Energy transfer in hybrid systems composed of TPD and CdSe/CdS/ZnS colloidal nanocrystals

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ABSTRACT

We studied the efficiency of energy transfer in systems composed of TPD organic semiconductor and CdSe/CdS/ZnS nanocrystals passivated with different organic ligands. It was demonstrated that increasing the thickness of the nanocrystal capping layer results in reduction of energy transfer rates from TPD to the nanocrystals as well as inter-nanocrystal energy transfer rates. The Förster mechanism was suggested to be responsible for the energy transfer observed.

1. Introduction

Spherical semiconductor colloidal nanocrystals (NCs) were first synthesized in 1993 [1]. These objects attract strong interest as they are a promising material for fabrication of novel photonic and optoelectronic devices. This interest is due to their unique properties such as size-dependent emission wavelength controlled during the synthesis, narrow photoluminescence and the ability to utilize liquid-phase deposition of these nanoparticles [2]. To date, several types of semiconductor-nanocrystal-based devices, e.g. organic light-emitting diodes (OLEDs) [3,4], photovoltaic cells [5], photodetectors [6] and visible tunable lasers [7] have been fabricated.

The standard structure of a light-emitting diode is composed of two electrodes, charge transport layers and an active layer providing radiative recombination of charge carriers. To suppress metal-induced luminescence quenching in the active layer it is necessary to introduce transport layers into the OLED structure.

Active emissive layer of light-emitting diodes with semiconductor nanocrystals as radiative recombination sites is often deposited from a mixture of the nanocrystals and one of the transport materials transferring energy to the nanocrystals [8]. Consequently, the process of energy transfer is one of the factors that governs the efficiency of electroluminescence.

Concentration of the nanocrystals in the transport layer matrix is an essential characteristic that provides high efficiencies and desired spectral characteristics of luminescence. Decreasing the concentration of the nanocrystals leads to decrease of their luminescence intensity. This also leads to inefficient energy transfer from the transport layer molecules to the nanocrystals as the energy transfer occurs only from the molecules located in close vicinity to the nanocrystals. Excessive increase in the nanocrystal concentration is untenable as it leads to deterioration in conductivity of the active layer and increase of the LED's operating voltage reducing the overall efficiency of the device. At high concentrations electronic excitation can be transferred from smaller nanocrystals to larger ones [9] inducing a red shift of the active layer emission spectrum [10].

The present paper is aimed at the investigation of the energy transfer from TPD (N,N′-bis(3-methylphenyl)-N,N′-bis(phenyl)-benzidine) organic fluorescent material acting as a hole transport layer [3,11] to CdSe/CdS/ZnS nanocrystals capped with different ligands. Energy transfer between neighboring nanoparticles is studied as well. One of the main tasks was to determine donor-acceptor energy transfer rates and to establish the mechanism of the transfer.

2. Experimental

CdSe/CdS/ZnS colloidal core/shell/shell nanocrystals with two I-type heterojunctions were synthesized according to the technique analogous to the one described in [12]. The stabilizers we used were ligands with curved and linear structures; namely, oleylamine

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($C_{18}H_{35}NH_2$), with its molecule twisted due to the presence of a double bond, as well as octane-1-thiol ($C_8H_{17}SH$) and dodecanethiol ($C_{12}H_{25}SH$) linear molecules. The nanoparticles coated with octane-1-thiol and dodecanethiol were obtained by replacement of the initial oleylamine ligands. This was achieved through extensive stirring of the initial nanocrystal dispersion in corresponding excessive alkylthiol with subsequent multistage refinement of the nanoparticles by precipitation in alcohols. The described procedures proved to have no effect on the structural properties of the nanocrystals.

The size of the nanoparticles was evaluated on the basis of the transmission electron microscopy image analysis by means of ImageJ software using the method described in [13]. The images were obtained with the use of JEOL JSM-7001F microscope at MIPT's Collective Use Center. Energy transfer was studied for the samples fabricated with the use of a MTI TC100 spin coater, as well as drop-casting of the nanoparticle and TPD solutions onto a precleared glass substrate. The film thickness could be varied from tens of nanometers to one micrometer depending on the deposition technique. The concentrations of TPD molecules and nanocrystals in all solutions were 5 mg/cm^3 and about 10^{15} cm^{-3}, respectively. The concentration of the nanoparticles was evaluated according to the technique described in [14].

Photoluminescence spectra were recorded with the use of an Ocean Optics Maya 2000 Pro spectrometer and 365 nm LED excitation. Absorption and excitation spectra were measured by a Perkin Elmer Lambda 45 spectrophotometer and a SDL spectrometer with a Hamamatsu H6240-01 PMT detector sensitive in the region of 300–850 nm. Photoluminescence decays were obtained with a PicoQuant MicroTime 200 confocal fluorescence microscope with application of time-correlated single photon counting technique. A PicoQuant LDH-375 (375 nm, 3.3 eV) semiconductor pulsed laser with 50 ps pulse duration and 2.5 MHz pulse repetition rate was used as the excitation source. Luminescence signal was registered with a τ-SPAD avalanche photodiode. Interference filters produced by Chroma (USA) were applied to single out the selected luminescence bands. The region of interest (ROI) was 80×80 μm. The measurements were conducted for film samples as well as for solutions of the studied substances in toluene poured into special vials. Laser intensity was kept constant during the scanning at different regions of the samples to provide relevant experimental data.
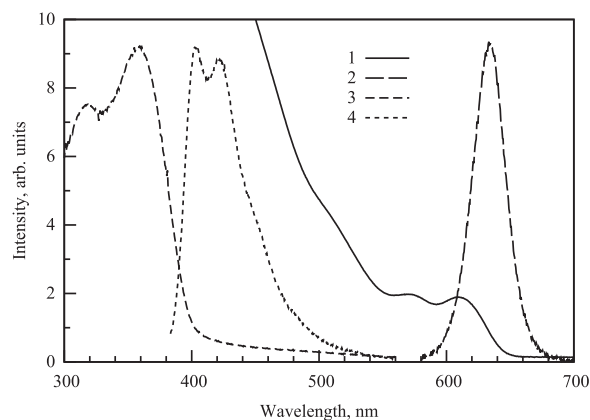

Fig. 2. Absorption and photoluminescence spectra for NC_1 nanocrystal film and TPD film. 1 – nanocrystal absorption, 2 – nanocrystal luminescence, 3 – TPD absorption, 4 – TPD luminescence.

3. Results and discussion

The images of the nanocrystals obtained with the use of a transmission electron microscope are given in Fig. 1; corresponding size distributions are given as well. Nanocrystal average sizes d including the thickness of the passivation layer are 8.1 ± 0.2 nm for NC_1, 8.3 ± 0.2 nm for NC_2 and 9.1 ± 0.2 nm for NC_3. Standard deviation of the nanoparticle size is about 1.3 nm.

Fig. 2 presents absorption and photoluminescence spectra for NC_1 nanocrystal films and a TPD film. The spectra of NC_2 and NC_3 nanocrystals are similar as they differ only by optically passive ligand capping. Emission spectrum of TPD and absorption spectra of the nanocrystals are overlapped. It suggests that both radiative and nonradiative channels of the energy transfer from TPD to the nanoparticles are possible. All nanocrystals under study exhibit Stokes shift of about 50 meV. Considerable width of the luminescence band (107 meV) can be ascribed to the size distribution of the nanoparticles. Optical excitation spectra for NC_1 as well as for the mixture of TPD and NC_1 are given in Fig. 3. The spectra were recorded for the maximum luminescence of the nanoparticles observed at 630 nm. Additional excitation band discovered for the TPD and NC_1 mixture is the evidence of the energy transfer from TPD to the nanocrystals.

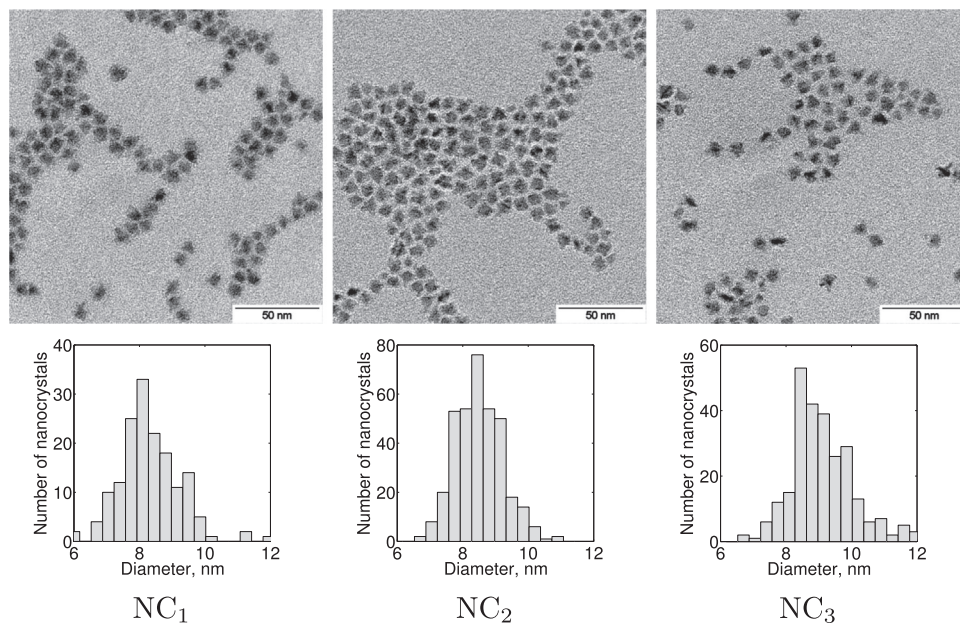Luminescence decays for a neat TPD film as well as for the films

Fig. 1. Microphotographs and size distributions for CdSe/CdS/ZnS nanocrystals with different types of capping ligands. NC_1 – octane-1-thiol-capped nanocrystals with 8.1 ± 0.2 nm average particle size including capping; NC_2 – dodecanethiol-capped nanocrystals with 8.3 ± 0.2 nm average particle size; NC_3 – oleylamine-capped nanocrystals with 9.1 ± 0.2 nm average size.