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CdSe Quantum Dots and SBMA/CdSe Nanocomposites Characterization by Optical and 2D DOSY NMR Methods

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Abstract We present experimental results on preparation and characterization of colloidal CdSe quantum dots (QDs) and polymer nanocomposite based on them. CdSe QDs were characterized by UV absorbance and visible photoluminescence (PL) spectroscopy as well as 2D DOSY NMR. The average CdSe particles size estimated from the UV-Vis absorption spectra was found to be in good correlation with results obtained from NMR measurements. Nanocomposite thin films were prepared on the base of styrene with butylmethacrilate copolymer (SBMA) (1:1). CdSe QDs were successfully incorporated into the SBMA copolymer matrix and thin films of CdSe/SBMA nanocomposites were characterized by UV-Vis and PL spectroscopy.

Keywords CdSe Nanocrystals, Quantum Dots, 2D DOSY NMR, Photoluminescence

1. Introduction

Colloidal luminescent CdSe quantum dots (QDs) remain the subject of great interest both for fundamental research and industrial development. Extensive research efforts have been developed over the last years on preparation and characterization of CdSe QDs because of their various applications in photonics, optoelectronics, medicine, etc., specifically for preparation of nanocomposite (NC) materials [1-3]. Application of CdSe QDs for preparation of polymer nanocomposites makes it possible to obtain materials with advanced properties for practical applications. In polymer nanocomposite the polymer is used both as a matrix, as well as passivation material for stabilization of CdSe nanoparticles properties.

The great advantage of QDs is the possibility they offer for tuning of their properties by varying the size of nanoparticles. The size of QDs can be easily controlled by different ways, for example by variation of the reaction time, or the temperature of the solvents, by variation of the concentration of the reaction compounds in solvents, etc. This gives a relatively simply and convenient technology for controlling the optical parameters of the nanocomposite structures for practical exploitation. For example, PL emission from colloidal CdSe quantum dots can be adjusted in a relatively wide spectral range. The technology makes it possible to prepare different sized nanocrystals with high PL efficiency and narrow PL band, while PL emission may cover a narrow spectral band, tuned from blue to read and even up to near infrared.

In this paper we present experimental results on preparation of colloidal CdSe QDs and their characterization by optical spectroscopy methods as well as by two-dimensional diffusion ordered NMR spectroscopy (2D DOSY NMR). The technology for synthesis of colloidal CdSe QDs was modified for preparation of SBMA copolymer nanocomposite based on them. The QDs have been incorporated into the copolymer matrix and the nanocomposite thin films were characterized by UV-Vis and PL spectroscopy. The mechanisms of PL emission and excited carries transport are discussed.

2. Preparation Details

2.1. Materials

Cadmium oxide (99.999%), oleic acid (90%), selenium (99.5%, 100 mesh), trioctylphosphine (90%), 1-octadecene (90%), tributylphosphine (90%), were purchased from Aldrich and used without further purification.

2.2. Synthesis

CdSe semiconductor nanocrystals were synthesized in a three-neck flask equipped with condenser, magnetic stirrer, thermocouple, and heating mantle. At the first step the stock solution was prepared: 180 mg of Se powder, 3 mL of

1-octadecene (ODE), 2 mL tributylphosphine (TBP) and 0.8 mL of trioctylphosphine (TOP) were mixed by intense stirring.

The Cd precursor solution was prepared from 80 mg of CdO powder, 3 mL of 1-octadecene, 1 mL of TBP and 4 mL of oleic acid. These compositions were mixed together by vigorous stirring. The precursor solution was heated up from the room temperature up to ~ 220°C for complete dissolving of CdO, which was determined visually. Then at the temperature 90°C 2 mL of the stock solution was quickly injected into the hot Cd precursor solution and then this mixture was kept at 90°C. Different-sized QDs were obtained by varying the reaction time. For obtaining the desired size of quantum dots the colloidal quantum dots solutions were collected at determined reaction time intervals (~ 90″) after the injection. Extracted sample solutions were further introduced in chloroform solvent for preserving and further investigations. The CdSe QDs were isolated and purified by adding acetone to the cooled solutions followed by centrifugation at 8000 rpm for about 30 min.

In order to prepare the polymer nanocomposites, the SBMA copolymer and CdSe QDs were separately dissolved in toluene solvent, to obtain the solutions with the density ρ = 111 mg/mL and ρ = 25 mg/mL, respectively. These solutions were mixed together in the proportion 1:1 by vigorous stirring. The nanocomposites thin films were prepared on glass substrates by spin-coating method at 800 rpm and dried out at 40°C.

3. Characterization Methods

CdSe nanoparticles have been characterized by UV-Vis absorption and photoluminescent spectroscopy as well as by 2D diffusion ordered NMR spectroscopy. The average CdSe particles size for three selected samples was estimated from the position of the first excitonic peak in the UV-Vis absorption spectrum as well as from experimental data on 2D DOSY NMR. PL spectra were measured under excitation of a laser beam 405 nm using a MDR-23 monochromator and a photon counting module H9319-12 connected to a PC.

The principle of operation of diffusion ordered nuclear magnetic resonance spectroscopy is described in details in many sources [6-8]. It was demonstrated by NMR measurements that even after multiple centrifugations and washing of colloidal solution of CdSe nanoparticles in organic solvent, there is a remaining of molecular film of oleic acid on the surface of the nanoparticles. This is applied for determination of the nanoparticles size in the method of high resolution 2D DOSY NMR.

The method is based on separation of the NMR signals of different species according to their diffusion coefficients. It is well known that the character of Brownian motion of the molecules in solutions is determined not only by the temperature and viscosity, but also by the size and shape of these molecules.

In order to obtain the diffusion coefficients of the specific molecules a series of spin echo spectra is measured with different pulsed magnetic field gradient strengths. Subsequent processing of the signal decay gives information on the magnitude of diffusion coefficient. The initial diffusion weighted NMR spectra of DOSY NMR are one-dimensional, while 2D DOSY increases the dimensionality by one. In the case of high resolution 2D DOSY NMR relatively small difference in diffusion coefficient can be resolved [7,8]. Pulsed field gradient NMR spectroscopy can be used to measure translation diffusion of molecules. By use a gradient of magnetic field the molecules can be spatially labeled. If they move after this encoding during the diffusion time (Δ), their new position can be decoded by a second gradient. The measured signal is the integral over the whole sample volume, and NMR signal intensity is attenuated depending on the diffusion time and the gradient parameters (g, δ) according to relation [8]:

$$I = I_0 \exp(-D\gamma^2 g^2 \delta^2 (\Delta - \delta/3)), \quad (1)$$

where I is the observed intensity; I_0 is the reference intensity; D is the diffusion coefficient; γ is the gyromagnetic ratio of the observed nucleus; g is the gradient strength and δ is the length of the gradient.

Experimental measurements on 2D DOSY NMR were carried out with BRUKER Avance III NMR 400 spectrometer at room temperature at the following parameters of the system: gradient calibration 0.5566 G/cm; Z gradient strength 5.57 G/cmA; gradient pulse duration 1 ms; delay for gradient recovery 0.1 ms.

4. Experimental Results and Discussion

Fig. 1 illustrates the absorption spectra of colloidal chloroform solution of the prepared QDs for different particles size. The excitonic absorption peaks appear very clear on each curve, indicating the presence of CdSe QDs.

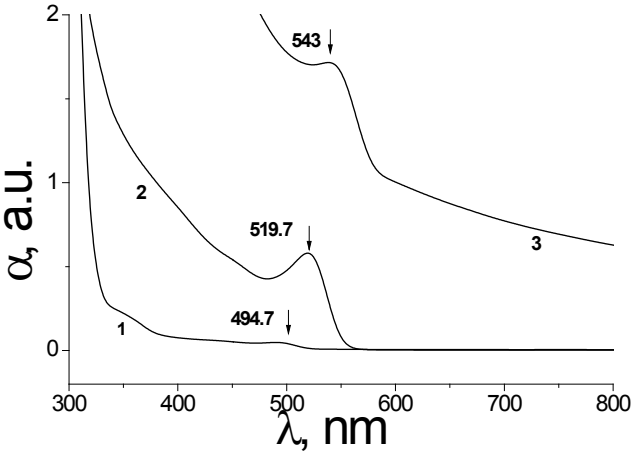

Figure 1. UV-Vis absorption spectra of suspension of CdSe quantum dots in chloroform grown at various reaction times (samples 1-3). The plots 1 - 3 correspond to three dots samples collected at 50 s time interval from the injection. The reaction times, t : (1) t_0 ; (2) t_0 +50 s; (3) t_0 +100 s.