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Enhancement of the photoluminescence in CdSe quantum dot–polyvinyl alcohol composite by light irradiation

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ABSTRACT

The effect of photo-induced enhancement (more than a tenfold) of room temperature deep-trap photoluminescence (PL) in CdSe quantum dots (QDs) embedded in polyvinyl alcohol (PVA) film has been found and investigated by the PL and X-ray diffraction methods. The effect is observed under illumination of the QD/PVA composite with LED's light of 409 or 470 nm at elevated temperatures and is shown to be caused by an increase of the activation energy of thermal quenching of defect-related PL. It is shown that thermal annealing of the composite by itself stimulates polymer crystallization and produces a small increase in the intensity of both the band-edge and defect-related PL bands of CdSe QDs. It is found that the effect of illumination decreases when the annealing temperature increases from 90 °C to 120 °C because thermal annealing at 120 °C per se results in strong enhancement of room temperature deep-trap PL. The effect of photo-induced enhancement of defect-related PL is found to be irreversible and is assumed to be related to the change of QD surface defect passivation or surface defect rearrangement. This is ascribed to partial destruction of PVA matrix as a result of interaction of QD/PVA interface with photocarriers generated in the QDs due to LED's light absorption.

1. Introduction

The development of new low-cost and "green" approaches for a colloidal synthesis of semiconductor quantum dots (QDs) in environment-friendly polymers is highly motivated by their potential application in opto- and photoelectronics, biology, medicine, etc. The polymers with embedded QDs demonstrate novel and distinctive properties owing to combination of the inherent characteristics of polymer matrices (such as easy processability, flexibility, high mechanical strength, etc.) and unique optical and chemical features of the QDs [1]. The latter includes size-tunable spectral properties, high photoluminescence (PL) quantum yield, broad absorption spectrum and narrow exciton emission band, high chemical stability and resistance to photochemical- and metabolic degradation, etc. [1].

It has been reported that the QDs embedded in a conductive polymer can improve its transport properties and increase the efficiency of polymer-based solar cells [1,2] and light-emitting diodes (LEDs) [1,3,4]. Colloidal QD-based LEDs have emerged as a competitive choice in thin film displays with improved color saturation and white lighting with a high color rendering index [4]. Specifically, in the QD-based white LEDs, white emission has been achieved using excitonic [5,6] or deep trap emission in the QDs [7,8]. In the last case an enhancement of the luminescence efficiency is the key problem.

Polyvinyl alcohol (PVA) is a hydrophilic biodegradable, biocompatible, nontoxic, noncarcinogenic polymer. It is used in various pharmaceutical, medical, cosmetic, food and agricultural products [9]. PVA is an optically transparent polymer which is characterized by good chemical resistance and film forming ability [10]. It is also considered as a good host material for metal nanoparticles and semiconductor QDs. PVA-protected Ag [11], Pt [12] and Au [13] nanoparticles as well as ZnO [14], PbS [15], CdS [16] and CdSe [17] QDs have been reported. However, PVA is known to undergo photochemical transformations under γ-quanta or UV-light irradiation [16,18]. This distinctive feature of PVA can affect also the properties of QD/PVA composite [16], since photoluminescent characteristics of QDs, especially quantum yield, are known to be influenced significantly by the extent of a passivation of QD undercoordinated surface atoms by organic ligands as well as by a chemical nature of passivating entities.

Here, we present the results of investigation of the photoluminescence (PL) and structural properties of composite PVA films with

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embedded CdSe QDs. The enhancement of deep-trap photoluminescence in the QDs under illumination of a composite film at elevated temperatures is demonstrated and discussed in details.

2. Experimental details

The QDs studied were produced by the reaction of cadmium chloride and sodium selenosulfate in aqueous solution of gelatin [19] and then transferred to PVA. The reagents purchased from Aldrich were used. The procedure applied for QD synthesis is of low cost approach that requires comparatively mild conditions and relatively low-toxic Cd(II) and Se(II) precursors. After the dialysis the QD–gelatin solution was mixed with 20% PVA solution. Hydrochloric acid was added to improve homogeneity of the polymer mixture. The solution was deposited onto glass slides and dried in dark at 15–20 °C for 3–5 days. The QD/PVA composite films were annealed for 5 min at T_{ann} = 90 °C or 120 °C in atmospheric ambience under illumination with the 409-nm or 470-nm light from a light-emitting diodes (LED). Before annealing the films were separated from the glass. To compare the PL transformations in the QD/PVA composite with those in pure PVA, the PVA films were also studied and treated similarly.

The PL spectra were measured in the temperature range of 77–400 K. The PL was excited by a LED's light of 470 nm and recorded using a prism monochromator equipped with a photomultiplier and a lock-in amplifier. X-ray diffraction (XRD) study was realized using a D-8 ADVANCE (Bruker) one-crystal X-ray diffractometer operating with the Cu Kα-radiation.

3. Results

Fig. 1 shows normalized optical absorption spectrum of the QD/PVA composite. A broad band with a maximum at about 2.5 eV and a blurred edge corresponds to optical absorption by CdSe QDs with an average diameter of about 2.3 nm [20]. It is obvious that the QD absorption is responsible for strongly pronounced yellow coloration of the composite film contrary to the colorlessness of the pure PVA film.

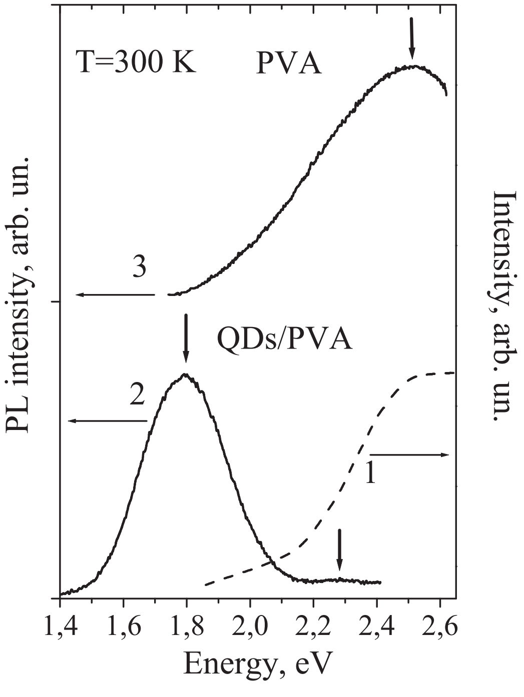

Fig. 1. Normalized optical absorption (1) and PL spectra (2, 3) of the CdSe QD/PVA composite (1, 2) and of pure PVA (3), T = 300 K, λ_{exc} = 470 nm.

The PL spectrum of the QD/PVA composite consists of two bands (Fig. 1, curve 2). The weak band at about 2.26 eV can be ascribed either to exciton radiative recombination or to band-edge PL in the QDs [21], while the intense band at 1.8 eV originates from the radiative recombination of carriers via deep acceptor level created by surface defects of the QDs [22]. A predominant contribution of the deep-trap emission in the PL spectrum of the composite is not surprising for the QDs of small size [21]. However, insufficient passivation of surface defects of the QDs by functional groups of PVA can also be assumed. This assumption is supported by the fact, that a higher contribution of the exciton band in the PL spectrum has been observed by us for the QD/gelatin composite synthesized in the way described in the present work [23].

In the PL spectrum of pure PVA film, a broad band centered near 2.5 eV is observed. The band apparently originates from the functional groups of PVA. The PL from the PVA matrix is found to be strongly quenched in the PL spectrum of the QD/PVA composite under used excitation. This is probably caused by a screening effect of CdSe QDs efficiently absorbing the 470-nm excitation light. Alternatively, the quenching of the PL from polymer matrix in the CdSe QD/polymer composites has been ascribed also to rapid charge transfer [24] or efficient Forster resonant energy transfer [25] from polymers to the QDs.

The investigation of the structural characteristics of the films denotes that the XRD patterns of the QD/PVA composite are dominated by the signals from the PVA matrix only (Fig. 2). In fact, the diffraction patterns of the pure PVA and of the QD/PVA composite show the same diffraction peaks. The most intensive peak is around $2\theta = 19.5°$. This peak is accompanied by a set of the signals of much lower intensity evidently caused by partially crystallized PVA matrix [16]. The peaks from crystalline CdSe phase are not observed that is apparently caused by low QD concentration (less than 1%, w/v). Thermal annealing of the pure PVA and of the QD/PVA composite films increases the intensity of the PVA-related peaks in both cases, indicating the expected increase of the degree of crystallinity of PVA matrix. It is found that the higher is the annealing temperature, the more pronounced are the peaks of crystalline PVA. The illumination of the films during annealing does not affect essentially the XRD patterns in comparison with the effect produced by the annealing per se.

The effect of the annealing on the PL spectra of the QD/PVA composite is shown in Fig. 3. Upon the annealing at T_{ann} = 90 °C in dark, the intensity of the band-edge and defect-related PL bands increases in 1.5–1.7 times at 77 K (Fig. 3a, curve 2) and in 2–3 times at 300 K (Fig. 3b, curve 2). However, if the annealing is carried out under illumination, a significant enhancement of defect-related PL band (more than a tenfold in some samples) is observed in the room temperature PL spectrum (Fig. 3b, curve 3). At the same time, the illumination during annealing does not affect (or affect slightly) the intensities of the band-edge and defect-related PL bands measured at 77 K (Fig. 3a, curve 3) as well as the intensity of the band-edge PL detected at room temperature (Fig. 3b, curve 3). However, the increase of the annealing temperature up to 120 °C decreases the effect of the illumination. In this case thermal treatment by itself produces strong enhancement of room-temperature defect-related PL band, whereas the effect of the illumination is small (Fig. 3c). For pure PVA film, the illumination has no effect on the PL intensity which increases in ∼1.5 times under the annealing either in dark or under illumination irrespectively of the annealing temperature.

Thus, thermal treatment of the QD/PVA composite increases the intensity of both PL bands. The increase of the annealing temperature from 90 °C to 120 °C stimulates mainly a pronounced enhancement of the room temperature deep-trap PL. The same effect is achieved under illumination during the annealing at

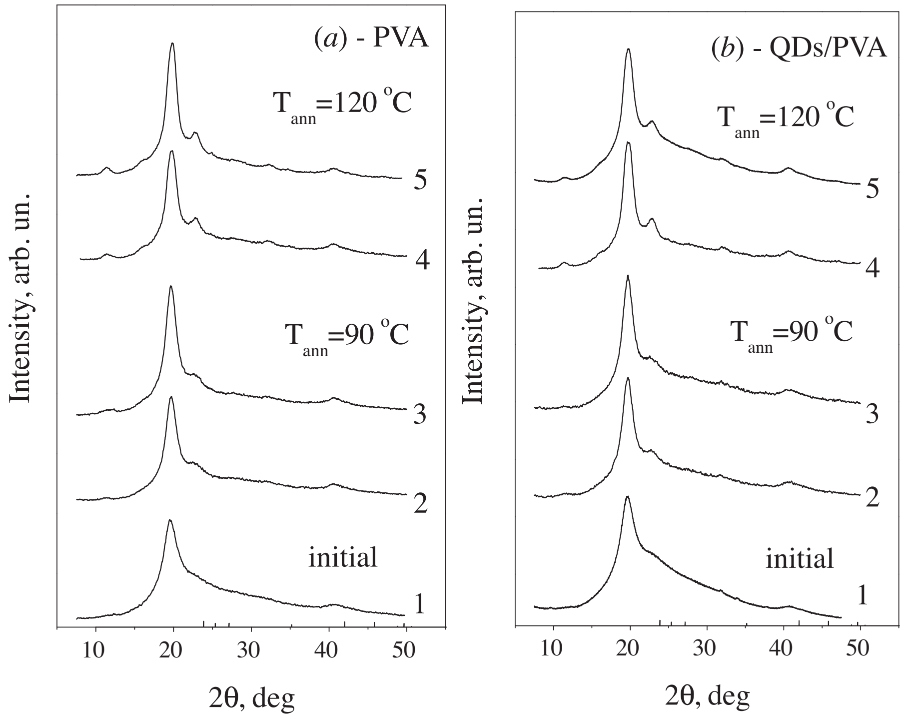

Fig. 2. X-ray diffraction patterns of pure PVA film (a) and the CdSe QDs in PVA matrix (b) before (1) and after annealing at 90 °C (2, 3) and 120 °C (4, 5) in dark (2, 4) and under illumination with LED's light of 409 nm (3, 5). The curves are shifted in vertical direction for clarity. The lines indicate the reflections for bulk hexagonal CdSe.

90 °C. The transformation of the PL spectra is found to be irreversible.

In order to have a deeper insight into the nature of the effect of photo-induced enhancement of the deep-trap PL, the temperature dependence of the PL spectrum of the QD/PVA composite was studied in the range of 77–400 K. Fig. 4 shows the Arrhenius plot of defect-related PL band intensity measured in the untreated composite film and in the film annealed at 90 °C under illumination with the light of 470 nm. When the temperature increases from 77 K up to about 300 K the PL intensity decreases, owing to the thermal quenching. However, further temperature rise causes the increase of PL intensity in the non-treated sample. This indicates that the effect of photo-induced PL enhancement in the QD/PVA composite starts already at 300 K and occurs also under irradiation by LED's light of 470 nm. This is proved by the kinetics of the PL intensity changes during continuous illumination at room temperature (see inset in the Fig. 4). After the annealing of the composite under illumination, only the quenching of the PL intensity occurs when the temperature elevates from 77 K to 400 K.

Fig. 4 shows that in the temperature range of 250–350 K the Arrhenius plots can be approximated by a linear dependence indicating that the PL intensity, $W(T)$, varies exponentially with

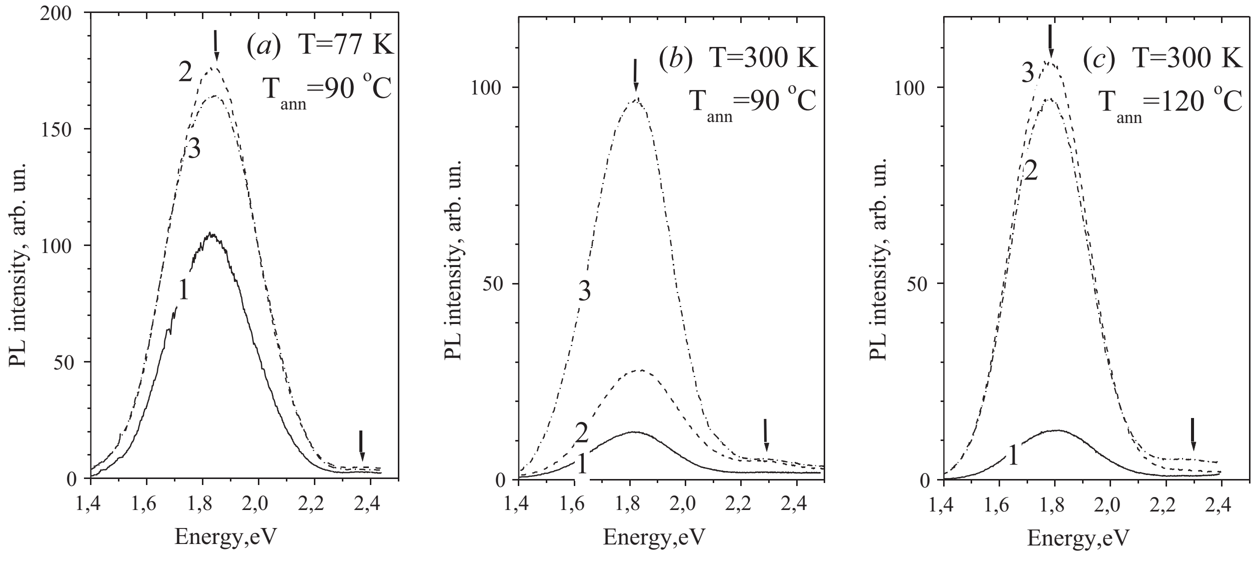

Fig. 3. PL spectra of the CdSe QDs in PVA matrix before (curves 1) and after annealing at 90 °C (a, b) and 120 °C (c) in dark (curves 2) and under illumination by LED's light of 409 nm (curves 3), measured at $T = 77$ K (a) and 300 K (b, c), $\lambda_{exc} = 470$ nm.

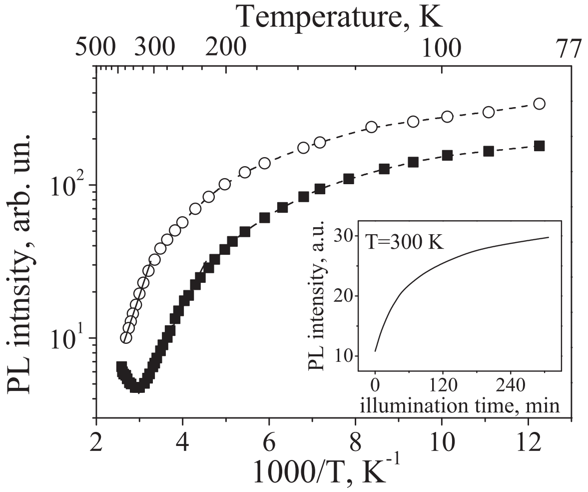

Fig. 4. Temperature dependence of defect-related PL band intensity of the CdSe QDs in PVA matrix before (solid symbols) and after (open symbols) thermal annealing at 90 °C under illumination with LED's light of 409 nm and their approximation by single-exponential dependence (soild lines), $\lambda_{exc} = 470$ nm. Inset: evolution of the defect-related PL band intensity upon illumination with LED's light of 470 nm at 300 K.

temperature T and can be fitted by a single exponential dependence:

$$W(T) = A + B \exp\left(\frac{-E_A}{kT}\right) \quad (1)$$

where A and B are the constants and E_A is the activation energy of PL thermal quenching. It is found that annealing upon illumination increases the activation energy of thermal quenching of the intensity of defect-related PL band in 1.5–2.0 times depending on the sample. For the dependencies presented in Fig. 4 the E_A magnitude increases from 110 meV to 170 meV. These values are close to the E_A values found by us for CdSe QDs embedded in gelatin matrix, as well as to those observed by other authors for colloidal CdS or CdSe QDs embedded in inert matrices [23,26,27].

4. Discussion

The results of both PL and XRD investigations show that thermal annealing of the QD/PVA composite in air increases the PL intensity in the QDs as well as the crystallinity of the PVA matrix. The latter is not surprised since thermal treatment of PVA at elevated temperatures is known to stimulate the breaking of hydrogen bonding between the macromolecules as well as between neighboring parts of a macromolecule and rearrangement of polymer chains [16]. Some polymer chains align parallel, fold together and form ordered regions, thus increasing the degree of polymer crystallinity.

At the same time, thermal annealing of the composite in the air can stimulate an oxidation of the PVA matrix. In the initial stage, the process of polymer destruction is accompanied by breaking of hydrogen bonding, splitting of polymer chains and formation of free radicals. In oxygen-containing atmosphere, a transformation of hydroxyl-groups of PVA into carbonyl groups can be expected. At elevated temperatures various transformations of free radicals, including chain-transfer reactions between free macro-radicals, give rise to a partial cross-linking of polymer chains.

In the QD/PVA composite, the individual functional groups of PVA as well as the fragments of the partially-broken polymer chains can passivate under-coordinated surface atoms of the QDs [13,14,17]. For example, in the CdSe QDs capped with PVA, formation of the chemical complex between the $-C{=}O$ group of PVA matrix and Cd^{2+} ion on the QD surface was proposed [17]. In the QD/PVA composite studied, the increase of the QD photoluminescence intensity both at 77 and 300 K under the annealing in dark can result from improvement of the passivation of non-radiative defects located on the QD surface. It can be supposed that the transformations in PVA structure occurred during oxidation result in a rearrangement of some functional groups or fragments of the polymer chains of PVA matrix and in the enhancement of the passivation of non-radiative defects on the QD surface, producing a PL intensity increase.

The effect of photo-induced enhancement of room temperature deep-trap emission in the QDs is also supposed to be the result of the transformation of functional groups or the fragments of the polymer chains of PVA matrix at the QD/PVA interface. Other possible reasons of photoinduced enhancement of the QD photoluminescence intensity, like passivation of non-radiative surface defect by photo-adsorbed oxygen and/or water molecules [28] or photo-induced recharging of the trapping centers on the QD surface [29], can be ruled out, because these processes should affect mainly the exciton PL in the QDs and they are usually partially reversible. At the same time, in the QD/PVA composite studied, the illumination influences the intensity of defect-related band mainly and the effect is found to be irreversible. Besides, the same effect is also produced by the annealing in dark at higher annealing temperature (at 120 °C). Therefore, it can be supposed that the illumination stimulates the same processes as thermal annealing in the air. However, these transformations are seems to occur not in the whole PVA matrix, but in the regions close to QD/PVA interface only. This is proved by the fact, that illumination has no additional effect on the PL spectra of pure PVA or on the crystallinity of PVA matrix. The latter is not surprised since photo-induced transformations in PVA are usualy observed under illumination with UV-light, which is strongly absorbed by PVA [18].

The role of light illumination in this effect can be understood as follows. In the QD/PVA composite the LED's light is absorbed by CdSe QDs mainly. The photocarriers generated in the QDs can initiate various secondary radical processes at the QD/PVA interface [16] resulting in destructive transformations of PVA. In a similar way, in [30] an enhancement of the photooxidation process in PVA in the presence of collagen was explained by the absorption of UV-light by chromophores in collagen and the energy transfer to PVA molecules. Therefore, we can suppose that photocarriers generated in the QDs promote formation of free radicals and their secondary reactions in PVA matrix, most likely near the QD/PVA interface. Photo-induced transformations of PVA polymer chains stimulate reconstruction of the ligands at the QD/PVA interface.

We find that under illumination the activation energy of thermal quenching of the deep-trap emission increases, while that of the band-edge PL does not change. Therefore, we can suppose that thermal quenching of defect-related band in the temperature range of 250–350 K is determined rather by thermal escape of a carrier (a hole seemingly) from the deep acceptor level of radiative defect to the level of non-radiative defect than by thermal escape of a carrier from the QD. These defects are obviously located on the surface of QD in close spatial proximity. Upon illumination of the QD/PVA composite at elevated temperatures, the height of potential barrier for carrier escape increases. This can be caused by a change of the energy position of the level of non-radiative defect or by variation of the type of a non-radiative defect, participating in the thermal quenching of defect-related PL. In both cases, the transformation of passivating ligands on the QD surface is assumed to occur.

5. Conclusions

The effect of annealing at 90 °C and 120 °C under illumination with blue LED's light on the PL and structural properties of polymer films of PVA with embedded CdSe quantum dots is investigated. X-ray diffraction study revealed that annealing increases a degree of crystallinity of PVA matrix, while the illumination has no noticeable effect on it. In the PL spectra, measured both at low and room temperatures, the annealing is found to result in the increase of the intensity of both the band-edge and defect-related PL bands in 1.5–3.0 times. The annealing at 90 °C under illumination is found to enhance significantly (more than a tenfold) the intensity of room temperature defect-related PL. The same effect is also produced by the annealing in dark at 120 °C. It is shown that the effect of photo-induced enhancement of defect-related PL is caused by the increasing of the activation energy of the PL thermal quenching. The effects of PL increase are found to be irreversible and ascribed to the improvement of QD surface defect passivation by functional groups or the fragments of the polymer chains of PVA matrix as well as to the surface defect rearrangement.

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