

Anisotropic absorption of the nanostructured material of CdSe/ZnS quantum rods embedded in polymer film

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Abstract

An approach to achieving of spatially homogeneous, ordered ensemble of semiconductor quantum rods in polymer film of polyvinyl butyral is reported. The CdSe/ZnS quantum rods are embedded to the polymer film. Obtained film is stretched up to four times to its initial length. A concentration of quantum rods in the samples is around 2×10^{-5} M. The absorption spectra, obtained in the light with orthogonal polarization, confirm the occurrence of spatial ordering in a quantum rod ensemble. Anisotropy of the optical properties in the ordered quantum rod ensemble is examined. The presented method can be used as a low-cost solution for preparing the nanostructured materials with anisotropic properties and high concentration of nanocrystals.

1. Introduction

Nanostructured materials, consisting of colloidal semiconductor nanocrystals, can be considered as a lowcost solution for various applications of photonics such as photovoltaic (Emin *et. al.* 2011) and thinfilm devices (Baker *et. al.* 2010), sources of polarized light (Wu *et. al.* 2010), light emission diodes (Anikeeva *et. al.* 2009), among others. A number of nanostructured and functional materials grows rapidly due to recent advances in the technologies of colloidal synthesis that allow controlling of optical, mechanical, electrical, magnetic, catalytic, and electronic properties of material.

The optical properties of semiconductor nanostructured material may be

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manipulated by a variation size (de Mello Donega *et. al.* 2009) and shape (Peng *et. al.* 2000) of its constituent nanoparticles. In particular, the shape anisotropy of CdSe Quantum Rods (QRs) leads to the anisotropy of its optical properties. It was calculated for the quantum rods with an aspect ratio greater than ca. 1.3 (Hu *et. al.* 2002) that the first electronic transition is polarized along the long axis of nanocrystals (Hu *et. al.* 2002), and the high energy transitions have components with orthogonal polarization (Li and Wang 2003). Experimental evidences of absorption (Kamal *et. al.* 2012) and photoluminescence (Chen *et. al.* 2001, Chen *et. al.* 2002, Artemyev *et. al.* 2003) anisotropy were obtained too, but only for the QR first electronic transition.

For all of the benefits nanostructured materials offer, their building blocks, colloidal nanocrystals, exhibit complex interaction between themselves, with matrix or substrate, that makes difficult to manipulate of nanocrystals and form the periodically ordered ensemble. There is a variety of approaches to nanocrystals ordering such as lithography techniques (Tamborra *et. al.* 2007), biomimetic (Dutta and Hofmann 2003), template- (Yin *et. al.* 2001) and matrix-assisted (Wu *et. al.* 2010, Mukhina *et. al.* 2012) approaches.

The nanocrystal-matrix interface and the morphology of the nanostructured material determine the degree of nanocrystals ordering in the matrix-assisted approach. Modification of the nanocrystal's surface with different types of solubilizers is required in most cases to achieve a good morphology of material (Mukhina *et. al.* 2012). However, chemical affinity of the material components allows to use blending without the nanocrystal's surface modification. In particular, Poly (Vinyl Butyral) (PVB) exhibits a good chemical compatibility with CdSe/ZnS quantum dots capped with Trioctylphosphine Oxide (TOPO) (Kagan *et. al.* 1996), so, the using of the PVB matrix is an effective way of the CdSe/ZnS nanocrystals ordering.

The well known matrix-assisted method to achieve macroscopic ordering in a particles ensemble is an ordering in the stretched polymer film. This approach was effectively used for ordering of dye molecules (Thulstrup *et. al.* 1970), liquid crystal molecules (Aoyama *et. al.* 1981) or iodine aggregates in PVB polarizer (Schuler 1979).

In this paper we use a modification of the method of a nanoparticles ordering in the stretched polymer film to obtain a CdSe/ZnS quantum rod ensemble with anisotropic optical properties, embedded to the PVB film.

2. Experimental section

In this study we used semiconductor core/shell CdSe/ZnS quantum rods. The rods had a diameter of 5 nm with an average aspect ratio of ~ 7 and exhibit a photoluminescence band with a peak emission at 645 nm. Nanocrystal's surfaces were capped by TOPO.

Nanostructured material was prepared by embedding the CdSe/ZnS QRs in PVB film. The solution of Polyvinyl Butyral (PVB) in tetrahydrofuran was mixed with the QR solution in tetrahydrofuran in a volume ratio of 1:3. To achieve an elastic polymer film dibutyl phthalate of 3% by volume was added to the mixture as a plasticizer. Afterwards a casting of the mixture of QRs, PVB and dibutyl phthalate on polyethylene substrate was used to obtain samples of film. A low adhesion of PVB film to the polyethylene substrate allowed to remove the samples from the substrates after a solvent

evaporation. The removed samples were stretched up to four times its original length to achieve a QR spatial ordering.

The optical characteristics of the samples were obtained using a Lumex Fluorat-02-Panorama spectrofluorimeter. The setup used for the measurements is shown in the schematic diagram in Figure 1. Transmission spectra in the vertically and horizontally polarized light was measured with a polaroid to estimate the degree of QR ordering. Depolarization of the excitation radiation and the radiation, transmitted through the sample, was carried out with an optical fiber for prevention of the instrumental effects related to a partial polarization of the light passing through a monochromator. A Zeiss LSM 710 confocal laser scanning luminescent microscope was used for characterization of the microstructure of the nanostructured material. Sample microstructure homogeneity was tested by an analysis of the QR luminescence microscopy images at 645 nm, obtained with 405 nm excitation from diode laser.

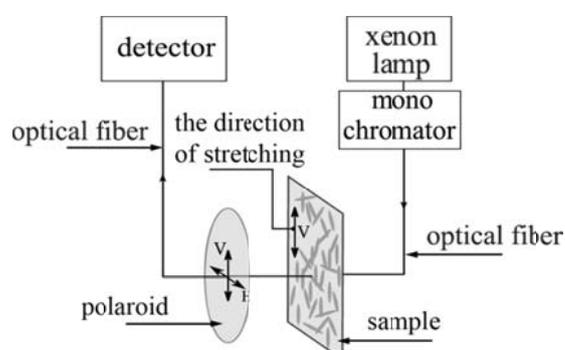


Fig. 1 Schematic diagram of experimental setup for absorption measurements.

3. Results and Discussion

To demonstrate the possibility of the stretched polymer induced ordering of the QRs, the nanocrystals were embedded in the PVB film. The samples of nanostructured polymer material were obtained by blending of the components in solution. Modification of the QR's surface was not required due to the chemical affinity of TOPO, a solubilizer of the QRs, and PVB, polymer matrix. Absorption spectra of the QRs both in tetrahydrofuran solution and embedded in the PVB film are shown in Figure 2. No significant spectral shift of the QR absorption band in the film, as compared with the solution, indicates that embedding of nanocrystals in the PVB film does not change their optical characteristics. The QR concentration in the film was to be calculated as 2×10^{-5} M.

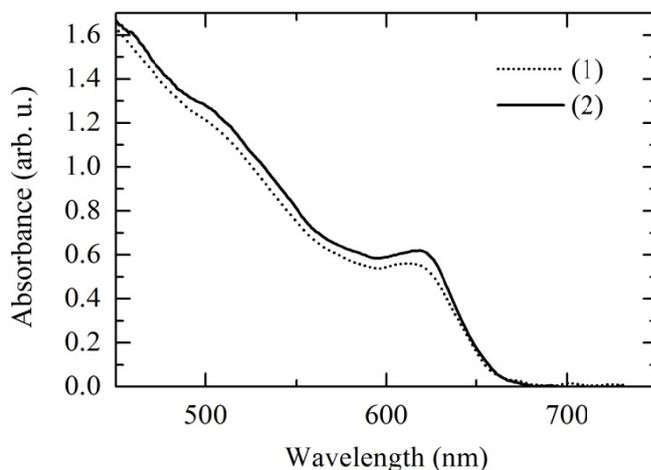


Fig. 2 Absorption spectra of the QRs in tetrahydrofuran solution (1) and embedded in PVB film (2), the spectrum of QR in solution was multiplied by 25.

Luminescence microscopy images of the QRs embedded in the PVB film shown in Figure 3 were recorded to examine homogeneity of the obtained material. The Figure demonstrates an absence of the QR aggregates. The observed spatial homogeneity of the polymer film with embedded QRs allows to use PVB as a matrix in the matrix-assisted approach to ordering of nanocrystals.

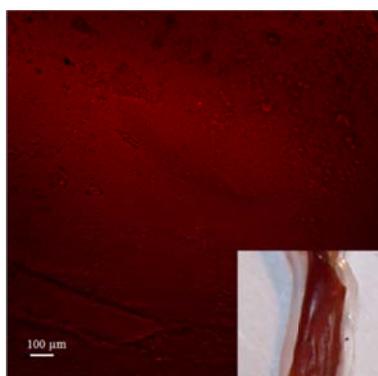


Fig. 3 2D luminescent confocal microscopy images of the QRs embedded in the PVB film. The excitation/registration wavelengths are 405/645 nm. Space bar is shown. The inset depicts photography of the sample of film.

To estimate the degree of the QR ordering in the PVB film stretched up to four times its initial length, the absorption spectra of the QRs embedded in the stretched PVB film were measured in polarized light. Figure 4 shows the components of absorption spectra, which were obtained in the light polarized parallel and perpendicular to the direction of the sample stretching.

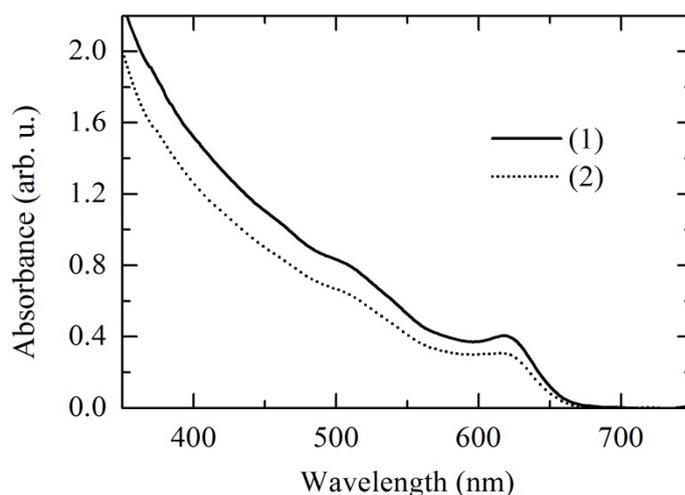


Fig. 4 Absorption spectra of the QRs embedded in the stretched PVB film: (1) component polarized parallel to the direction of stretching; (2) component polarized perpendicular to the direction of stretching.

The degree of absorption anisotropy

$$P = \frac{(D_{\parallel} - D_{\perp})}{(D_{\parallel} + D_{\perp})} \quad (1)$$

is calculated using the absorption spectra shown in Figure 4, where D_{\parallel} and D_{\perp} are the components of absorbance with the polarization direction that are parallel and perpendicular to the direction of the sample stretching, respectively. The degree of absorption anisotropy for the first electronic transition was calculated to be 16-25 %.

4. Conclusions

The samples of the nanostructured material with a high concentration of the QRs, viz. 2×10^{-5} M, were obtained using the matrix-assisted approach for embedding the CdSe/ZnS QRs in the PVB film. An absence of nanocrystals aggregates, confirmed by the confocal luminescent microscopy method, indicates a relatively high spatial homogeneity of a QR ensemble. The stretching of polymer matrix was used to estimate possibility of the QRs ordering in the PVB film. Anisotropy of the optical properties of the ordered QR ensemble, which was obtained in the stretched PVB film, was examined by a method of absorption spectroscopy. The degree of absorption anisotropy was calculated to be 16-25 % for several samples of the material. Such a high degree of spatial ordering of an QR ensemble in the stretched PVB film let us considered the obtained nanostructured material as a good solution for a variety of photonics applications as well as a useful instrument for investigation of anisotropy of the optical properties of the colloidal semiconductor nanocrystals.

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