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Photodegradation of IR luminescence of Ag_2Se colloidal quantum dots

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Received October 31, 2024
Revised October 31, 2024
Accepted November 25, 2024

Photodegradation of exciton and trap-state luminescence, in bands with maxima at 705 and 905 nm respectively, of hydrophilic Ag_2Se colloidal quantum dots (QD), passivated with 2-mercaptopropionic acid molecules (Ag_2Se/2MPA) was established. Herewith, the exciton band is characterized by complete quenching of luminescence of Ag_2Se/2MPA QD as the sample gets exposed. Trap-state luminescence experiences quenching by 40−60%. The quenching of trap-state luminescence is accompanied by an acceleration of luminescence kinetics and a decrease in the decay time from 280 to 210 ns. In this case, photodegradation of luminescence in this band is reversible. After 24 h of storage of the exposed colloidal solution of Ag_2Se/2MPA QDs, a long-wave shift of the trap-state luminescence band to the region of 960−1200 nm occurs, with an even greater decrease in its decay time to 170 ns. The regularities gained are explained by the formation of core/shell systems Ag_2Se/SeO_2 with a type I heterojunction.

Keywords: luminescence, luminescence decay time, photodegradation, quantum dot, core/shell system, silver selenide.

DOI: 10.61011/EOS.2025.01.60570.7279-24

Introduction

In recent years, semiconductor colloidal quantum dots (QDs) with size-dependent luminescence have attracted great practical interest in the development of optical sensors for various purposes [1–3]. An essential issue delineating the potential of this luminescence application in various areas of modern photonics is forecasting the quantum luminescence yield of colloidal QDs [4]. At that, great attention is paid to the processes of photoactivation [5,6] and photodegradation [7] of QDs luminescence that occur as a result of photochemical reactions involving both a semiconductor nanocrystalline core and an organic shell. These reactions change the structure and size of QDs due to photo-corrosion and photo etching of QDs [6,8]. Under the action of exciting quanta in one case a flaring of QD photoluminescence is observed, and in the other — its quenching (degradation or „fatigue"). In this case, photodegradation can be both reversible and irreversible [6,7,9]. The issues of photoactivation and photodegradation of luminescence are considered in detail for colloidal QDs of CDs, CdSe, CdTe, Ag_2S [5–8,10–15]. The main mechanisms discussed are the processes leading to changes in the quantum yield of luminescence: photo-destruction and photo-desorption of passivator molecules, photolysis of nanocrystals, and photocatalytic oxidation and dissolution reactions in the presence of O_2 [6,7,11,12,14,15].

In one of the first experiments on the problem in question, the process of increasing the quantum yield (photoactivation) of CdSe QDs luminescence under prolonged illumination with natural light was demonstrated [10,11]. This process is associated with elimination of dangling dangling bonds on CdSe QDs interfaces during the photocatalytic formation of SeO_2 shell. After absorption of the radiation quantum, a photoexcited electron is injected onto an oxygen molecule (O_2) in solution near QD interface, and the ion $O_2^{\cdot -}$ is formed. The Se hole captured in the dangling bond contributes to the formation of SeO_2. Thus, the bright luminescent QDs of type „core−shell" CdSe/SeO_2 are formed, where the non-radiative decay of excitons is no more prevailing over the radiative one [11]. For colloidal Ag_2S QDs and CdS with sizes 2.6−3.2 nm passivated with thioglycolic acid (TGA) [12–13], a decrease in photoluminescence intensity was found as the samples were exposed to radiation with a wavelength of 445 nm, starting from the values of the effective power 10 mW. It was also found that a decrease in optical density along the entire contour of the absorption spectrum is associated with photodegradation of the passivating shell. In addition, signs of a photochemical reaction accompanied by the formation of non-radiative recombination channels have been established for Ag_2S QDs [7,12].

Prolonged exposure of the core/shell QDs (CdSe/ZnS QDs) to radiation revealed that ZnS shell is destructed, which leads to an increase in the probability of non-radiative transitions and lower luminescence intensity of CdSe QDs [16,17]. In paper [18] it was found that in conditions of vacuum and absence of oxygen and water vapor the photo-induced processes CdSe/ZnS are not

activated. In this case, degradation in air occurs due to predominance of photo-corrosion (decrease in luminescence efficiency) over passivation of surface defects (increase in luminescence intensity).

The transfer of excited charge carriers from the QD core to surface ligands or surrounding molecules is also an effective way of luminescence quenching. The photoinduced degradation or luminescence stability is attributed to the mutual arrangement of energy levels of HOMO-LUMO of surface ligands and QDs. In papers [10,11], it is noted that in the presence of oxygen and metal chalcogenide nanocrystals, superoxide formation reactions can occur as a result of electron photo-transfer according to the mechanism $O_2+e^- \rightarrow O_2^{(-)}$. In its turn the hole may lead to oxidation of both, the chalcogen atoms [14], and the passivator molecules [15]. This process affects the ratio of the concentration of luminescence centers and non-radiative recombination, and also leads to passivator desorption and poorer QD stability. However, in papers [10,11] it was found that similar process leads to higher luminescence of CdTe and CdSe QDs due to formation of core/shell-structures $CdTe/TeO_2$ and $CdSe/SeO_2$.

In recent years, there has been a rising interest in the control of IR luminescence of colloidal QDs from narrow-band semiconductors, such as Ag_2Se, Ag_2Te, PbS, PbTe, etc. In particular, due to the dimensional effect for Ag_2Se QDs it is possible to control the absorption and luminescent properties in the range of 800−2000 nm [19–23]. However, an in-depth analysis of the luminescence patterns in Ag_2Se QDs, including the problem of its photo stability, has not yet been performed. The data available in the literature on the size dependences of the luminescence spectra of Ag_2Se QDs synthesized by different methods using different precursors, Stokes shift, and achievable quantum yield are contradictory [20–24].

The findings presented in this paper are aimed at clarifying the regularities of photo processes that determine degradation of exciton- and trap-state IR-luminescence of the quantum dots Ag_2Se/2MPA.

Samples

All chemicals (silver nitrate ($AgNO_3$), 2-mercapto-propionic acid (2MPA), sodium hydroxide (NaOH), selenium (Se), sodium sulfite (Na_2SO_3)) had HP or UHP purity class and were used without additional purification.

Colloidal Ag_2Se QDs were synthesized in water using one common method [19]. 2 MPA was used as a passivator, which is characterized by a minimum yield of sulfur ions, which prevents the formation of Ag_2S phase.

Ag_2Se QDs were synthesized based on the use of 2 precursors: silver precursor Ag^+/2MPA, fabricated from the solution of 1 mmol $AgNO_3$ in 50 ml water and 2 mmol 2MPA at pH 10 and selenium precursor — from selenium (Se) and sodium sulfite (Na_2SO_3) in the ratio 1 : 0.5. It is worth noting that without addition of the selenium precursor, Ag^+/2MPA solution remained colorless and transparent, indicating the absence of sulfur ions from 2MPA. Selenium precursor was added to Ag^+/2MPA solution by drops. There were fabricated three samples of Ag_2Se/2MPA QDs with the ratio of concentrations [Ag] : [Se], equal 1 : 0.2 (further $Ag_2Se(0.2)$ QDs), 1 : 0.3 (further $Ag_2Se(0.3)$) and 1:0.4 (further $Ag_2Se(0.4)$). Subsequent addition of the selenium precursor resulted in loss of colloidal stability of the solution and sedimentation.

To determine the effect of molecular oxygen on the photo stability of Ag_2Se QDs, a series of $Ag_2Se(0.3)$/2MPA QDs with different concentrations of sodium sulfite acting as an antioxidant was synthesized [25]. The used concentrations ratios of $[Na_2SO_3] : [Na_2SeSO_3]$ were 0.5 : 1, 1 : 1 and 5 : 1.

Fig. 1 illustrates TEM-images of Ag_2Se QDs obtained through the use of different concentrations of selenium. Analysis of TEM images of the quantum dots $Ag_2Se(0.2)$/2MPA showed that the average size of nanocrystals is 2.1nm with a dimensional spread of 7−10%. For the quantum dots $Ag_2Se(0.3)$/2MPA the average size increased to 2.3 nm, and dispersion - up to 20%. For the quantum dots $Ag_2Se(0.4)$/2MPA the nanocrystals were observed with an average size of 2.6 nm with a dispersion over 35%.

Research procedures

Structural composition of synthesized Ag_2Se QDs was certified by using transmission electron microscopy on Libra 120 TEM (CarlZeiss, Germany) with an accelerating voltage of 120 kV. Data on QDs size distribution were obtained by digital analysis of TEM images.

For detection of the optic absorption and luminescence spectra within 200−900 nm the spectrophotometer USB2000+(Ocean Optics, USA) was used with the source of radiation USB-DT. Optical absorption spectra in the range of 900−1400 nm were recorded using G9203-256 spectrometer (Vision2Go, Russia) with an incandescent lamp as a radiation source. To detect the luminescence spectra excited by radiation with a wavelength of 660 nm in the range of 900-1400 nm, an automated complex based on a diffraction monochromator with a 600 mm^{-1}¡3 mm $grating^{-1}$ equipped with a PDF10C/M photodetector (Thorlabs, USA) was used. The spectra were adjusted to the detector's spectral sensitivity function measured using a reference incandescent lamp. To detect the excitation spectra in the region of 500−1300 nm, a second diffraction monochromator with a grating 1200 mm^{-1} with an incandescent lamp was used.

The time-resolved luminescence in the region of below 900 nm was registered using PMT PMC-100-20 (Becker&Hickl, Germany), and in the region of 900−1400 nm — using a module with a single-photon avalanche diode InGaAs KIT-IF-25C (Micro Photon Devices, Italy) using the time-correlated photon counting

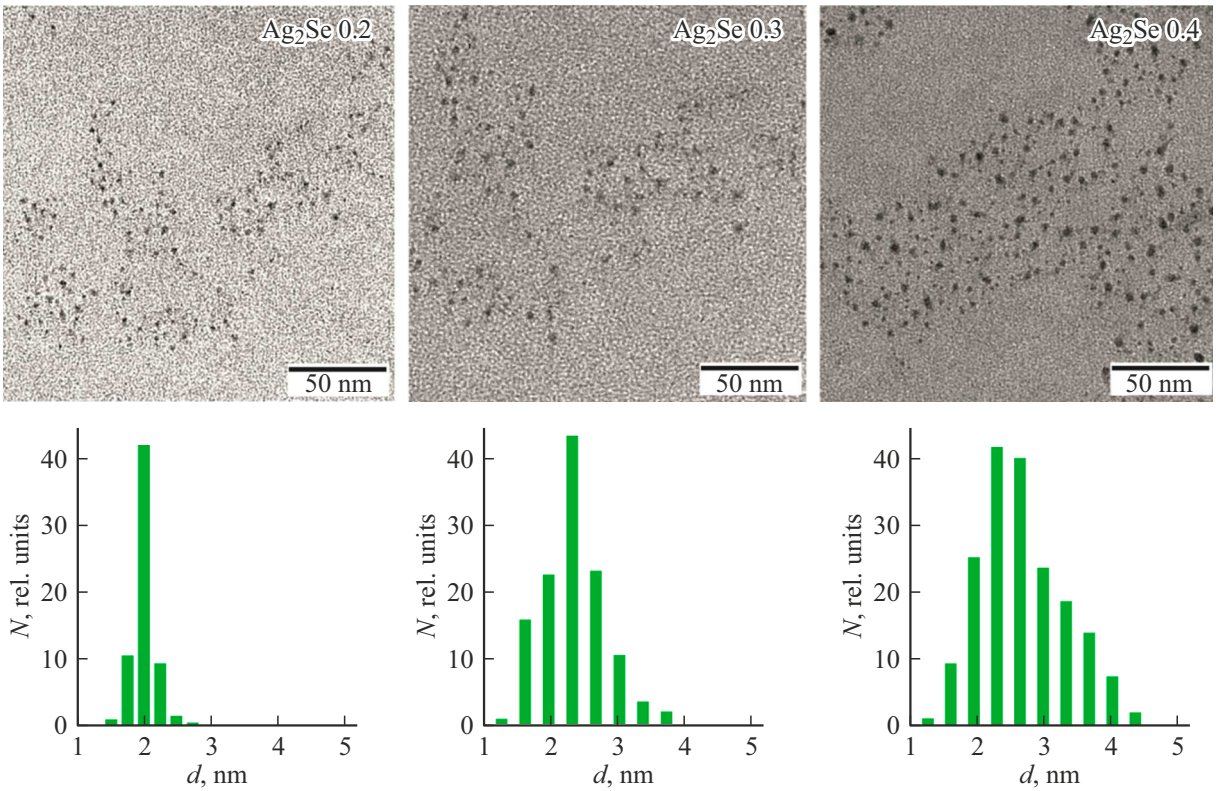

Figure 1. TEM-images and histograms of distribution of the sizes of studied samples Ag_2Se/2MPA QDs.

board TimeHarp 260 (PicoQuant, Germany). The temporal resolution in the visible spectrum region was 0.2 ns, and in IR spectrum — 0.5 ns. The samples were excited with a PICOPOWER LD660 semiconductor pulsed laser (Alphalas, Germany) with a wavelength of 660 nm and a pulse duration of 60 ps.

Photodegradation of luminescence was recorded by measuring the photoluminescence intensity of Ag_2Se QDs in the maximum of the luminescence band under radiation with wavelengths of 462, 532 and 660 nm and power of 50 mW for 1 h. The radiation power was monitored with an optical power meter PM100A Thermal Power Sensor Head S401C (Thorlabs, USA). The excitation sources were semiconductor laser diodes NDB7675 (Nichia, Japan) with a wavelength of 462 nm, PM-G80 (CST, China) — 532 nm and LPC-826 (Mitsubishi, Japan) — 660 nm. The measurements were carried out at room temperature, the QD sample was mixed during excitation, the sample's area illuminated by the exciting radiation was 0.5 cm^2, the incident beam on the sample was perpendicular to the cuvette plane. The QDs concentration in the solution was about 10^{16} QDs/ml.

Results and discussion

Figure 2 shows spectral luminescent properties of Ag_2Se/2MPA QD samples before and after exposure to radiation with wavelengths of 462, 532, and 660 nm and a power of 50 mW/cm^2.

In the optical absorption spectra of Ag_2Se/2MPA QD samples, the wide bands were observed shifted to the short-wavelength region relative to the edge of the fundamental absorption of single crystals Ag_2Se ($E_g = 0.4$ eV) and featuring specific singularities in the region of main exciton transition. For $Ag_2Se(0.2)$/2MPA QDs a distinct exciton absorption in 640 nm region was clearly seen in the absorption spectrum. The presence of a structure in the spectrum indicates a small size dispersion of QDs, which is consistent with the TEM data.

As the ratio [Ag] : [Se] increased to 0.3, a blurring of the exciton structure and a long-wavelength shift of the absorption edge by 20–30 nm were observed, with a slight increase in the average size and size dispersion of nanocrystals. A further increase of [Ag] : [Se] ratio to 0.4 led to a shift of the exciton structure in the absorption spectrum to 720 nm due to the dimensional effect and its even greater blurring due to an increase in the size spread of nanocrystals. Thus, there is a correlation between the TEM data and the QDs absorption spectra.

In the luminescence spectra of $Ag_2Se(0.3)$/2MPA QDs, two luminescence bands with maxima located in the region of 705 and 905 nm were observed. For the first band, the Stokes shift relative to the exciton absorption peak was 0.15 eV and the luminescence decay time was —2.43 μs, and for the second — 0.54 eV and 290 ns, respectively. The

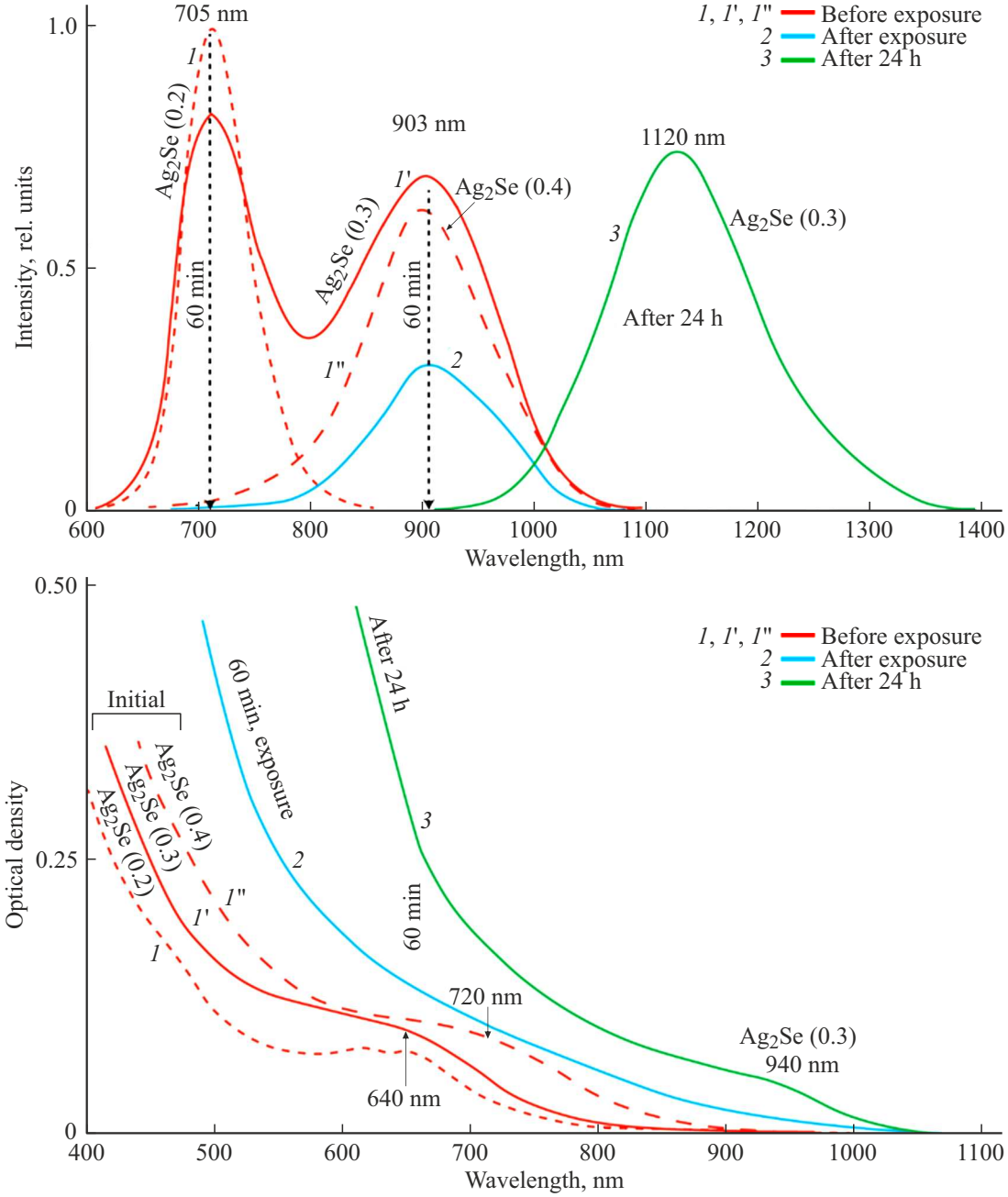

Figure 2. Luminescence (top) and absorption (bottom) spectra of Ag_2Se/2MPA QDs before illumination (red lines), after illumination (blue lines) and after 24 hours in the dark (green lines, for samples illuminated by 462 nm radiation). Dashed lines — luminescence recovery after exposure to radiation with the wavelength of 660 nm.

obtained values indicate the exciton nature of luminescence in the first band and trap-state nature in the second. For colloidal Ag_2Se QDs synthesized with the ratio [Ag] : [Se] reduced to 0.2, it led to a more bright short-wave exciton luminescence band in the region of 705 nm and disappearance of the trap-state luminescence band with a maximum at 905 nm. An increase in the ratio of [Ag] : [Se] to 0.4, on the contrary, led to complete quenching of the exciton band while maintaining trap-state luminescence with a maximum at 905 nm.

Figure 3 shows the results demonstrating changes in the spectral luminescent properties of Ag_2Se QDs as they are exposed to radiation with wavelengths of 462, 532 and 660 nm and a power of 50 mW. The regularities found in the luminescence were similar. Within an hour, the exciton luminescence was completely extinguished and the intensity of trap-state luminescence decreased by 60, 40, and 20%, respectively, for wavelengths of 462, 532 and 660 nm. At the same time, the kinetics of photo degradation of luminescence was complex, not exponential (Fig. 3).

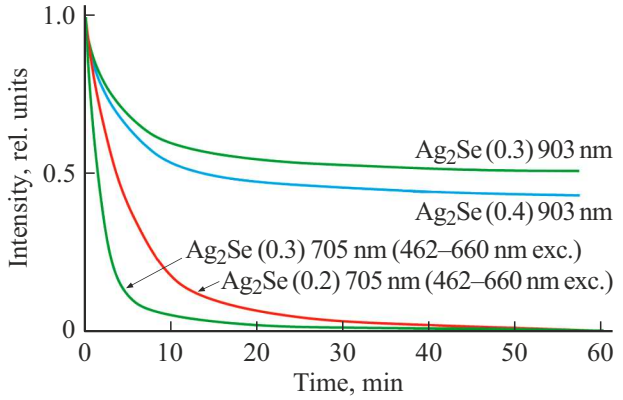

Figure 3. Normalized dependence of the luminescence intensity of Ag_2Se/2MPA QDs at the band maximum on the exposure time to radiation within wavelengths of −660 nm.

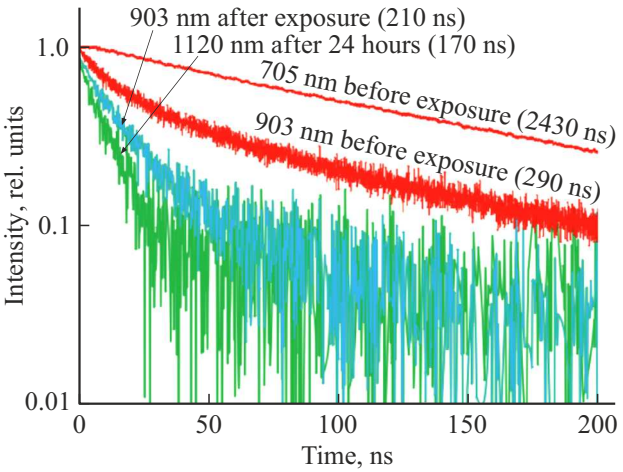

Figure 4. Luminescence decay curves for $Ag_2Se(0.3)$/2MPA QDs before, after exposure to 462 nm radiation, and after dark recovery.

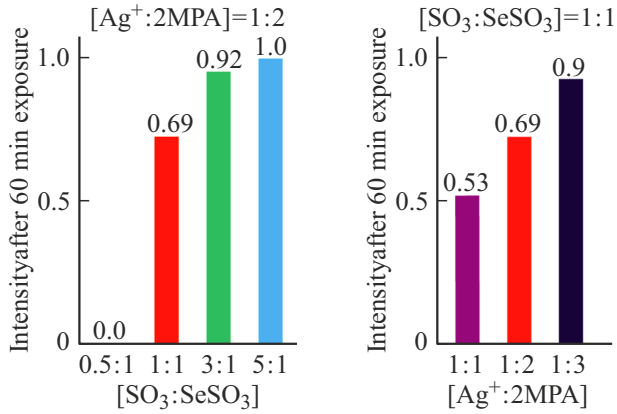

Figure 5. Histograms of luminescence intensity for $Ag_2Se(0.3)$ QDs after 60 min exposure to radiation with a wavelength of 462 nm, 50 mW: on the left — at different concentration of Na_2SO_3 and constant ratio of $[Ag^+] : [MPA] = 1 : 2$; on the right - at different ratio of $[Ag^+] : [MPA]$ and constant concentration Na_2SO_3.

Thus, the intensities of both, exciton and trap-state luminescence experienced maximum photodegradation during the first 10−15 min of exposure. After that, the luminescence quenching rate decreased. After 30−40 min of exposure, photodegradation of trap-state luminescence practically stopped. The exciton band was quenched during 40−50 min. The rate of luminescence degradation for samples with a high selenium content was higher than for samples with a lower selenium content. QDs exposure did not shift the maximum of the trap-state luminescence band.

After exposure, colloidal Ag_2Se QDs were kept in the dark at room temperature for 24 hours. Finally, an increase in the intensity of trap-state luminescence and a shift of the peak to the long-wavelength region to 930−1230 nm were observed for all samples. Exciton luminescence was not restored. The magnitude of the shift of trap-state luminescence peak during its restoration increased with growing concentration of Se precursor. At the same time, the half-width of the trap-state luminescence band decreased from 0.35 to 0.26 eV. For the samples of $Ag_2Se(0.2)$/2MPA QDs, which did not initially exhibit trap-state luminescence, its occurrence was observed in the region of 910−1025 nm. These features indicate the involvement of photochemical reactions involving selenium in the mechanism of degradation/restoration of luminescence. The long-wavelength shift of the luminescence band maximum is accompanied by a shift of the exciton absorption maximum to the region of 730−1040 nm, which indicates the nanocrystals size increase to 15−20%. At the same time, the Stokes shift in the trap-state luminescence band decreased from 0.55 to 0.25−0.3 eV (depending on the selenium concentration and exposure wavelength).

The kinetics of luminescence decay for Ag_2Se QDs also undergoes changes as a result of exposure. Figure 4 shows the luminescence decay curves of $Ag_2Se(0.3)$/2MPA QDs recorded at wavelengths of 705 and 905 nm near the peaks of both luminescence bands. All luminescence decay curves are non-exponential. The average luminescence decay time was determined by approximating empirical decay curves by the sum of several exponentials:

$$I(t) = \sum_{i=1}^{3} a_i \exp[-t/\tau_i], \quad (1)$$

$$\langle \tau \rangle = \sum_{i=1}^{n} a_i \tau_i / \sum_{i=1}^{n} a_i, \quad (2)$$

where a_i and τ_i — amplitude and time constant of i-th component.

The average luminescence decay time for Ag_2Se QDs was about 2400 ns for the exciton band and 280 ns for the trap-state band. Exposure of colloidal solutions resulted in complete quenching of the exciton luminescence band and a partial decrease in the intensity and decay time of trap-state

luminescence to 210 ns. After holding of exposed QDs in the dark, despite a threefold increase in the quantum yield of luminescence, the luminescence decay kinetics was further accelerated („τ“ = 170 ns). The mismatch between the decay kinetics and the quantum yield of luminescence here is apparently determined by the mechanism of luminescence itself. Indeed, for trap-state luminescence, a simple two-level model in which the quantum yield of luminescence and the decay time are directly proportional is not applicable. The radiation process does not directly compete with non-radiative trap-state at the same center. The variety of photo processes occurring before trap-state luminescence makes the relationship between luminescence kinetics and quantum yield non-trivial.

The next stage in studying the photodegradation patterns of IR luminescence of Ag_2Se/2MPA QDs was to determine the effect of oxygen-related processes on it, in particular, photo-transfer of charge carriers to oxygen molecules, destruction/desorption of the passivator, and subsequent oxidation of the QD surface. To test this hypothesis, a series of $Ag_2Se(0.3)$/2MPA QD samples with different levels of passivator 2MPA and different concentrations of antioxidant Na_2SO_3were synthesized and the photo stability of the synthesized samples was examined. The results are illustrated in Fig. 5.

The introduction of Na_2SO_3into the colloidal solution and an increase in its concentration leads to improved photo stability of luminescence. Thus, with a ratio $[SO_3] : [SeSO_3] = 0.5$ the exciton luminescence band is completely extinguished in 705 nm. An increase in the ratio $[SO_3] : [SeSO_3]$ to 1 resulted in that IR luminescence of $Ag_2Se(0.3)$/2MPA QD in the exciton luminescence band (705 nm) photo-degraded only by 31% after being exposed to radiation with a wavelength of 462 nm (for 60 min). An increase in the ratio $[SO_3] : [SeSO_3]$ to 5 contributed to preserving the intensity of exciton luminescence without its decrease during excitation of $Ag_2Se(0.3)$/2MPA QDs.

Similarly, an increase in the passivator concentration with a constant amount of antioxidant ($[SO_3] : [SeSO_3] = 1$) led to an improvement in the photo stability of the quantum dots. Thus, with a concentration ratio of [Ag] : [2MPA] equal to 1 : 1, the quenching of exciton luminescence was only 47% within an hour. With the ratio [Ag]:[2MPA] equal to 1 : 2, the quenching of the exciton luminescence band was 31%, and with the ratio 1 : 3 it was 10%. Thus, it is concluded that not only molecular oxygen, but also the process of passivator desorption is involved in the photo degradation of IR luminescence of Ag_2Se/2MPA QDs.

Improved photo stability of IR luminescence of Ag_2Se/2MPA QDs in the presence of an antioxidant, binding the molecular oxygen, indicates that molecular oxygen takes part in the photodegradation of the QDs luminescence. Moreover, since no spontaneous degradation of Ag_2Se/2MPA QDs' IR luminescence is observed during storage of the sample in the dark, it is presumed that it occurs because of a photochemical reaction. The deceleration of photo degradation of IR luminescence with the growth of the passivator concentration in the solution indicates that the first stage in the process of luminescence degradation is the passivator photo-destruction/photo-desorption. This process slows down in the presence of high concentrations of passivator, since in this case the passivator sorption/desorption equilibrium shifts towards sorption. In its turn, at a low concentration of the passivator, its desorption and oxidation of QD surface with oxygen occur with the formation of selenium dioxide layer SeO_2. Selenium dioxide is a wide-band semiconductor with a band gap of 3.7 eV. Thus, the findings of this study indicates that QDs surface becomes oxidized and SeO_2 shell is formed around it.

The formation of a shell from wide-band selenium oxide leads to the formation of core/shell systems of Ag_2Se/SeO_2, the energy properties of which indicate that they have a hetero-system of I type. This assumption is also confirmed by regularities in the kinetics of luminescence decay. When luminescence is restored, a decrease in the average lifetime is observed with a growing intensity of the glow. This, in turn, indicates higher efficiency of radiative trap-state due to formation of a wide-band shell.

Conclusion

This paper outlines the findings of the studies of photodegradation and dark restoration processes for the exciton (705 nm) and trap-state luminescence (905 nm) of hydrophilic colloidal quantum dots (QDs) of Ag_2Se coated with 2MPA molecules. It was found that exciton luminescence is particularly sensitive to exposure of colloidal solution — it is characterized by the complete disappearance of photoluminescence when illuminated for 1 h by radiation with wavelengths 462−660 nm and power of 50 mW. At the same time, quenching at 40−60% at similar exposures is observed for trap-state radiation.

Studies of the kinetics of trap-state luminescence decay time-correlated single photon counting have shown that luminescence quenching is accompanied by a reduction in the decay time from 280 to 210 ns. It was found that holding of exposed colloidal solutions of Ag_2Se QDs without any light for 24 h is accompanied by an increase in the quantum yield of luminescence. In this case, the peak of trap-state luminescence shifts to the long-wavelength region to 960−1200 nm, and the luminescence decay time is reduced to 170 ns.

The discovered luminescence regularities are explained by photochemical reactions, as a result of which the core/shell systems Ag_2Se/SeO_2 with a type I heterojunction are formed.

Acknowledgments

Transmission electron microscopy results were obtained using Libra 120 microscope provided by the Common Use Center of „Voronezh State University“.

Funding

This study was funded by the Russian Science Foundation as part of research project № 22-12-00232.

Conflict of interest

The authors declare that they have no known financial conflicts of interest or personal relationships that could affect the study presented in this paper.

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Translated by T.Zorina