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Up-converted emission of colloidal nanocrystals containing dendrimers

K. Dou[a,b], Z. Xu[b], X.J. Wang[c,d,*], A. Apblett[b], T. Collins[a]

[a] *Department of Physics Oklahoma State University, Stillwater, OK 74078, USA*
[b] *Department of Chemistry, Oklahoma State University, Stillwater, OK 74078, USA*
[c] *Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics, and Physics, Chinese Academy of Sciences, Changchun 130033, China*
[d] *Department of Physics, Georgia Southern University, Statesboro, GA 30460, USA*

Abstract

The spectroscopic and microscopic investigation of polystyrene nanocrystals containing dodecanamide-modified poly(propyleneimine) dendrimers was performed. Nearly monodisperse colloidal particles have diameters of 60 nm. Up-converted emission in the deep blue around 430 nm was observed upon excitation with lower-energy photons from 480 to 540 nm. The intersystem crossing time constant was estimated to be 11 ps through an up-converted emission measurement.

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Keywords: Nanocrystals; Nanostructured materials; Excited state dynamics; Up-conversion

1. Introduction

There has been increasing interest in photonic crystals known as photonic band-gap materials because they are composed of ordered structures with regular periodicity comparable to the wavelength of an electromagnetic wave [1,2]. Three-dimensional (3D) photonic crystals have been developed for the manipulation of light transmission in visible and infrared range and this will create new aspects for micro- to nano-scale device fabrication and integration with special properties. Significant applications of photonic crystals have been demonstrated in the fields of photon trapping, light-beam bending and light emitting [3–7].

Recently, we reported a spectroscopic and microscopic investigation in polystyrene photonic crystals [8–10]. Emulsion copolymerization of a 2-hydroxyethyl methacrylate (HEMA) with styrene leads to latexes with a spherical structure. The scanning electron microscopic (SEM) images show a monodisperse distribution of the colloidal crystals. Spectral investigation on polystyrene spheres revealed that the size distribution led to a narrow emission in excitation spectra. Up-converted blue emission by yellow light excitation was

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*Corresponding author. Department of Physics, Georgia Southern University, Statesboro, GA 30460, USA. Tel.: +1-912-681-5503; fax: +1-912-681-0471.

E-mail address: xwang@gasou.edu (X.J. Wang).

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also observed. A stop band for this up-converted emission was found to appear at 550 nm.

In this paper, the spectroscopic investigation was performed in 60-nm colloidal polystyrene nanocrystals containing dodecanamide-modified poly(propyleneimine) dendrimers. The transmission electron microscopy (TEM) images show a monodisperse distribution of colloidal particles. Spectral investigation indicated that blue emission resulting from an up-conversion process appeared for a range of excitation wavelengths from 480 to 540 nm.

2. Experimental

The strategy of the method for synthesizing colloidal polystyrene nanocrystals containing poly(propyleneimine) dendrimers is monodisperse dendrimers or dendrimer-surfactant aggregates of low polydispersity as templates for the growth of particles of low polydispersity [11]. Emulsion polymerization led to latexes with a final size of spheres of 60 nm. Colloidal layers were deposited on quartz by vertical-evaporation deposition. Particle sizes were determined using both methods of TEM and dynamic light scattering (DLS). The TEM images were obtained at 80 keV with a JEOL JEM 100 CXII instrument (Tokyo). DLS measurements provided the diffusion coefficients of particles subsequently used to calculate particle sizes.

Spectral measurements of excitation, emission and selective excitation were performed using a Spex Fluorolog F112A fluorometer (0.22 m double grating spectrometer and thermo-electrically cooled R928 PMT detector). Photo-up-converted luminescence spectra were obtained using a dye laser pumped by an excimer laser. Maximum output-pulse energy from the dye laser was 4.0 mJ at a pulse width of 15 ns. The dye laser was tunable over 460–520 nm for Coumarin 102 and over 525–610 nm for Coumarin 153 in methanol solutions. A short pass filter was used to eliminate the effect of laser light on the up-converted emission measurements. All spectra were corrected for instrumental response and all measurements were performed at room temperature.

3. Results

3.1. Spectral measurements

Colloidal nanocrystals of polystyrene with dendrimers (PSD) observed with TEM display a broadband UV and visible photoluminescence upon UV excitation in spectral measurements. Fig. 1 shows emission spectra of PSD nanocrystals at a variety of excitation wavelengths of 280, 320, 350, 380 and 400 nm. A broadband emission excited by both 280 and 320 nm was found peaking around 430 nm. A longer wavelength excitation at 350 nm produces a strong emission with a broadband structure at 430 nm overlapped with 470 nm. Excitation at 400 nm is more efficient and gives rise to the 470 nm band. A multiband structure was found to appear at 378, 399 and 422 nm in the excitation spectra (Fig. 2). The particle-size distribution may be responsible for this broadband emission. The emission spectra in Fig. 1 exhibit two bands at 430 and 470 nm (also seen in Fig. 2(c)) which possibly arise from two types of luminescent centers. The 430-nm emission may be attributed to monodisperse nanocrystals, while the longer wavelength emission at 470 nm may be attributed to a photoaggregate of nanocrystals.

The emission measurements for a variety of select excitation wavelengths are also used to study the up-converted-emission behavior.

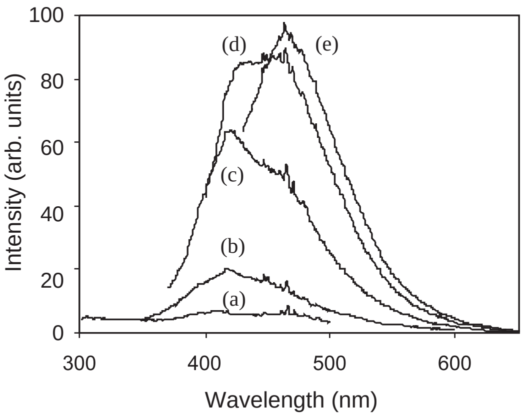

Fig. 1. Emission spectra of polystyrene-dendrimer nanoparticles with a diameter of 60 nm at various excitation wavelengths of (a) 280, (b) 320, (c) 350, (d) 380 and (e) 400 nm.

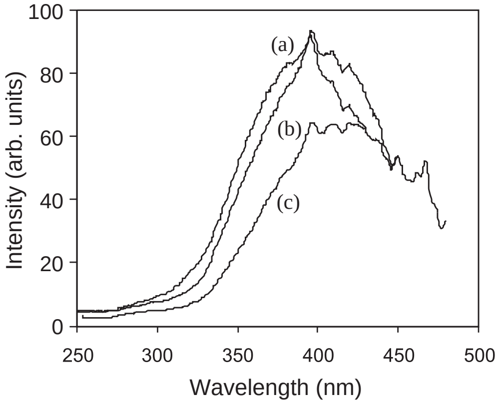

Fig. 2. Excitation spectra of polystyrene-dendrimer nanoparticles with a diameter of 60 nm at different monitoring wavelengths of (a) 450, (b) 470 and (c) 500 nm.

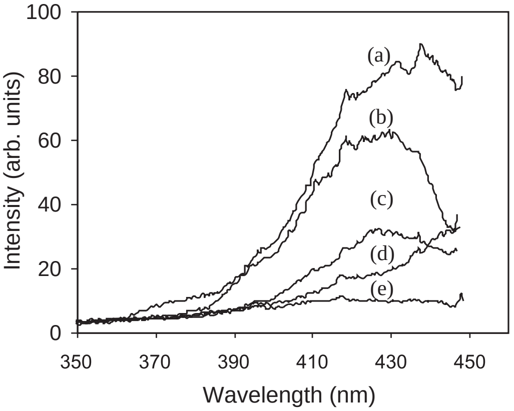

Fig. 3. Up-converted emission spectra of polystyrene nanoparticles with a diameter of 60 nm at various excitation wavelengths of (a) 480, (b) 500, (c) 532, (d) 550 and (e) 600 nm.

Photoluminescence from the PSD nanocrystals exhibits up-converted emission as shown in Fig. 3, where emission of a broad band of 410–440 nm centered at 430 nm is confirmed using three different excitation wavelengths of 480, 500 and 532 nm. A complete cut-off excitation wavelength for this up-converted emission (known as a stop band) was found at 600 nm. There is almost no up-converted emission found from the PSD nanoparticles at this cut-off wavelength excitation. Up-converted emission from PSD nanoparticles (Fig. 3) is measured to be 10 times weaker than the emission using normal excitation (Fig. 1).

3.2. Dynamic analysis

A dynamic model associated with both singlet $\{S\}$ and triplet states $\{T\}$ [12] in energy excitation, absorption, transfer and emission used for molecules will be employed to analyze up-converted processes in the PSD nanoparticles. The initial excitation corresponds to the $S_1 \leftarrow S_0$ transition, followed by an $S_n \leftarrow S_1$ absorption transition, where S_n represents all the singlet states above S_2. Two-photon processes of the $S_1 \leftarrow S_0$ and $S_n \leftarrow S_1$ two-stepwise transitions result in the $S_2 \rightarrow S_0$ transition leading to up-converted luminescence. S_2 can be populated through $S_n \rightarrow S_2$ nonradiative transitions. The emission intensity of the $S_2 \rightarrow S_0$ transition is expressed as

$$I_{S_2} \propto 1/\tau_{S_2} \int_0^{\infty} n_{S_2}(t)\,\mathrm{d}t, \tag{1}$$

where n_{S_2} represents the electron population in S_2 state. The following rate equations are numerically calculated to obtain n_{S_2} in order to get I_{S_2} :

$$\begin{aligned}
\frac{\mathrm{d}n_{S_0}}{\mathrm{d}t} &= -\frac{\sigma_{\mathrm{g}} I}{\hbar\omega} n_{S_0} + \frac{n_{S_1}}{\tau_{S_1}} + \frac{n_{T_1}}{\tau_{T_1}} + \frac{n_{S_2}}{\tau_{S_2}},\\
\frac{\mathrm{d}n_{S_1}}{\mathrm{d}t} &= \frac{\sigma_{\mathrm{g}} I}{\hbar\omega} n_{S_0} - \left(\frac{1}{\tau_{S_1}} + \frac{1}{\tau_{\mathrm{ST}}} + \frac{\sigma_{\mathrm{SE}} I}{\hbar\omega}\right) n_{S_1} + \frac{n_{S_2}}{\tau_{21}},\\
\frac{\mathrm{d}n_{S_2}}{\mathrm{d}t} &= -\left(\frac{1}{\tau_{21}} + \frac{1}{\tau_{S_2}}\right) n_{S_2} + \frac{n_{S_n}}{\tau_{n2}},\\
\frac{\mathrm{d}n_{S_n}}{\mathrm{d}t} &= \frac{\sigma_{\mathrm{SE}} I}{\hbar\omega} n_{S_1} - \frac{n_{S_n}}{\tau_{n2}},\\
\frac{\mathrm{d}n_{T_1}}{\mathrm{d}t} &= \frac{n_{S_1}}{\tau_{\mathrm{ST}}} - \left(\frac{1}{\tau_{T_1}} + \frac{\sigma_{\mathrm{TE}} I}{\hbar\omega}\right) n_{T_1} + \frac{n_{T_n}}{\tau_{T_n}},\\
\frac{\mathrm{d}n_{T_n}}{\mathrm{d}t} &= \frac{\sigma_{\mathrm{TE}} I}{\hbar\omega} n_{T_1} - \frac{n_{T_n}}{\tau_{T_n}},
\end{aligned} \tag{2}$$

where $\{n_p\}$ ($p = S_0, S_1, S_2, S_n, T_1$ and T_n) denote the population in the corresponding energy level, where T_n represents all the triplet states above T_1; $\{\tau_q\}$ where $q = S_1, S_2, S_n, T_1$ represent the corresponding inverse transition rates to ground state (S_0) and $q = T_n$ the inverse transition rate to state T_1; the inverse τ_{21} and τ_{n2} are the transition rates from the S_2 and S_n to S_1 and S_2 levels, respectively; σ_{SE}, σ_{TE} and σ_{g}, stand for the absorption cross-sections for the singlet, triplet and ground state, respectively. I and $\hbar\omega$ are the incident laser intensity and photon energy, respectively. Fig. 4

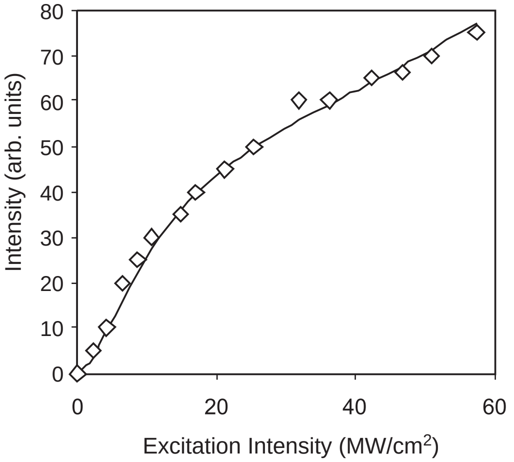

Fig. 4. Intensity dependence of up-converted emission at an excitation wavelength of 500 nm. The intersystem crossing time constant obtained from the fit of the numerical calculation to the experimental data is 11 ps.

depicts the intensity dependence of up-converted emission of both the experimental data (shown by diamonds) and theoretical calculation (solid line) for an excitation wavelength of 500 nm. Parameters used for the numerical calculation presented in Fig. 4 were $\sigma_{SE}=\sigma_{TE}=\sigma_g=1.5\times 10^{-17}\,cm^2$, $\tau_{S_1}=1.0$ ns, $\tau_{S_2}=10$ ps, $\tau_{21}=\tau_{T_n}=\tau_{n_2}=1.0$ ps, and $\tau_{T_1}=0.1$ ms. τ_{ST} was used as an adjustable parameter in this calculation. Finally, τ_{ST} was obtained to be 11 ps for the theoretical plot shown in Fig. 4. The $S_1\rightarrow T_1$ intersystem crossing was found to saturate the up-converted emission because it reduced the electron source for the S_2 level. Increasing the $S_1\rightarrow T_1$ intersystem crossing may reduce the probability for the $S_n\leftarrow S_1$ process, consequently leading to a decrease in the $S_2\rightarrow S_0$ emission.

4. Summary

Up-converted emission was demonstrated in polystyrene nanocrystals containing dendrimers of size 60 nm. The intersystem crossing time constant was estimated to be 11 ps by fitting the experimental data for the up-converted emission versus the excitation intensity.

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