Photoluminescence and structural properties of CdSe quantum dot–gelatin composite films

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ABSTRACT

Optical and structural properties of composite films of CdSe quantum dots (QDs) embedded in gelatin matrix have been investigated by photoluminescence (PL), optical absorption and X-ray diffraction (XRD) methods. The optical absorption of the composite in the visible spectral range is found to be determined mainly by light absorption in the QDs. The decrease of the film transparency and the shift of the absorption edge to lower energies observed upon thermal annealing of the films at 140–160 °C are ascribed to the formation of chromophore groups in gelatin matrix. XRD patterns of the composite revealed helix to coil transition in gelatin matrix under thermal annealing of the composite at 100–160 °C. It is found that PL spectra of the composite are dominated by exciton and defect-related emission of the QDs and also contain weak emission of gelatin matrix. It is found that thermal annealing of the composite at 100–160 °C changes PL intensity and produces the shift of the PL bands to lower energies. As the annealed composite was kept in air for several months, the shift of exciton-related PL band position restored partially and the PL intensity increased. It is proposed that the increase of the PL intensity upon the thermal annealing of composite at 140 °C can be used for enhancement of the QD-related PL. Changes that occurred in the PL spectra of composite are ascribed to structural and chemical transformations in gelatin matrix and at the QD/gelatin interface.

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1. Introduction

An interest in luminescent II–VI quantum dots (QDs) produced by "wet" colloidal chemistry techniques is aroused by their promising biomedical applications including bioimaging, labeling, and sensing [1]. Specifically, QD-conjugates can be used for *in vivo* fluorescent labeling and tracking of drug molecules, live cells, tissues and organs [1–3]. However, to be used *in vivo* the QDs must meet the requirements of stability and biocompatibility. The cytotoxicity of QDs is known to be highly dependent on the core composition, size and surface functionality [2,4]. The main cyto-toxic effect associated with the QDs is ascribed to the leakage of metallic ions from the QD core into surrounding tissue. In fact, cytotoxicities of CdTe and CdSe QDs are attributed mainly to release of Cd^{2+} ions from the QD core in response to ultraviolet radiation as well as to photo-oxidation processes [4,5]. Therefore, various surface stabilizing and coating materials and protocols

have been applied for making monodispersed, bio-inert and highly stable luminescent QDs [6,7].

Recently, gelatin was proposed as a surface capping agent to reduce the toxicity of II–VI QDs [8]. Gelatin is a readily available, cheap, natural nontoxic, water-soluble and biodegradable polymer derived from collagens [9,10]. Gelatin has long being used in food, pharmaceutical and medical industries [10]. In the last decade, gelatin nanoparticles have been under development as safe and efficient drug- and gene delivery systems [10–12]. Gelatin can also be used as a stabilizing agent during the synthesis of colloidal QDs [13–15]. Possibilities to encapsulate CdSe [16], CdTe [17], PbSe [18] and CdHgTe [19] QDs into gelatin nanoparticles via dessolvation methods have been demonstrated. The *in vitro* cytotoxicity tests have proved that QDs embedded in gelatin nanoparticles have no or reduced toxic effect on cells [8,16] and show inherent stability against photo-oxidation damage and salt effect [16–19].

However, pure gelatin dissolves rather quickly in aqueous solutions and rapidly degrades *in vivo*. To be suitable for long-term biomedical applications, gelatin materials must be submitted to cross-linking procedure, which improves the mechanical prop-erties of gelatin and reduces polymer dissolution. Usually, it is realized by adding of chemical agents – crosslinkers (*e.g.*

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formaldehyde or glutaraldehyde). However, the use of chemical crosslinkers can lead to toxic side-effects owing to unreacted residues [20]. Thermal treatment of gelatin microspheres at 110 °C for tens of hours has been proposed as an alternative method for cross-linking of gelatin [21]. The annealing does not affect the size and the shape of gelatin particles, but their color becomes progressively brown. It has been shown [21] that by increasing thermal conditions the extent of microsphere swelling decreases and the solubility of microspheres decreases. Though the effect of thermal annealing on the mechanical properties of gelatin materials has been intensively investigated [9,21–24], thermal stability of the QD-gelatin composites as well as the effect of thermal treatment on the emission spectra of the composite has not been studied in detail [25].

Here we present results of our investigations of the effect of thermal annealing at 100–160 °C on the photoluminescence (PL), optical and structural properties of CdSe QDs embedded in gelatin films.

2. Experimental details

Composite films of CdSe QDs embedded in gelatin matrix as well as the films of pure gelatin were studied. Both gelatin and reagents for synthesis of colloidal CdSe nanocrystals were purchased from Sigma-Aldrich and used without an additional purification. CdSe QDs were produced by the reaction of Na_2SeSO_3 and $CdCl_2$ in aqueous solution of gelatin at 6 °C [13]. After the dialysis the QDs solution was kept at 90 °C for 2 h to promote growth of QDs in size. Thin films were obtained by applying 4 ml QDs solution onto cleaned glass slides and drying for 2 days in a black-out drying box at 20 °C and natural ventilation. A thickness of polymeric films on a glass was measured to be 0.18–0.20 mm to within ± 0.01 mm. The mass fraction of the QDs in a gelatinous matrix was less than 1% w/v. The increase of the QDs mass fraction over this value results in deterioration of optical properties of the films evidently caused by QD coagulation.

The films studied were annealed for 1 h at 100, 140 and 160 °C in the atmospheric ambience. Before annealing the films were removed from glass.

The PL spectra were studied at 77 and 300 K. The PL was excited with light of 470 nm from a light-emitting diode (LED) and recorded using a prism monochromator equipped with a photo-multiplier and an amplifier with synchronous detector. The optical absorption spectra were measured at room temperature using light of a halogen lamp passed through a grating monochromator and recorded by a Si photodiode. X-ray diffraction (XRD) study was realized using X-ray powder diffractometer ARL X'TRA with a Cu anode.

3. Experimental results

3.1. Optical absorption study

The films studied were homogeneous and smooth. The non-treated films of pure gelatin and of the composite were transparent in the visible spectral range. The films of pure gelatin were completely colorless (Fig. 1b, curve 1), while the composite films had yellow color. The optical absorption spectra of non-treated composite (Fig. 1a, curve 1) contain a shoulder at about 2.29 eV on the absorption edge caused by exciton absorption in the QDs. The average diameter of the QDs estimated from spectral position of the shoulder is about 2.9 nm [26]. It is obvious that the QD absorption is responsible for the strongly pronounced coloration of the composite film. The optical absorption spectra measured on different sections of the films were the same within the error margin suggesting that distribution of the QDs in a gelatinous matrix was homogeneous.

Thermal annealing of the films at 100 °C does not change noticeably the optical absorption spectra. However, as the annealing temperature was increased up to 140 °C, darkening of both composite and pure gelatin films occurred. The darkening is caused by the decrease of the film transparency in the whole spectral range and the shift of the absorption edge to lower
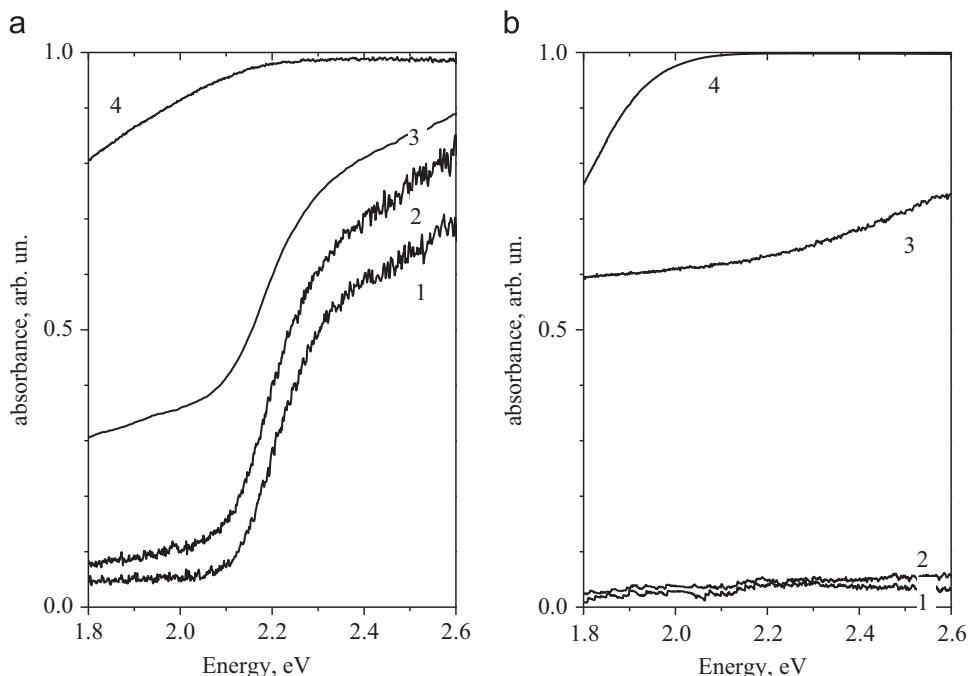

Fig. 1. Optical absorption spectra of the QDs-gelatin composite (a) and pure gelatin (b) films before (curve 1) and after thermal annealing at 100 °C (curve 2), 140 °C (curve 3) and 160 °C (curve 4), T=293 K.

energies. The annealing at 160 °C resulted in further decrease of the film transparency and the increase of the shift magnitude. Appearance of the films indicates that both the composite and pure gelatin films undergo partial melting during the thermal annealing at 160 °C. Being fully flexible before the annealing they became brittle after thermal treatment. It is found that the higher is the annealing temperature, the more brittle the gelatin film becomes.

3.2. Photoluminescence spectra investigation

The PL spectra of the composite films before and after thermal annealing are shown in Fig. 2. The low temperature PL spectra of non-treated composite (Fig. 2a, curve 1) are dominated by two bands. The high-energy PL band can be ascribed to exciton radiative recombination in the QDs or radiative recombination of carriers through the shallow surface traps, while the low-energy band is apparently caused by radiative recombination of carriers via deep levels of surface defects in the QDs [27]. The relative contribution of the bands to the PL spectrum changes with temperature because of different thermal quenching of the excitonic and defect-related bands [25]. At room temperature PL spectra of the composite, the excitonic band dominates, while the defect-related band is poorly resolved (Fig. 2b, curve 1). The shape of PL spectra does not depend on the concentration of CdSe QDs both in starting colloidal solutions and in the final polymer films. The PL intensity grows linearly with CdSe concentration both in colloids and the films till the absorption saturation is achieved.

It is found that thermal annealing of the composite changes PL intensity and produces the shifting of the PL bands to lower energies (the redshift effect). The redshift is observed both at 300 and 77 K and is larger for the excitonic band. In the films annealed at different temperatures, the shift magnitude ranges between 30 and 60 meV; the higher the annealing temperature,

the larger the shift magnitude. The annealing of the composite films at 100 and 160 °C resulted in a decrease of the PL intensity. In the composite annealed at 100 °C, the decrease of the PL intensity is observed both at 77 and 300 K, being larger at 77 K. In the composite annealed at 160 °C, the decrease of the PL intensity is observed at 77 K only, while the room temperature PL intensity increases. It is found that only the annealing at 140 °C stimulates the increase in the intensity of the excitonic PL bands both at 77 and 300 K.

It should be noted that PL spectra of the composite also show the plateau at about 2.3–2.4 eV of weak intensity. To elucidate the origin of this emission the PL spectra of pure gelatin films were studied. In the PL spectrum of gelatin film, a broad band covering the whole visible spectrum is observed (Fig. 3). The band apparently originates from the functional groups of gelatin. The band is centered at about 2.4 eV under 470 nm LED's light excitation both at low and at room temperatures (Fig. 3, curve 1). It seems that the PL of gelatin matrix contributes also to the PL spectrum of the composite film, but its intensity is strongly reduced as compared to that of pure gelatin film. This is probably caused by strong absorption of 470-nm excitation light by the QDs in the composite film.

It is found that thermal treatment of pure gelatin films at 100 and 140 °C produces the increase of the PL intensity and the shifting of the PL band to lower energies (Fig. 3, curves 2 and 3). These effects are observed both at low and room temperatures. Further increase of the annealing temperature up to 160 °C resulted in a pronounced decrease of the PL intensity and strong shift of the PL band to low energy region up to 2.08 eV (Fig. 3, curve 4).

Changes in the PL spectra of composite upon annealing are found to be partially reversible. Storage at room temperature for about a week of the composite film annealed at 100 °C resulted in full recovery of the PL peak position, while in the composites annealed at 140 and 160 °C only a partial recovery of the PL peak
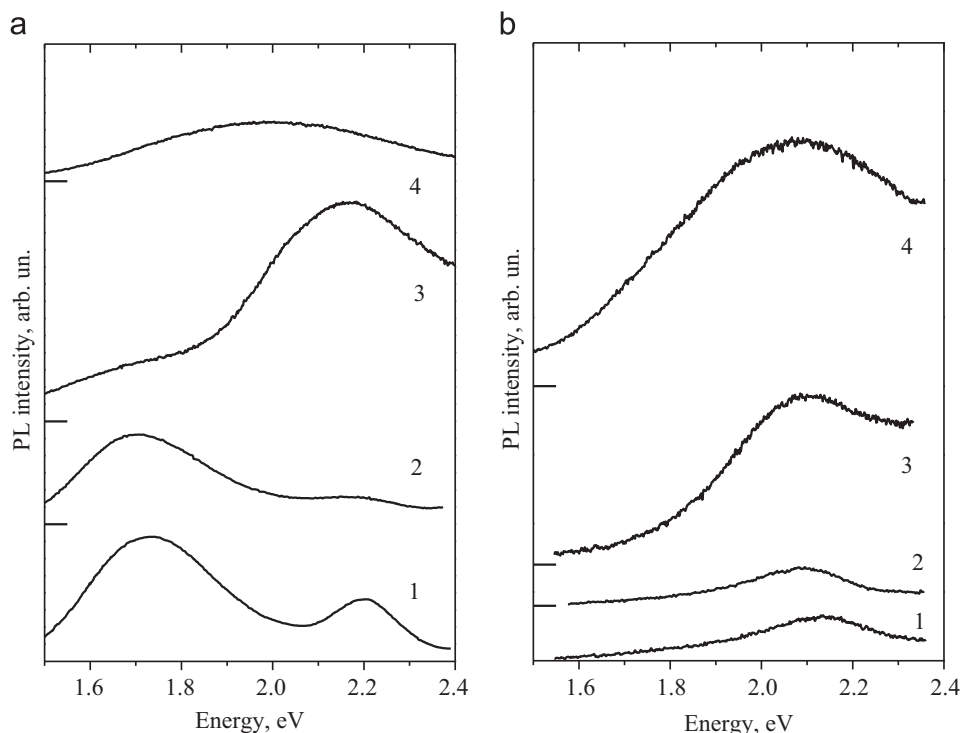

Fig. 2. Photoluminescence spectra of the QDs-gelatin composite recorded at 77 K (a) and 293 K (b) before (curve 1) and after thermal annealing at 100 °C (curve 2), 140 °C (curve 3) and 160 °C (curve 4), $\lambda_{exc}=470$ nm.
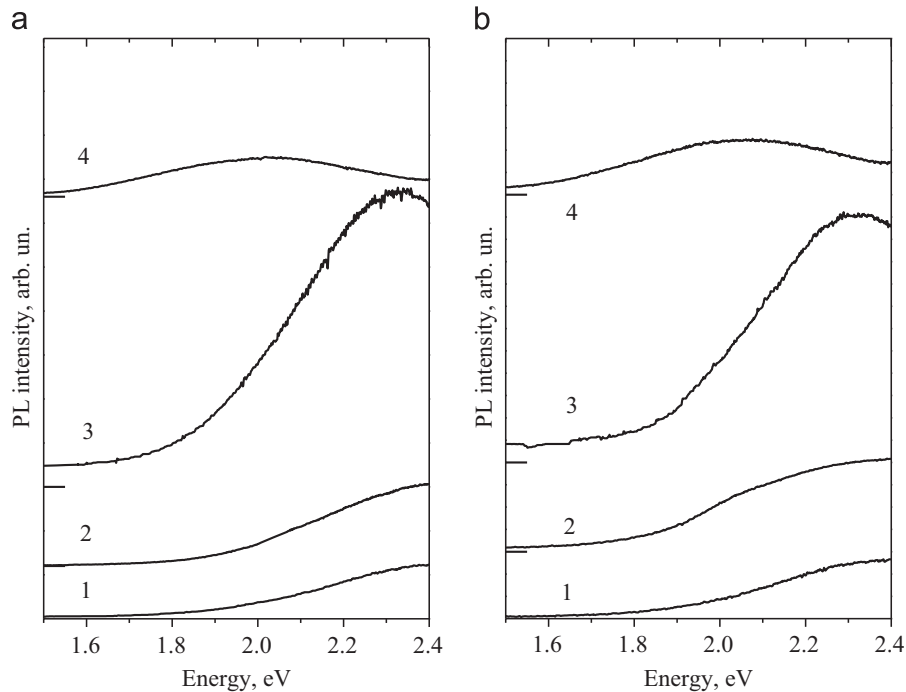
Fig. 3. Photoluminescence spectra of pure gelatin film recorded at 77 K (a) and 293 K (b) before (curve 1) and after thermal annealing at 100 °C (curve 2), 140 °C (curve 3) and 160 °C (curve 4), λ_{exc}=470 nm.
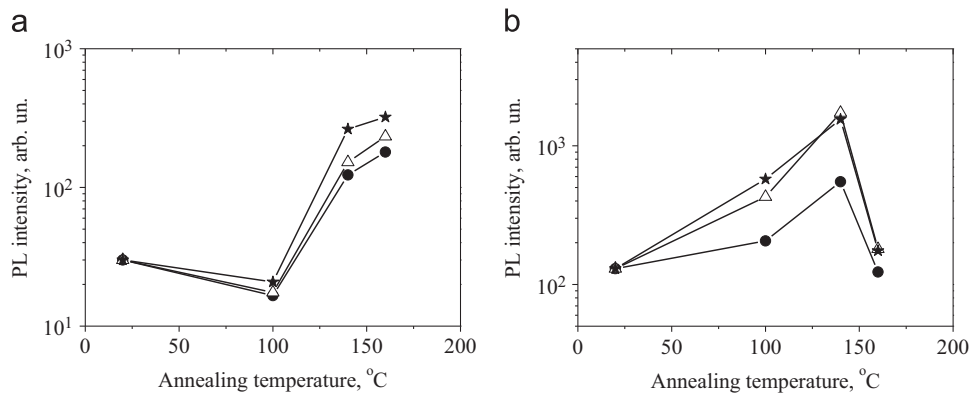

Fig. 4. Photoluminescence intensity *vs* annealing temperature for the QDs-gelatin composite (a) and pure gelatin (b) films recorded just after annealing (circles) and after 1 (triangles) and 2.5 (stars) months of storage in air, T=293 K, λ_{exc}=470 nm.

position was observed even after several months of storage. In the annealed gelatin films, spectral position of the gelatin-related PL band did not get restored. For all thermally treated composite and gelatin films the increasing of the PL intensity was observed during the storage (Fig. 4). It should be noted that neither optical transmission nor the flexibility of the annealed films was restored during the storage.

3.3. The XRD investigations

The XRD patterns of the QD-gelatin composite show only the signals from the gelatin matrix of partially crystalline nature (Fig. 5). The peaks from crystalline CdSe phase are not observed apparently because of a low QD concentration in the composite. The peak at 2θ=7.8 grad observed for both untreated films (Fig. 5, curve 1) is usually assigned to the triple-helical crystalline structure in collagen and renatured gelatin [28,29]. The presence of this peak in the XRD patterns is not surprising. The triple helix is the

defining feature of the collagen molecule. It consists of three parallel left-handed helical polypeptides coiled about each other to form a right-handed triple helix. When gelatin gel is obtained from collagen by partial hydrolysis and denaturation, the regular triple helix structure is broken down to form random gelatin coils. However, at temperatures below 35–40 °C the gelatin chains undergo a progressive conformational change, which is known as the coil-to-helix transition. Since the films studied were dried on a glass substrate below this temperature, the triple-helical crystalline structure was formed in both composite and gelatin films. Fig. 5 shows that the intensity of the peak at 2θ=7.8 grad decreases drastically in both composite and pure gelatin films upon annealing at 100 °C indicating the helix to coil conformational transformation of solid gelatin macromolecules. This phenomenon is accompanied by release of water molecules, which form hydrogen bonded bridges stabilizing the helix [9]. The increase of the annealing temperature up to 140 and 160 °C produces further decrease of the peak intensity.
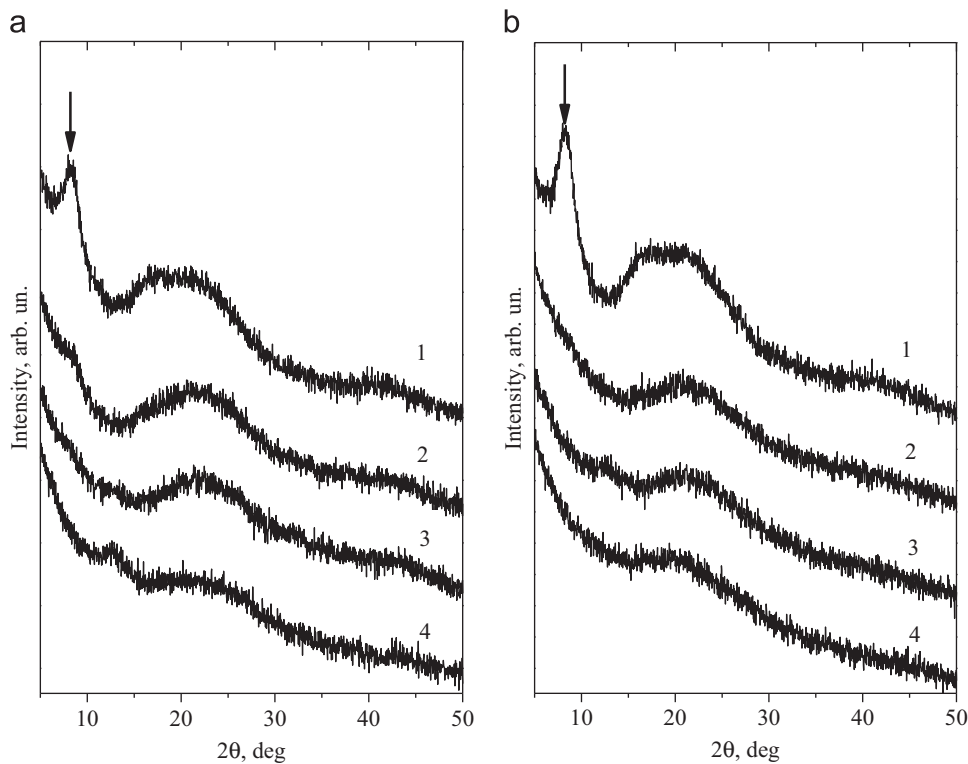
Fig. 5. X-ray diffraction patterns of the QDs-gelatin composite (a) and pure gelatin (b) films before (curve 1) and after thermal annealing at 100 °C (curve 2), 140 °C (curve 3) and 160 °C (curve 4), $T = 293$ K.

4. Discussion

The results obtained indicate that thermal annealing of the QDs-gelatin composite strongly influences the PL characteristics of the QDs. The annealing changes the PL intensity and produces the redshift of the PL bands. These changes can be caused by structural transformations in the QD ensemble as well as by structural and chemical transformations in gelatin matrix and at QD/gelatin interface.

Specifically, the redshift in the emission and absorption spectra of CdTe and CdSe colloidal QDs upon surface ligand exchange and thermal annealing has been usually explained by: (i) nanoparticle aggregation and efficient energy transfer from smaller to larger QDs in the ensemble [30,31]; (ii) the extension of exciton wave-function to the outer ligands due to their change [32,33].

We should suppose that the redshift effect is caused not by QD coalescence, but by changes in QD passivating ligands resulting from structural transformations in gelatin matrix. This is proved by partial recovery of the excitonic band position during the storage of thermally treated composite films. In addition, the changes in the absorption spectra of the composite under annealing indicate that the redshift effect is not due to the change of the exciton confinement energy in the QDs. In fact, the absorption edge caused by QD absorption does not shift to the red upon annealing at 100 °C. The changes in the absorption spectra of composite upon annealing at 140–160 °C are apparently caused by the formation of chromophore groups in gelatin matrix. The formation of some functional groups which adsorb and emit within the HOMO–LUMO energy gap of gelatin is proved by the increase of the optical absorption and PL intensity in thermally treated gelatin films.

The chromophore groups appearing in gelatin matrix can be of different nature. Some collagen chromophores that produce fluorescence in the ultraviolet and visible spectral range are supposed to be tyrosine-related [34]; other are identified as pentosidine and pyridinoline and suggested to be the products of cross-linking [35,36]. The collagen fluorescence in the visible spectral range had been proposed to be of excimer nature and attributed to phenylalanine residues [37]. The annealing of gelatin at elevated temperatures stimulates breaking of hydrogen bonds between the macromolecules as well as between the neighboring parts of a macromolecule, splitting of polymer chains and formation of free radicals. The transformation of free radicals, including chain-transfer reactions between free macro-radicals, can give rise to a partial cross-linking of gelatin chains [9,38,22] and formation of carbonyl ($C{=}O$) and carboxyl (–COOH) groups as well as of polyene units, which are known to be quite common absorbing and light-emitting species in polymers [39,40]. The formation of a three-dimensional network by the interchain covalent cross-linking effect had been supposed for thermally treated gelatin films [22]. Thermal cross-linking mechanism was proposed to be a condensation reaction between a carboxyl group and an amine group of adjacent gelatin chains with excessive dehydration [22]. It can be supposed that some of these processes promote passivation of surface defects in the QDs and are responsible for the increase of the PL intensity in the composite annealed at 140 °C. The above mentioned transformations can occur both under annealing at elevated temperatures and during storage of annealed polymer at room temperature. The latter can explain the increase of the PL intensity in the annealed films during their storage in air for months.

The decrease of the PL intensity in the composite film occurring under annealing at 100 °C can be caused by dissociation of coordination bonds between surface Cd atoms and amino-groups of gelatin molecules. We have observed a similar effect in the composite films of CdSe QDs in gelatin matrix upon thermal annealing at 100 °C [25]. The XRD investigations show that the helix to coil transition in the gelatin matrix already occurs at 100 °C. As the result of this transition some of the amino acid strands in gelatin become detached from one another. It is

supposed that these strands become detached from the QD surface too. Recovery of the PL band position and PL intensity during the film storage can be explained by re-bonding of Cd surface atoms with amino-groups of gelatin molecules.

The decrease of the PL intensity in the films subjected to the thermal annealing at 160 °C can be the result of strongly increased visible light absorption in the gelatin matrix (Fig. 1, curve 4). In the composite films annealed at 160 °C, both 470-nm excitation light and the QD-related exciton emission are absorbed by gelatin matrix. In pure gelatin films annealed at 160 °C, the reabsorption of the PL light in gelatin matrix can be responsible not only for the decrease of the PL intensity, but also for the redshift of the PL peak position. Appearance of the films annealed at 160 °C indicates that the films undergo partial melting during thermal treatment. In fact, the temperature of melting transition in gelatin varies from 156 °C [41] to 210 °C [9]. It has been mentioned that in gelatin heated above 140 °C both thermal and thermo-oxidative destruction of gelatin occur [9]. We can suppose that some of these processes promote formation in gelatin matrix of chromophore groups responsible for strongly increased light absorption.

The results of the PL investigations of thermally treated composite films show that the annealing at higher temperatures (140–160 °C) is more attractive for an improvement of the PL properties of QD-gelatin films. This is due to the fact that the annealing stimulates PL increase owing to improved passivation of surface defects in the QDs. The fact that the spectral shift occurred upon annealing relaxes only partially seems not to be critical for possible biomedical applications because the shift magnitude is found to be a few times smaller than PL band halfwidth and its relaxation occurs during the months. The results of XRD investigations show that thermal annealing in the whole temperature range stimulates dehydration of gelatinous matrix that should decrease solubility of gelatin in aqueous solutions and make it suitable for biomedical application. However, the higher the annealing temperature, the more brittle the gelatin films become. Moreover, the annealing at 160 °C promotes melting of gelatin and so it seems to be undesirable for the processing of QD-gelatin composite. Therefore, thermal annealing at 140 °C is supposed to be more attractive for improvement of PL and structural properties of the QD-gelatin films.

5. Conclusion

PL, optical absorption spectra and the XRD patterns of CdSe QDs-gelatin composite and pure gelatin films as well as their transformation under the thermal annealing in the air at 100–160 °C have been investigated. It is found that PL spectra of the composite under excitation with visible light are dominated by the QD-related PL, while the intensity of the emission from gelatin matrix is strongly reduced. It is shown that the thermal annealing of the composite changes PL intensity and produces the shifting of the PL bands to low energy region. The storage of the annealed films in the atmospheric ambience stimulates partial recovery of the QD-related PL peak position and the increase of the PL intensity. The decrease of the transparency of composite film under annealing is ascribed to the formation of chromophore groups in gelatin matrix. It is supposed that strongly increased visible light absorption in gelatin matrix is responsible for the decrease of the PL intensity in the films annealed at 160 °C. The XRD study shows that the thermal annealing stimulates helix to coil transition in gelatin matrix already at 100 °C. The effect of annealing on the PL spectra of the QDs is supposed to be caused by change of surface defect passivation in the QDs resulting from

structural transformations in gelatin matrix. It is proposed that the thermal annealing of CdSe QDs-gelatin composite at 140 °C can be used for the increase of the QD-related PL intensity.

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