

High resolution method for measuring local quantum yield of photoluminescence and phototransformation using confocal scanning microscope

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ABSTRACT

With the help of confocal scanning microscope capable of mapping the intensity of luminescence and transmittance, as well as luminescence spectra, with diffraction-limited resolution, local quantum yields of photoinduced transformations and photoluminescence of molecules and nanocrystals can be measured. The values of luminescence quantum yields of quantum dots distributed uniformly or aggregated in different locations of a polymer film are shown to differ by a factor of 3.5. To measure quantum yield of a photochemical reaction, the latter is induced by a scanning focused beam within a small area, and thus modified intensity of luminescence and transmitted light is monitored. The agreement of optical density measured using the microscope with its standard values depends on numerical aperture of the objective lens.

Keywords: measuring quantum yield; confocal microscopy; semiconductor nanocrystals; fluorescence;

1. Introduction.

Quantum yield (QY) is one of the most important characteristics of photoinduced processes such as photoluminescence and photochemical transformations. Quantum yield depends on intrinsic properties of molecules, nanocrystals, and other species as well as on their interactions with environment. As a rule, only average values of QY can be measured, while the information about their microscopic local values is hidden.

Nanocomposites with luminescent semiconductor nanocrystals (quantum dots, QD) are widely used in different areas, such as microelectronics, solar energetics, biology and medicine (Rajeshwar *et. al.* 2001, Tomczak *et. al.* 2009) due to their unusual optical, electrical and structural properties (Bukowski and Simmons 2002). Spatial

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heterogeneity of properties is a common feature of nanocomposite materials. Tendency of nanocrystals to aggregate may lead to considerable inhomogeneity of light intensity, decrease of luminescence caused by nonradiative energy transfer. The distribution of QY could be regarded as a quantitative measure of nanocrystal and molecules interactions and provide information about efficiency of nanocrystal incorporation in the polymeric matrix. Bulk polymers themselves are known to be spatially inhomogeneous, and luminescent dyes dissolved in them may serve efficient probes for testing the microheterogeneity.

There are two fundamentally different approaches to measuring QY of luminescence and photoreactions - direct and comparative (Krauss and Carlson 2007). The traditional techniques of QY measurements are described in detail in the review Demas and Crosby (Demas and Crosby 1971). The direct method of measuring absolute QY q consists in determining the ratio of number of photons emitted per unit time by the sample m_{lum} to the number of photons absorbed per unit time m_{abs} :

$$q = \frac{m_{lum}}{m_{abs}} \quad (1)$$

Various techniques intended for measurement of absolute luminescence and photoreaction QY are known, such as that using a spectrophotometer with integrating sphere (Gaigalas *et al.* 2009) or the dual-beam thermal lens technique (Bindhu *et al.* 1995), but most of them do not make it possible to determine local characteristics of the samples.

To determine QY of single particles, correlated atomic-force and single-particle fluorescence microscopies were applied (Ebenstein *et al.* 2002), resulting in a combined map of the topography and the single-particle fluorescence, however it can not be applied to investigate thick samples with inhomogeneous spatial distribution of the luminophores or organic dyes in the bulk.

The present work is aimed at development of a technique for measurement and mapping of local quantum yields of luminescence and phototransformation using a confocal laser scanning microscope.

2. Experimental part

2.1 Experimental set-up and calibration measurement

The proposed method for measuring local quantum yield of luminescence and phototransformation has been developed with help commercial confocal luminescence scanning microscope (LSM 710 with Axio Imager Z1, Carl Zeiss, Germany). The principle of confocal microscopy is shown in the schematic diagram presented in Fig. 1. Confocal scanning microscopy allows for obtaining images with high axial resolution

due to confocal pinhole which is to suppress scattered and emitted light from out-of-focus optical slices.

In our experiments, different laser lines from the microscope were used to induce photochemical reactions and excite fluorescence. The 405 nm diode and 488 nm argon line lasers had been used for excitation of luminescence and inducing phototransformations, 543 nm HeNe laser source was used for calibration.

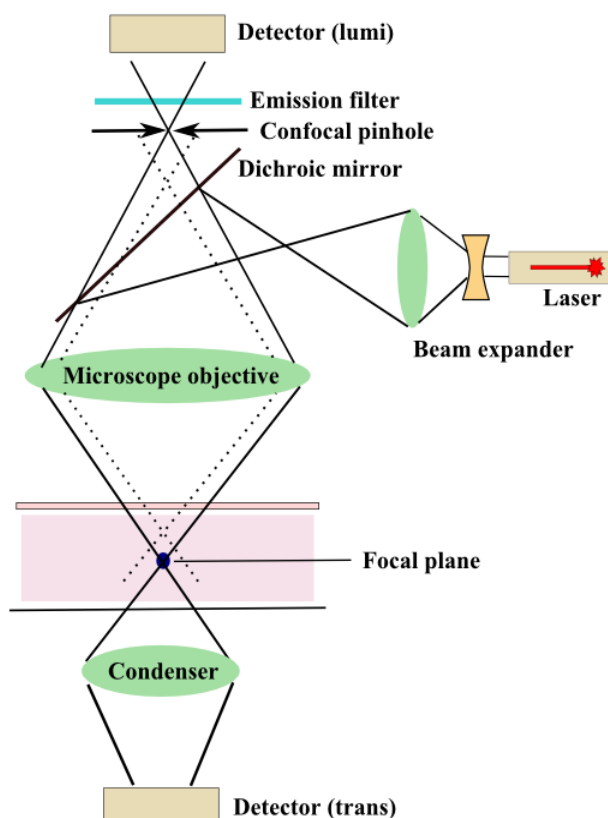


Fig. 1 Schematic diagram of confocal microscope for luminescent and transmittance measurements.

The first step needed before establishing the technique for measuring QY with confocal laser scanning microscope is calibration of optical density and optical slice thickness for correct measurement of light transmittance and right geometry of the experiment correspondently. For calibration of optical density we use a standard light absorber with well defined transmittance (glass covered with a metal layer). The optical density measured with the microscope versus the etalon optical density is shown in Fig. 2a, from which the range of linearity can be estimated. When using high-resolution lenses with large numerical apertures, significant deviation of the measured values from real shall be taken into account. Optical layer thickness (axial resolution) strongly depends on numerical aperture, too (Fig. 2b).

2.3 Preparing the samples

In this work we used 1) semiconductor core/shell CdSe/ZnS QDs capped by TOPO (trioctylphosphineoxide), whose average diameter is 2,5 nm, maximum luminescence at 531 nm with QY in hexane about 13%, and 2) an organic dye phenanthrenequinone (PQ) capable of photoreduction with hydrogen abstraction (Carapellucci et al., 1969), also known as a component of light-sensitive materials for holograms recording (Veniaminov et al., 2008).

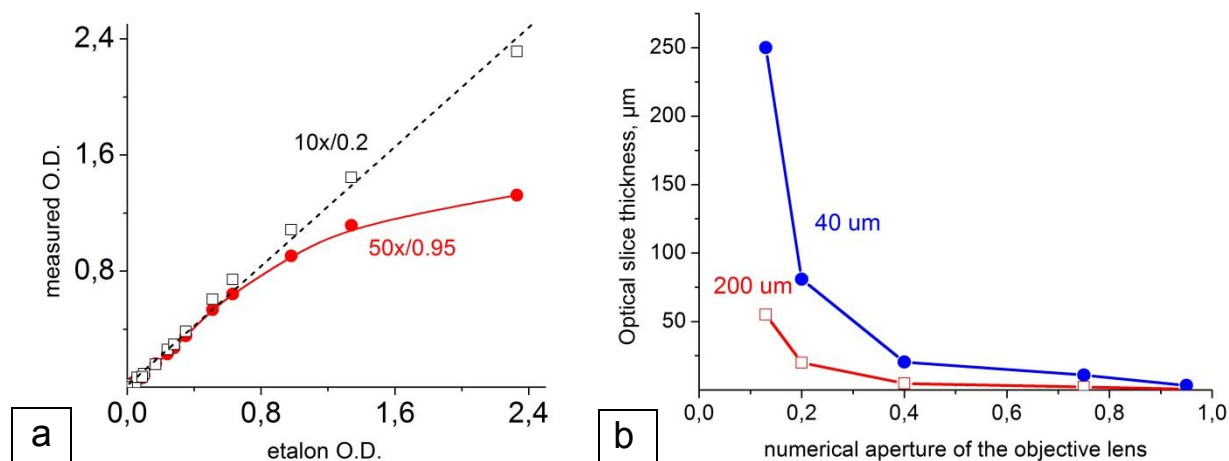


Fig. 2 a) Optical density of an etalon absorber measured using the confocal microscope with different objectives vs. its real optical density measured with parallel beams;
b) Optical slice thickness as a function of a numerical aperture of the objective lens, at different pinhole diameters (40 and 200 μm)

3. Results and Discussion

3.1 Quantum yield of phototransformation

Polymer film with phenanthrenequinone (PQ) was produced from PMMA (polymethyl methacrylate). We applied 488 nm laser exposure to 50x50 μm squares of polymer film for bleaching (photoreduction) of PQ molecules. As a result of the reaction, intensities of both transmitted light and luminescence increased (Fig.3), meaning that the absorption was mainly due to PQ, while the luminescence belonged to the photoproduct rather than to PQ itself. The quantum yield of phototransformation was found to decrease with exposure, too, probably due to photoselection caused by microscopic spatial heterogeneity of the polymer film. For measurement QY of photoinduced transformation we measured the number of photons in the excitation light and the number of modified molecules dye and calculated QY – φ , using Eq. 2:

$$\varphi = \frac{\Delta D A S h c}{\varepsilon W \lambda (1 - T) t}, \quad (2)$$

where ΔD - the optical density, A - Avogadro number, S - glow area, h - the Planck constant, c - speed of light, ε - extinction coefficient, W - the power of laser light, λ - excitation wavelength, T - transmittance, t - time of exposure. The curves of the change in optical density and photoluminescence intensity (Fig. 3 (b)) demonstrate mechanism transformation of dye molecules.

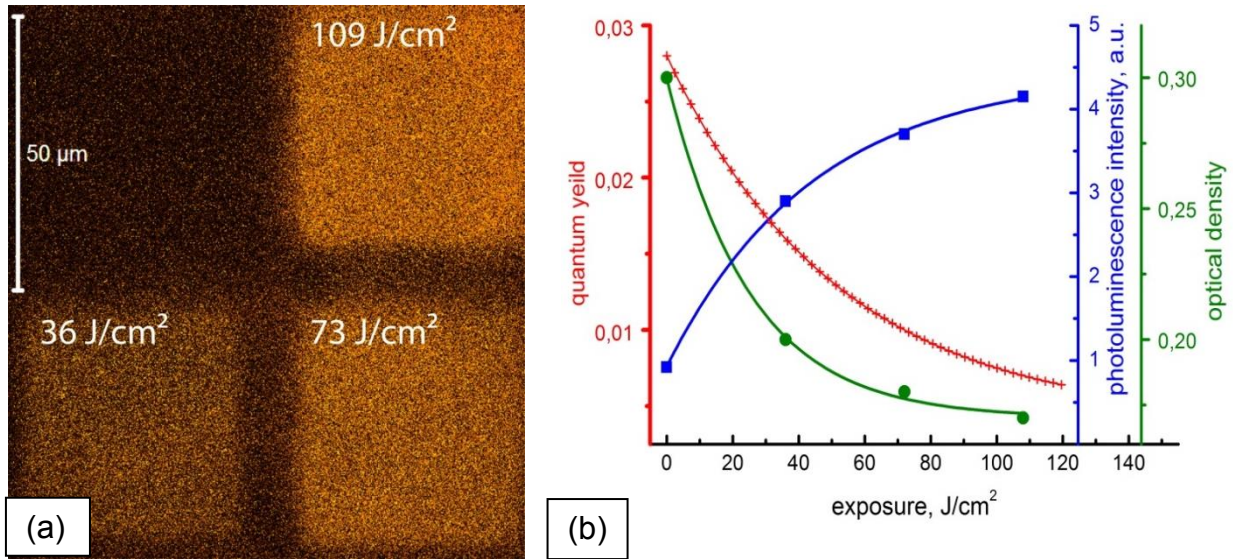


Fig. 3 (a) - Luminescent image of a 100x100 μm part of a PMMA film with PQ partially bleached with 488 nm laser light, (b) quantum yield (red), optical density (green) and photoluminescence intensity (blue) as functions of exposure.

3.2 Luminescence quantum yield

A method for determining the relative luminescence quantum yield involves comparing of the integrated intensity of the luminescence of the sample and the reference luminophor with a known quantum yield. The equation below instructs for the calculation:

$$\varphi = \varphi_0 \frac{1 - T_0}{1 - T} \frac{\int_{\lambda} I(\lambda) S(\lambda) d(\lambda) n^2}{\int_{\lambda} I_0(\lambda) S_0(\lambda) d(\lambda) n_0^2}, \quad (3)$$

where φ_0 , T_0 , I_0 , n_0 , S_0 - quantum yield, transmittance, intensity of luminescence, refractive index and luminescence area of reference sample correspondently, λ - is wavelength of excitations. Polymer film with quantum dots was produced from PC (polycarbonate) by solution method. For dissolved polymer granules and nanocrystals we used dichloromethane and ultrasonic bath. As a result of preparation, thin film (about 10 μm) with different distribution QDs was created (Fig. 4). Local spectra and QY of luminescence were measured from red and green regions (layer with uniformly

distributed and agglomerated QDs, respectively), as a reference sample, we used polymer film rhodamine dye film with a known QY. Red shift the emission spectrum from agglomerate regions (on 10 nm, Fig. 4 (b)) was found. The QY of luminescence of marked areas was calculated by Eq. 3 and amounted 40% within the red square and 12% in the green circle. The nanocrystals were uniformly distributed in polymer film have a high QY of luminescence and a small spectral shift relative to the solution.

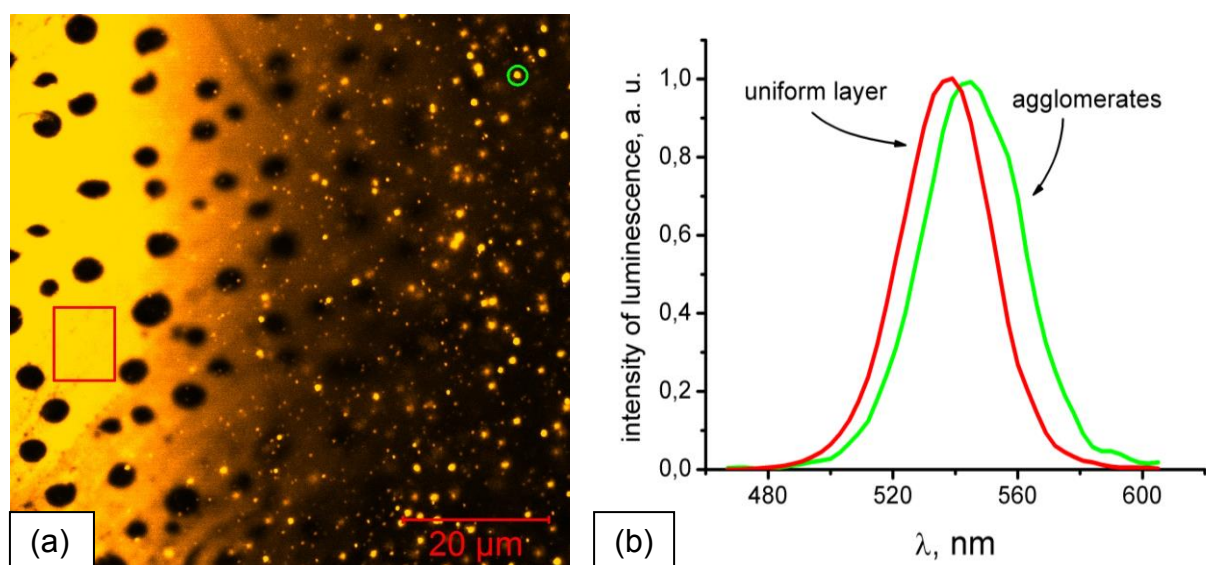


Fig. 4 (a) Luminescent image of film area with CdSe/ZnS nanocrystals; excitation at 405 nm, quantum yields are 40% within the red square and 12% in the green circle (b) luminescence spectra of red and green regions (layer with uniformly distributed and agglomerated QDs, respectively) from (a).

4. CONCLUSIONS

In this contribution, we have shown how a confocal scanning microscope can be used as a tool for measuring local quantum yields of luminescence and photochemical transformations, due to its ability to produce spatial distributions of the intensities of transmitted and emitted light, local luminescence spectra, and apply photochemically active light to small regions of interest. Such measurements provide important information on microstructure of composite materials, the degree of their heterogeneity, and can be useful if only a small amount of specimen is available for investigation.

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