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Comparative Analysis of Methods for Enhancement of the Photostability of CdTe@TGA QD Colloid Solutions

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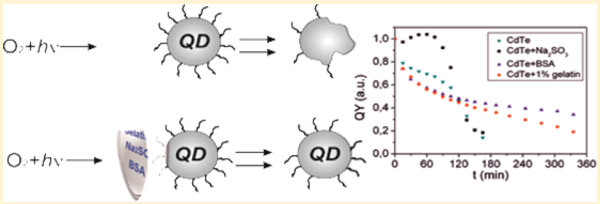
ABSTRACT: The employment of colloid quantum dots in a number of applications is limited by their instability under light irradiation. Additional methods of photostability enhancement of UV+visible-irradiated TGA-stabilized CdTe quantum dots are investigated. Photostability enhancement was observed via either addition of sodium sulphite in the role of chemical oxygen absorber or addition of 1% gelatin, or, finally, by additional stabilization by bovine serum albumine (BSA). The latter method is the most promising, since it not only enhances the quantum dots' photostability but also makes them more biocompatible and extends the possibilities of their biological applications.



INTRODUCTION

Semiconductor nanocrystals (colloid quantum dots (QDs)) have attracted great attention in recent years due to numerous possible applications, e.g., in life science,[1−3] in sensorics,[4−6] in display technology,[7] as LEDs,[8,9] and in solar energy harvesting.[10−12] The progress in these studies is sometimes hindered by the limitations of chemical stability and photostability of QDs in solution.[13] The latter is especially important in the physical regimes when QDs undergo long-lasting or multiply repeated optical irradiation. Such regimes occur, for example, when QDs are utilized for cellular labeling and biological imaging,[14,15] or in the processes of self-assembly of QDs into the structures of predefined geometry in the field of laser radiation.[16] The role of dissolved oxygen in the photoinduced instability of colloidal QDs is well-known.[14] Ma et al. argued that optical irradiation stimulates generation of a reactable state of oxygen, with the sequent oxidation of both stabilizer and the surface of QDs, and final destruction or aggregation of QDs. Enhancement of QD solution photostability is known to be attained either by chemical extraction of oxygen from the solution or by additional stabilization of QDs via preventing oxygen access to the QDs. Serum albumin (BSA) is a well studied and widely used protein which enables modification of nanoparticle surfaces with the size of several tens of nm[17,18] or for their binding.[19] Employment of BSA as the additional surface passivation agent allows obtaining stable and biocompatible QDs with improved luminescent properties.[20] Interaction of QDs with BSA leading to their mutual binding[21−26] as well as their pH stability[27,20] is well documented. On the other side, the photostability of several BSA−QD complexes was surprisingly flabbily studied. Let us mention just a few. Improvement of QD photostability in 10% gelatin solution under 400 nm irradiation was demonstrated in a paper.[28] Improvement of BSA−QD photostability under 405 and 800 nm irradiation was evidenced.[29] Let us also mention that regardless of well-known fact that photooxidation, degradation, and aggregation of QDs are most pronounced under UV irradiation[13,30] there are no any sufficient studies in the literature on the additional stabilization efficiency under UV irradiation. The purpose of the present study is the investigation of photostability improvement of QDs under UV irradiation using all known approaches, namely, chemical oxygen extraction, viscosity modification of the solution by gelatin, and additional stabilization with BSA.

EXPERIMENTAL SECTION

Materials and Sample Preparation. Water-soluble CdTe QDs under study were produced by PlasmaChem and then were stabilized by thioglicole acid (TGA). All solutions were prepared using the phosphate buffer (0.02M) with pH 6.9. The reference sample containing only TGA-stabilized QDs was prepared by mixing 1960 μL of buffer solution and 40 μL of QD solution ($C = 3 \times 10^{-4}$ M). The sample for a chemical oxygen absorber test was prepared using the buffer solution (1940 μL), Na_2SO_3 (20 μL of 1 M solution), and 40 μL of QDs solution ($C = 3 \times 10^{-4}$ M). The fraction of sodium sulphite content in this sample was chosen to be 10 times higher than that necessary to remove all dissolved oxygen. The 1% gelatin (Fluka) solution was prepared by dissolving 52.7 mg of dry gelatin in 5.27 mL of buffer under continuous stirring in a magnetic stirrer and 80 °C heating. The sample for the gelatin efficiency test was prepared with 1960 μL of 1% gelatin solution and 40 μL of CdTe solution ($C = 3 \times 10^{-4}$ M). BSA solution ($C = 5 \times 10^{-4}$ M) was prepared right before the BSA efficiency

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test experiment using 5.3 mg of dry BSA and 160.6 μL of phosphate buffer. The sample for the BSA efficiency test was prepared using 1910 μL of buffer, 50 μL of BSA solution ($C = 5 \times 10^{-4}$ M), and 40 μL of CdTe solution ($C = 3 \times 10^{-4}$ M).

Instrumentation. Absorption spectra were recorded in a quartz cuvette (10×10 mm^2) using a Lambda 35 UV–vis spectrophotometer (PerkinElmer). PL spectra were excited at 480 nm and recorded using a Fluorolog 3 spectrofluorometer (HORIBA JobinYvon) with excitation and emission slit widths of 1.2 nm. All measurements were performed at room temperature. Colloid solutions were illuminated using a DRSh-250-3M mercury lamp. The irradiance spectrum of this lamp is plotted in Figure 1 and contains a number of intense

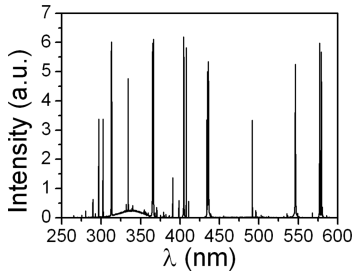

Figure 1. Spectra of the DRSh-250-3M mercury lamp used for CdTe QD solution illumination.

lines in the range from 275 to 600 nm. The power of radiation over the aperture of colloid solution was measured by a thermopile light sensor and was found to be $P = 0.067$ W.

RESULTS AND DISCUSSION

Absorption and Photoluminescence Spectra. Absorption and photoluminescence spectra of the samples before irradiation are shown in Figure 2. The luminescence of CdTe

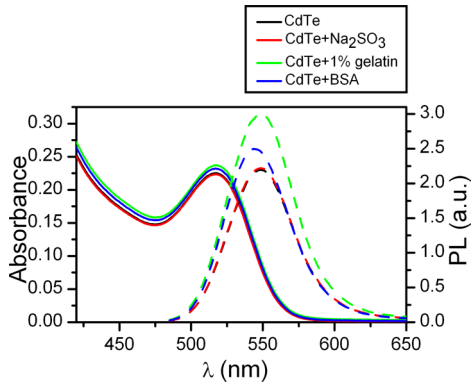

Figure 2. Optical density of 0.9 cm thick CdTe solution (solid line) and photoluminescence spectra (dashed line).

QDs in 1% gelatin solution is approximately 50% higher than that of reference sample (QDs in pure buffer solution), and the luminescence band peak wavelength experiences no shift, while absorption remains almost the same, compared with both the position and amplitude of the CdTe QD exciton peak. The luminescence of BSA-stabilized QD solution is about 25% higher than that of the reference sample, while the luminescence peak experiences a 5 nm blue shift. Again, absorption in this case experiences no changes. The impurity of Na_2SO_3 as the oxygen absorber does not change the optical properties of the QD solution.

QD solutions were irradiated for 165 min (reference sample and Na_3SO_3-containing sample) or 335 min (gelatin-stabilized and BSA-stabilized samples). Photostability was examined repeatedly, by recording absorption and photoluminescence spectra after each 15 min period of irradiation.

Figure 3 shows recorded absorption spectra of the samples. One can see that QDs in the buffer solution exhibit weak

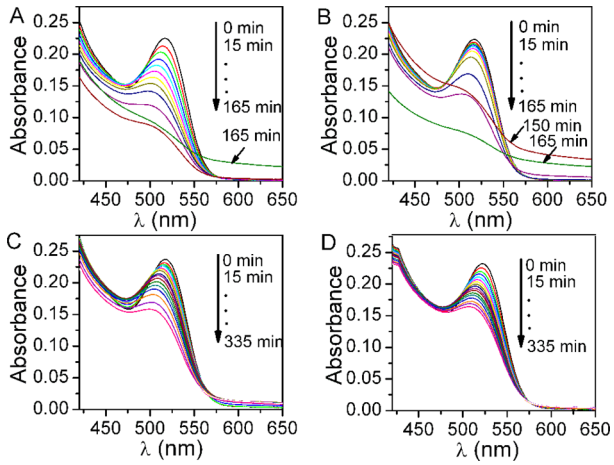

Figure 3. Variation of absorption spectra of QD solutions in the course of irradiation: (A) CdTe in the buffer, (B) CdTe in the presence of Na_2SO_3, (C) CdTe in 1% gelatin solution, and (D) CdTe stabilized by BSA.

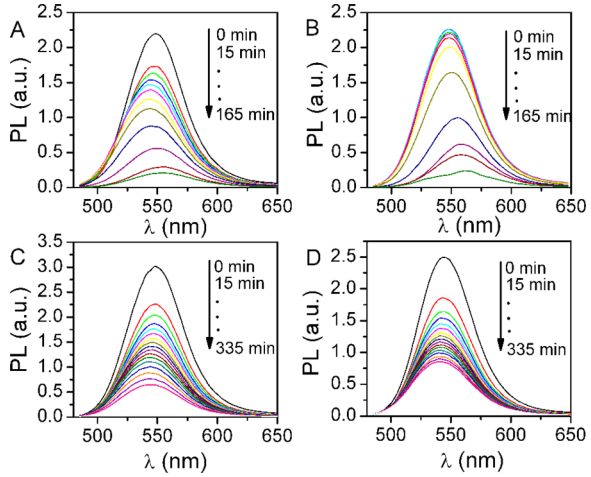

Figure 4. Variation of photoluminescence spectra of solutions: (A) CdTe in a buffer solution, (B) CdTe with Na_2SO_3, (C) CdTe in 1% gelatin solution, and (D) CdTe stabilized by BSA.

photostability (Figure 3a and Figure 4a), since optical density at the wavelength of the exciton peak and luminescence peak drops during the first 15 min of irradiation by 5 and 20%, correspondingly. Absorption experiences a 19% drop after the first 60 min of irradiation. The next 105 min of irradiation results in a decrease of these values by 60 and 91%, correspondingly. Simultaneously, the optical density at the wavelengths larger than the exciton absorption peak wavelength of isolated QD increases. Both of these facts originate either

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due to variation of the quantum confinement effect or due to QD aggregation. As was already discussed above, all current studies of photodegradation or any other kind of degradation of QD solutions imply the key role of oxygen. Photochemical reaction of oxygen with the stabilizer results in a gradual loss of antiaggregation stability and subsequent aggregation. Photochemical reaction of oxygen with the surface of QD leads to decreasing QD size, resulting in a blue shift of the exciton peak, as clearly seen in Figure 3a.

Impurity of sodium sulfite (NSO) to QD solution results in reduction of the oxygen content fraction in the sample. As a consequence, the photostability of the corresponding solution becomes higher and the solution behavior under irradiation is noticeably modified. The drop of the optical density of NSO-stabilized QDs (Figure 3b) after the first hour of illumination is about 5%, while that of the reference solution is 19%. However, during the second hour of illumination, the drop of optical density becomes more and more pronounced achieving 60% after 135 min. One can see in Figure 3b that at time 150 min (red line) the optical density increases compared to the one at 135 min (violet line). This effect is connected with increased scattering of light in the spectrometer during the initial stage of aggregation. Hence, the addition of NSO leads to an increase of QD photostability during an hour of irradiation of used power (P = 0.067 W), while at larger irradiation times this effect gradually vanishes. Luminescence intensity, in contrast, exhibits a minor increase of 2% after the first 75 min of illumination, followed by a sharp drop in the range 70−120 min, resulting in 90% loss of luminescence after 165 min of irradiation, and finally resulting in termination of stabilization by NSO. This behavior of luminescence correlates in time with the initial stage of aggregation. However, both absorption and luminescence evolution for NSO-stabilized sample within a 165 min period is not as gradual as in the case of the reference sample. The latter can be connected with two processes occurring in the solution containing Na_2SO_3. As was shown in a number of studies,[31,32] CdSe quantum dots dissolved in water with an impurity of sodium sulphite can be used for production of hydrogen by irradiation of the solution. In this case, sodium sulphite acts as the donor of electrons,[31,32] which recombine with photoinduced holes in the valence band of QDs, and cadmium serves as the electron acceptor. Since the electron acceptor is absent in our experiments, irradiation of the solution must lead to charging of QDs and emerging of a situation which is analogous to A-type blinking of a solitary QD.[33] Herewith, the process of hydrogen production starts after a certain delay[32] with the duration being determined by the initial sodium sulfite fraction in the solution. During that delay, sodium sulfite acts as the oxygen absorber, thus preventing QDs from oxidation and preserving the luminescence brightness of QDs. The second process occurring in NSO-stabilized QD solution is the transfer of oxygen from the ambience surrounding to a solution due to diffusion and convective flows that occur due to inhomogeneous heating of the cell by the optical radiation. As a result of the two processes described above, the sodium sulfite impurity falls to zero during the irradiation time. The onset of both QD oxidation and "blinking" leads to a sharp collapse of the QD luminescence observed in our experiment after 90 min of illumination irradiation.

Gradual introduction of sodium sulfite into the QD solution during the course of irradiation promises a further increase of photostability, though this method can meet the limitation in view of the growth of the ionic strength of the solution which may influence the chemical stability of the QDs.

Since the QD photodegradation rate depends on the presence of free oxygen in a solution,[34,35] decrease of its diffusion rate allows reduction of both the rate of collisions between QDs and oxygen molecules and the rate of oxygen transfer from the ambience to a solution. Addition of, e.g., 1% gelatin to the buffer solution is shown[36] to increase its viscosity by 2.3, leading to a 2.3-fold decrease of the oxygen diffusion rate. In our experiment, 10-fold photoluminescence quenching occurs during 165 min of illumination of CdTe QDs in the buffer solution. Gelatin-stabilized solution exhibits photoluminescence quenching by 84% during 330 min, that is, approximately 2 times slower, in accordance with the expected variation of the oxygen diffusion rate.

As pointed out above, QD solution illumination leads additionally to photodegradation of a stabilizer playing an important role in the formation of QD optical properties. Employment of BSA as an additional stabilizer of QDs must lead to stronger protection against oxygen penetration to both the QD surface and TGA molecules and, as a consequence, to improvement of QD photostability. In our experiment, QDs stabilized by joint action of TGA and BSA exhibit enhanced stability as compared with those in the solution with 1% gelatin. The photoluminescence intensity decrease was 70% of the initial value after 6 h of illumination, while for gelatin-containing solution it was 84%. The mechanism of degradation of TGA+BSA-stabilized QDs must be the denaturation of BSA primarily under UV irradiation. Particularly, decrease of BSA luminescence at 350 nm under 254 nm irradiation was reported and treated as the proof of BSA denaturation.[37] In our experiment, the intensity of irradiation at 254 nm is negligibly small. To check the presence of the denaturation process under illumination with the radiation with the spectrum presented in Figure 2, we examined BSA luminescence behavior under the same conditions as those used for experiments with QDs. We have found that BSA luminescence at 350 nm decreases by 60% after 15 min of irradiation (Figure 5). According to Figures 3d and 4d, the most pronounced variation of QD spectra associated with their photodegradation is observed in this very time period after the start of illumination.

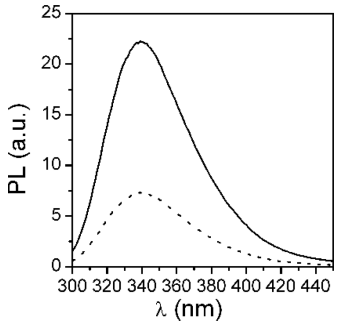

Figure 5. 295 nm excited luminescence spectra of BSA before irradiation (solid line) and after 15 min of irradiation (dashed line).

Variation of Spectral Maxima for QD Excitonic Absorption and Photoluminescence under Illumination. The spectral shift of QD absorption and photoluminescence maxima under the illumination is commonly connected either with the variation of their size[13] or with their aggregation.[38]

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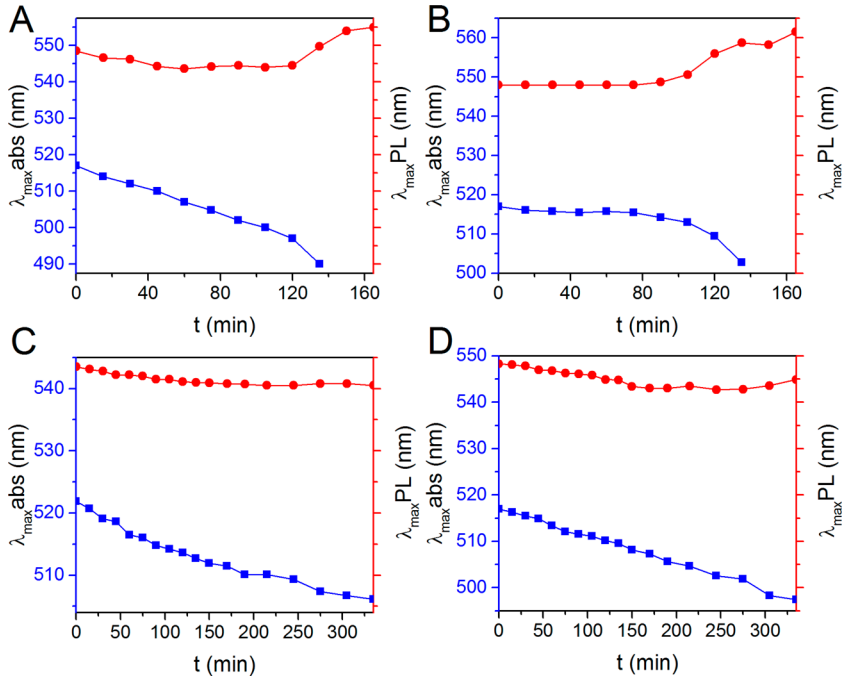

Figure 6. Absorption and photoluminescence maxima shift of QDs in the course of irradiation: (A) CdTe in the buffer solution, (B) CdTe with addition of Na_2SO_3, (C) CdTe in 1% gelatin solution, and (D) CdTe additionally stabilized by BSA.

Corresponding data obtained in our experiment are presented in Figure 6.

Blue shift of both absorption and photoluminescence maxima was observed for QDs in the buffer solution (Figure 6a). Note that for irradiation time more than 135 min the determination of absorption maximum was impossible due to inhomogeneous broadening of the spectrum. This broadening must be explained by the formation of large aggregates and by the electrodynamical interaction of the particles within these aggregates that produces strong modification of spectra.[39] Addition of Na_2SO_3 stabilizes both absorption and photoluminescence maxima positions for 90 min of irradiation. At irradiation times more than 1.5 h, the maxima begin to shift; however, absorption and photoluminescence maxima experience a shift of opposite sign. Specifically, the absorption maximum exhibits a blue shift until 135 min, while at larger illumination times strong light scattering by massive naked-eye-seen aggregates prevents the absorption maximum position from being determined. The photoluminescence maximum experiences a red shift, evidencing simultaneity of aggregate formation and reduction of individual QD size. Absorption and photoluminescence maxima in gelatin-containing and TGA+BSA-stabilized solutions exhibit just the same behavior. In these two cases, the synchronous blue shift of both spectral maxima evidences the reduction of QD size. Loss of transmission due to scattering of light by massive aggregates was not observed both for gelatin-containing and TGA+BSA-stabilized solutions. Therefore, at the examined illumination durations, QDs remain stabilized against aggregation to a sufficient extent.

Kinetics of QD Photodegradation. The square under the curves describing a band in a photoluminescence spectrum can be treated under certain conditions as the measure of a number of QDs participating in the emission, and therefore as the measure of QD photostability. Figure 7 presents the dependencies of the luminescent band's area (S) on the irradiation time as well as their best-fit exponential approximations.

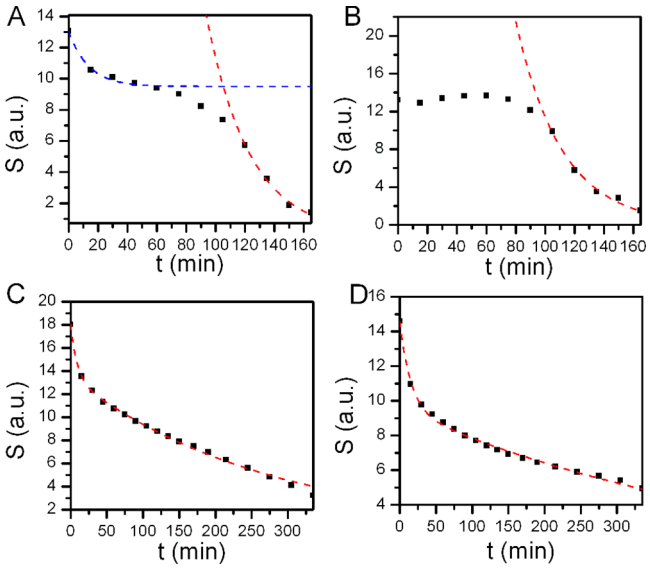

Figure 7. Time dependence of the area under the luminescent band curve (S) for (A) QDs in the buffer solution, (B) QDs in buffer solution with addition of Na_2SO_3, (C) QDs with addition of 1% of gelatin, and (D) TGA+BSA-stabilized QDs.

The luminescent band area decay for QDs in the buffer solution evidently is a two-stage process with a certain time delay between the first stage and the onset of the second stage (Figure 7a). The first stage is governed by the exponent with a time constant of 13 min and must be ascribed to QD surface degradation and QD size reduction. The first stage is governed by the exponent with a time constant of 13 min and must be ascribed to degradation of the TGA stabilizing layer.

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Degradation of TGA leads to three consequences overlapping in time, namely, QD surface degradation, QD size reduction, and gradual loss of stability against aggregation. The decrease of luminescence intensity initially is due to the first two factors, while aggregation becomes evident at the second stage, when the density of QDs with the degraded TGA layer becomes sufficient. This second stage is governed by the exponent with a time constant of 30 min and becomes completely evident after 120 min of irradiation. The time constant of the first stage is determined by the diffusion of oxygen, while the time constant of the second stage is due to QD diffusion that is slower due to the larger diameter of QDs. The decrease of luminescence at the second stage is due to the sedimentation of large enough aggregates from the solution.

The corresponding dependence for QDs with Na_2SO_3 (Figure 7b) contains a time period where the luminescent band area can be considered as a constant. The duration of this period is approximately 90 min, and this period must be ascribed to the preserving action of sodium sulfate against the oxygen-mediated photodegradation of QDs. After 90 min, the decay of the luminescent band square is governed by the exponent with a 32 min time constant. This time constant is close to that detected in the pristine buffer solution and must be associated with the onset of aggregation. Decay dependence for gelatin-stabilized solution is described by biexponential law with time constants of 9 and 277 min. The same behavior is observed for TGA+BSA-stabilized solution, with the time constants being 15 and 502 min. The smaller time constant in the case of gelatin stabilization can be associated with the action of oxygen dissolved in the close vicinity of every QD, while in the case of TGA+BSA it is the time constant of BSA denaturation. Large time constants observed at the second stages of illumination of these two kinds of solutions evidence noticeable enhancement of QD photostability when using gelatin or TGA+BSA.

While stabilization methods using either gelatin or BSA improve long-term stability, they cannot protect QDs from short-period degradation caused by neighboring oxygen. Therefore, we can expect that combination of gelatin or BSA stabilization with preaddition of a small amount of sodium sulphite may help to remove this initial stage of photodegradation.

The photostability of the QDs is extremely urgent for a number of applications. One of the approaches is the coating by other materials such as dielectric ones (e.g., SiO_2[40]) or core−shell structuring with semiconductors.[41] These methods efficiently protect the core of initial QDs by the price of certain changes in optical properties; however, they do not protect the antiaggregation layer against deterioration, and aggregation will nevertheless limit the photostability. Additionally, variation of the electrical properties of QDs after dielectric coating is expected that may change the properties of ensembles formed of them, and therefore limit the range of possible applications. Probably, the required level of photostability can be achieved by a combination of approaches investigated in the present paper with those employing the additional coating of QDs.

CONCLUSIONS

Additional enhancement of TGA-stabilized CdTe QD photostability under UV irradiation is demonstrated. The methods employed are chemical removal of oxygen, solution viscosity increase, and additional passivation of TGA@QD complexes. Introduction of excessive oxygen-binding Na_2SO_3 enables perfect photostability during the time period of the order of hours, until the expenditure of this stabilizer. Control of solution viscosity by gelatin addition produces a 2-fold increase of QD photostability. The combined TGA+BSA stabilization of QDs must be considered as the most promising one, since it not only enhances the photostability but also makes QDs more biocompatible and extends the possibilities of their applications in biological media.

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Notes

The authors declare no competing financial interest.

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