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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.

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 cytotoxic 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 properties 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 $\pm$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 photomultiplier 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

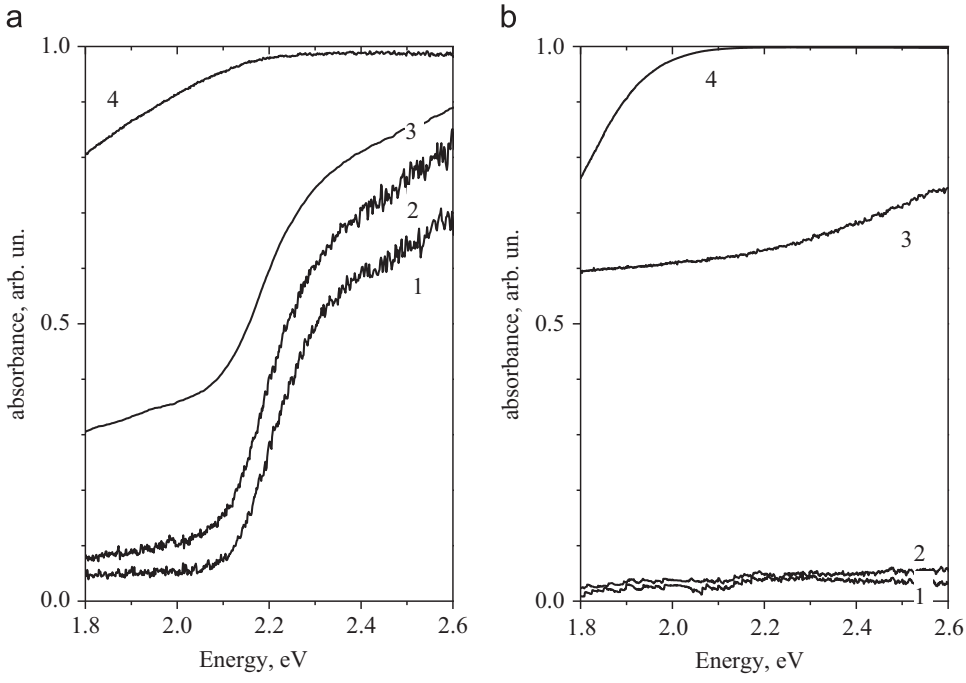

Fig. 1. Optical absorption spectra of the QDs-gelatin composite (a) and pure gelatin (b) films before (curve 1) and after thermal annealing at 100 °C (curve 2), 140 °C (curve 3) and 160 °C (curve 4), T=293 K.