the QDs' surface and this not only leads to aggregation but also to the alteration of the individual particles' properties.

Conclusion

In conclusion, the irradiation of TGA-stabilized CdTe QD solutions at a 0.4-W/cm^2 visible radiation intensity for 75 min leads to a decrease in luminescence; meanwhile, the absorption of QDs both in the exciton band and in the interband transition region remains untouched. This effect is explained by the action of a single process, namely the photodegradation of the stabilizing layer via TGA photodissociation. In contrast, in the case of UV irradiation falling into the interband transition range, two simultaneous processes are confirmed, namely the photooxidation of TGA and the photoinduced size reduction of CdTe QDs. In this case, a decrease was discovered in both the excitonic absorption magnitude and the luminescence intensity. Longer-time irradiation by UV + visible light forces the onset of QDs' aggregation. The maxima of excitonic absorption and luminescence bands undergo a blue shift during the first irradiation stage, which turns into red shift during the aggregation stage. The latter red shift is ascribed to the electrodynamic interaction of close QDs within an aggregate.

Therefore, the height of the barrier preventing spontaneous aggregation can be lowered under UV irradiation. Hence, the laser-induced self-assembly of CdTe QDs is recommended to be performed for a period of between 80 and 100 min after the low intensity (0.4 W/cm^2) UV irradiation begins under conditions equivalent to those used in this study. During this time interval, the height of the aggregation-preventing barrier already decreases; meanwhile, there is no noticeable drop in QDs' content.

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