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Optical memory based on photo-activated fluorescence of core/shell CdSe/CdS quantum dots embedded in poly(butylmethacrylate)

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ABSTRACT

This work presents the observation of a photo-activated fluorescence from core/shell quantum dots of CdSe/CdS incorporated in a poly(butylmethacrylate) matrix. Upon illumination with UV-light, the intensity of fluorescence from the quantum dots increases as seen by naked eyes at ambient conditions. This allows its utilization in optical memory media based on thin films of CdSe/CdS polymer nanocomposites suitable for practical application. The quantum dots are synthesized by the hot-injection method and embedded in poly(butylmethacrylate) matrix by radical polymerization with 1,1′-azobis-(cyclohexanecarbonitrile). The fluorescence of quantum dots quenched during the polymerization process, but appeared again after illumination of the nanocomposite material with UV-light. The fluorescence properties of quantum dots are governed by the presence of trioctylphosphine oxide in the matrix, which allows control of the optical memory effect.

1. Introduction

Semiconductor nanocrystals, known as quantum dots (QDs) possess unique optical properties due to the so-called quantum confinement effect [1–3] and hence find many important practical applications [4–6]. That is why, a wide variety of synthesis methods for QDs have been developed. Although the water-based syntheses [7,8] are relatively fast and simple the hot-matrix syntheses in organic solvents produce QDs of higher quality [9–12] as the one utilized by us here. QDs have been incorporated in various polymers [13–16], glasses [17–20] and organic semiconductors [5,21] in order to prepare nanocomposite materials with novel properties.

This paper presents the preparation of a nanocomposite material of core/shell CdSe/CdS QDs and polybutylmethacrylate (PBMA) by means of radical polymerization. It was found that this nanocomposite material possesses the so-called photo-activated fluorescence—an interesting phenomenon, which can be utilized in optical memory devices. Similar memory based on simple CdSe QDs deposited as a dry thin film on substrate has been previously described [22]. However, it is demonstrated here that the utilization of CdSe/CdS-PBMA nanocomposite material as optical memory media could be much more efficient by offering higher reproducibility, better mechanical properties, longer durability of information storage and much higher signal-to-noise ratio. The effect of trioctylphosphine oxide (TOPO) on the fluorescence of QDs is studied during the polymerization process by means of controlling the optical memory effect.

2. Experimental section

2.1. Chemicals

Cadmium oxide (CdO, 99%), sulfur (S, purum, 99.5%), Rhodamine 6G (for fluorescence) and pulverized selenium (Se, pure, 99.5%) were from Fluka. Tributylphosphine (TBP, 97%) was from Aldrich. Liquid paraffin and stearic acid were from RA.M.Oil SpA (Italy) and Hatkim SA (Turkey), respectively. Chloroform was of analytical reagent grade from Labscan Ltd. (Ireland). Toluene, chloroform, methanol and acetone were purified by distillation. All other chemicals and solvents were used as received, without additional purification. Tributylphosphine sulfide (TBP-S) solution (0.125 M) was prepared by reaction of sulfur (40 mg, 1.25 mmol) and TBP (0.34 ml, 1.35 mmol), and then dilution with liquid paraffin (10 ml). Tributylphosphine selenide (TBP-Se) solution (0.125 M) was prepared by dissolving selenium (100 mg) powder in TBP (0.5 ml) and then diluted with liquid paraffin (9.5 ml). Butylmethacrylate monomer and 1,1′-azobis-(cyclohexanecarbonitrile) were from Fluka.

2.2. Synthesis of quantum dots

For a typical preparation of CdSe cores, a mixture of CdO (50 mg, 0.39 mmol), stearic acid (0.600 g, 2.1 mmol) and liquid paraffin (15 ml) were heated up to ~260 °C. A solution of tributylphosphine selenide, TBP-Se (1.0 ml, 0.125 M), was then fast injected into the reaction solution [12]. The reaction solution was then cooled down by dissolving it in cold toluene (70 ml) 20 s after the injection of TBP-Se. The obtained

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QDs were purified by standard procedures [10]. For the deposition of CdS shells, CdO (50 mg) was dissolved in a mixture of stearic acid (600 mg) and liquid paraffin (5 ml) at 180 °C in open air and then cooled down to 120 °C. CdSe cores, obtained from the synthesis above, were transferred into the mixture. Tributylphosphine sulfide (TBP-S) solution (2 ml; 0.125 M) was injected at 100 °C and the reaction temperature was raised up to 250 °C within 8–10 min. The obtained CdSe/CdS QDs were purified [10] and dissolved in chloroform (10 ml). Before usage, the dispersion was heated to obtain clear dispersion. The obtained core/shell QDs possessed red-shifted absorbance and fluorescence spectra in comparison with the initial CdSe core QDs, which were considered as evidence for the successful growth of CdS shell, as previously described [12].

2.3. *Characterization of QDs*

The absorbance spectra of quantum dot dispersions in organic solvent were measured by Jenway 6400 spectrophotometer. The fluorescence spectra were measured by Carl-Zeiss monochromator, equipped with a photomultiplying tube (the samples were excited with UV-light of $\lambda = 370$ nm). Quartz cuvettes were utilized in both absorbance and emission measurements. The nanocrystals were imaged by a transmission electron microscope (TEM) JEM-2100F (JEOL) operated at 200 kV of acceleration voltage. The chemical composition of nanoparticles was analyzed by the EDS (energy dispersive spectroscopy) microprobe of the microscope. X-Ray diffraction (XRD) spectra were recorded at room temperature on a powder diffractometer (Siemens D500 with CuKα radiation within 2θ range 10–80 deg and step 0.05 deg 2θ and counting time 2 s/step).

2.4. *Preparation and optical properties of QD-poly(butylmethacrylate) nanocomposites*

The QD-polymer nanocomposites were prepared in the following way. Butylmethacrylate monomer (Fluka) was polymerized by radical polymerization; the monomer was used as received without further purification. 1,1′-Azobis-(cyclohexanecarbonitrile) (Fluka, >97%) was used as a radical initiator in concentration 1.8 mg ml^{-1}. The samples were polymerized at uniform conditions: sealed in Eppendorf tubes and heated for maximum 2 h in a boiling water bath. For the purpose, 0.5 ml of QDs in chloroform (prepared as described above) was dispersed by ultrasonication for 30 min in butylmethacrylate monomer (24 ml) until optically clear dispersion was obtained. A total amount of 44 mg initiator was dissolved in the so obtained dispersion and the resulting dispersion was divided in two equal parts. TOPO (440 mg) was dissolved into the first part to obtain TOPO-coated QDs (denoted as TOPO-QDs), and the second part of the dispersion of stearate-coated QDs (denoted as St-QDs) was left as a control. The obtained dispersions of QDs were sealed into Eppendorf tubes and were put into boiling water to be polymerized. Samples of TOPO-QDs and St-QDs in PBMA (both polymerized for 2 h) were illuminated with UV-light (Hg-lump; maximum emission at 370 nm; light power density at the sample position 2.5 mW cm^{-2}) for maximum 120 h at room temperature. The respective control samples were kept on ambient light. Fluorescence spectra of the UV-illuminated and the control samples are measured at regular time intervals. The light radiation of the UV-source was measured with Research Radiometer (Ealing Electro-optics, Inc.).

2.5. *Preparation of QD-polymer films for optical memory*

In order to prepare a material suitable for an optical memory device the QDs were embedded into PBMA films in the presence of TOPO. QDs were embedded in PBMA film (about 1 mm thick) formed by radical polymerization in the presence of TOPO at 100 °C for 2 h. A mask was then put over the QD-PBMA film and illuminated with UV-light for 12 h, a time interval necessary to observe intensive photo-activated fluorescence from the illuminated regions of the film.

3. Results and discussion

Core/shell QDs of CdSe/CdS with an average total size of 4.3 nm were used in all the experiments (TEM image of the QDs is given in supplementary material). The QDs could be dispersed well in butylmethacrylate monomer upon ultrasonication and remained luminescent. In all the cases optically clear polymer nanocomposites were formed after 2 h of polymerization, however, the fluorescence of QDs dramatically decreased during the polymerization process, especially if TOPO is added (Fig. 1). The decrease in fluorescence intensity is represented with the relative integrated fluorescence intensity (PL/PL$_0$). The integrated fluorescence of each sample (PL) is divided by the integrated fluorescence of the initial sample (before polymerization or before photo-activation, respectively) (PL$_0$) (the respective absorbance spectra of the samples before and after polymerization are given in supplementary material). We suppose that the fluorescence quenching during polymerization results from the introduction of defects on the nanocrystals surface. Such defects can be centers for non-radiative relaxation of the excited state thus leading to fluorescence quenching. It is interesting to observe that the addition of TOPO facilitates the fluorescence quenching. Most probably, TOPO molecules stabilize (by coordination) Cd(II) ions rather than QDs in the polymerizing medium. It means that TOPO is not a suitable surface capping agent for the investigated conditions, if one desires effective surface protection of QDs. However, utilizing TOPO in this case may be useful to prepare nanocomposite materials, exhibiting optical memory.

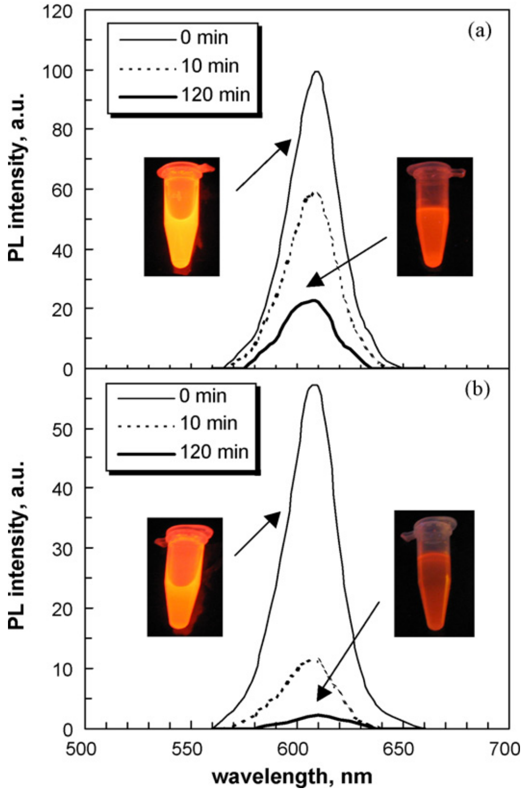

Fig. 1. Changes in the fluorescence spectra during butylmethacrylate polymerization in the cases of (a) St-QDs and (b) TOPO-QDs. All fluorescence spectra were measured at constant conditions.

If illuminated with UV-light, the fluorescence of both St-QDs and TOPO-QDs in PBMA was increasing (Fig. 2). In the case of TOPO-QDs in PBMA, the increase in fluorescence intensity was much more pronounced and accompanied by significant blue shifting of the emission maximum (Fig. 2b). The respective absorbance spectra in this case also become blue-shifted after UV-illumination, which corresponds to decrease of the nanoparticle size (dissolution of nanocrystals). Both, the absorbance and fluorescence spectra show broadening of the QDs size distribution after UV-illumination (the respective exciton absorbance and emission bands are broadened). For the case of St-QDs in PBMA these processes are less pronounced. These results indicate that TOPO facilitates the surface destruction of QDs as well as the defocusing of size distribution upon UV-illumination of the nanocomposite material.

The following hypothetical mechanism of photobleaching during polymerization and of photo-activation upon UV-illumination emerges based on the above facts. The initial QDs (before polymerization) are fluorescent, with low concentration of surface defects. During the polymerization process, reactive species (TOPO, radi-