# Accounting for scattering and reabsorption in the analysis of luminescence spectra of nanoparticles

V.I. Kochubey, Ju.G. Konukhova, I.V. Zabenkov, E.K. Volkova

***Abstract.*** **An algorithm and a program are developed allowing the correction of experimentally measured luminescence spectra of nanocomposite materials with the aim to determine the luminescence spectra of the nanoparticles or of the local regions of the sample. The optical characteristics of CdS nanoparticles synthesised in a high-pressure polyethylene and in the orthoxylene solution are studied. It is shown that the luminescence spectra of the nanoparticles differ from those experimentally observed due to the scattering and reabsorption in the samples. In the region of wavelengths 500 – 550 nm a ghost band may arise due to the scattering and reabsorption of the luminescence in the sample near the edge of the CdS absorption band.**

***Keywords***: *nanoparticle, luminescence spectrum, scattering, reabsorption.*

## 1. Introduction

One of the promising methods of nondestructive investigation of the internal structure of biological tissues and its changes is the optical tomography, using laser radiation for imaging. The advantages of this method are high sensitivity, possibility to work with biological objects of submicrometer size and to monitor fast processes with the characteristic subpicosecond time scale [1], nonionising action of the probe laser radiation, relative simplicity, and sufficiently low cost. However, the use of laser radiation for studying biological objects or in laser medicine meets serious problems due to the processes of scattering, refraction and reflection of optical radiation in biotissues.

Scattering arises due to inhomogeneities of the refraction index in cells, macrostructures, etc. In strong-scattering media the optical path length of photons, travelling in the sample, is increased (and, therefore, the absorption is increased too), and the depth of light penetration into the sample is decreased, which limits the spatial resolution and the depth of probing. The light scattering may be reduced by means of optical clearing of the biological tissue, based on matching the refractive indices of its structural elements and

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their environment by introducing the immersion liquid into the sample, as well as by choosing such a wavelength of the incident light that reduces the mismatch of the refractive indices (the shift towards the long-wave spectral region). Application of the new optical diagnostic method, the fluorescence optical tomography, may solve the problem of getting a signal from the studied volume, located at some depth inside the biological object, by introducing a small amount of fluorescent probing substance (dye or luminescent nanoparticles) sufficient for detection but physiologically harmless. At the same time this method allows suppressing the light, scattered by the volumes closer to the surface, using the spectral filtration of the exciting radiation. In our previous paper [2], using the mathematical modelling based on the Monte Carlo method, we demonstrated the possibility of imaging the objects that luminesce under the action of the probing laser radiation. The objects located in the skin at the depth of more than 1 mm from the surface can be imaged with the lateral resolution of hundreds of micrometres under the conditions of surface clearing of skin.

Using the luminescent agents in the method of fluorescence optical tomography, one should pay particular attention to the effect of the environment on the luminescence. The interaction with the environment affects both the structure of the substances and their luminescent characteristics. The changes can occur both in the position and in the intensity of luminescence bands, e.g., due to the radiationless energy transfer to the molecules of environment. Therefore, one of the methods to study biological objects may be to investigate the changes in the luminescence spectrum of the probing substances depending on the composition and properties of the surrounding biological medium under the excitation by laser radiation with the appropriate intensity at the prescribed depth. However, because of multiple scattering and reabsorption in the biological tissues, the measured spectra of absorption and luminescence of the sample are subject to perturbation by the upper layers. As a result, even at the same spectral characteristics of the radiation, the measured spectra will be different for the sites located at different depths. Therefore, to obtain the real view of luminescence, it is necessary to reconstruct the true spectra, taking the scattering and reabsorption into account.

The goal of the present paper is to study the influence of the scattering and reabsorption processes on the luminescence spectra of samples, containing luminescent nanoparticles. This study was performed in the model media (suspensions of nanoparticles in orthoxylene and nanoparticles in a polyethylene matrix).

The choice of nanoobjects as luminescent agents is stimulated by the expansion of the field of their biological and medical applications [3]. The increasing interest of researchers to nanoobjects is promoted by the discovery of their exotic physical and chemical properties, caused by the so called quantum-dimensional effects. Optical, electronic and catalytic properties of nanoparticles essentially differ from those of bulk substance and depend upon the particle size (the effect of dimensional quantisation). Therefore, by variation of the particle size one can control their optical, electrical and structural properties. At present the unique physical properties of nanoparticles are the subject of intense studies.

In the papers, devoted to the study of the optical properties of nanoparticles and nanocomposite materials [4–7], the main subject of attention is the influence of scattering on the absorption spectra. The influence of scattering on the formation of luminescence spectra of nanoobjects is studied insufficiently.

## 2. Methods and materials

Two types of samples were studied: (i) nanocomposite samples, produced at the Saratov Branch of Kotel'nikov Institute of Radio Engineering and Electronics of RAS and comprising CdS nanoparticles, synthesised in the bulk high-pressure polyethylene matrix (HPPM) via the decay of precursors of the appropriate complexes [8–10]; (ii) CdS nanoparticles in orthoxylene, synthesised by us following the original technique [11, 12]. In the second case the synthesis of free small-size CdS nanoparticles was implemented by holding the mixture of cadmium pivalate $Cd(piv)_2$ and elementary sulphur S, dissolved in orthoxylene, at the temperature $120\,°C$ during the prescribed time.

To calculate the luminescence spectrum of a local volume inside the sample, one should know the coefficients of absorption and scattering of the sample. Therefore, besides the luminescent characteristics of the samples, we measured the spectra of total reflection and total transmission.

The spectra of total reflection and total transmission were recorded my means of the double-beam Lambda 950 spectrophotometer (PerkinElmer) using the integrating sphere. The spectra of luminescence and excitation were measured by means of the LS-55 luminescence spectrometer (PerkinElmer). The spectra were corrected taking the power of exciting radiation and the spectral sensitivity of the device into account. Cuvettes made of 100-μm-thick LiF were used for the experiment. The measurements were carried out at room temperature. All luminescence spectra were recorded under the excitation at the maxima of the bands in the measured spectra of luminescence excitation.

## 3. Method of calculating the luminescence spectrum of a local volume inside the sample

We developed an algorithm for calculating the true luminescence spectra of nanoparticles using the spectral dependences of the transport scattering coefficient $\mu_s'(\lambda)$ and the absorption coefficient $\mu_a(\lambda)$, as well as the experimentally measured luminescence spectrum of the sample under study. The algorithm is based on the idea that the ratio of luminescence intensity, measured by the photodetector, and the luminescence intensity from a vanishingly small volume

of substance, located inside the bulk nanocomposite sample, characterises the reduction of the initial luminescence intensity due to the scattering and reabsorption in the sample. In this case the luminescence spectrum of the considered volume of substance is much closer to the luminescence spectrum of nanoparticles than the experimentally measured one because of small reabsorption. Therefore, it is sufficient to calculate the spectral dependence of this ratio, i.e., the correcting curve $[f(\lambda)]$ for the chosen model luminescence spectrum. The luminescence spectrum of the local volume inside the sample $I_{lum}(\lambda)$ in this case may be obtained by division of the experimental luminescence spectrum $I_{exp}(\lambda)$ by $f(\lambda)$:

$$I_{lum}(\lambda) = \frac{I_{exp}(\lambda)}{f(\lambda)}.$$

Taking the multiple incoherent scattering into account, the radiation transport process in a scattering medium is considered within the framework of the radiation transport theory [13]. Since the analytic solution of the radiation transport equation is difficult, different numerical methods became widely used [14]. In the present work the transport of exciting radiation and following luminescence through the layer of the sample was modelled using the Monte Carlo method, based on calculating multiple random photon trajectories in the scattering medium, the optical properties of which determine the length and shape of individual trajectories. We used the modification of the method with variable free path length of a photon [15–17] and with the multilayer structure of the sample taken into account [18]. In the modelling we assumed that nanoparticles are uniformly distributed over the sample volume. The algorithm developed accounts for the realistic geometry of the experiment and, via the presentation of the sample as layered structure, for the optical characteristics of the cuvette, in which the sample is placed.

The multilayer medium model is presented in Fig. 1. The basic input parameters for modelling are the absorption coefficient $\mu_a(\lambda)$, the transport scattering coefficient $\mu_s'(\lambda)$, and the refractive index of the medium. The optical characteristics $\mu_s'(\lambda)$ and $\mu_a(\lambda)$ were calculated from the measured spectra of total transmission and total reflection of the samples using the inverse adding–doubling method [19]. For biological objects the anisotropy factor is $0.8–0.85$; however, since in the nanocomposite materials, in
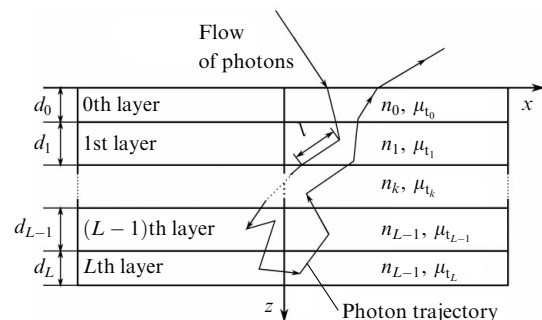


**Figure 1.** Schematic diagram of the photon scattering process in the inner regions of a multilayer sample. $l$ is the free path length of the photon, $n_k$ and $\mu_{t_k}$ are the refractive index and the total attenuation coefficient for the relevant layer ($\mu_t = \mu_s' + \mu_a$).

which we modelled the radiation transport, the scatterers are nanoparticles with sizes much less than the wavelength of light, we took the phase function in the Henyey–Greenstein form with the zero anisotropy factor. The number of photons of the exciting radiation at the front surface of the sample was taken equal to $10^8 - 10^{12}$.

At the first stage the propagation of $N$ photons of exciting radiation in the sample was modelled. The photons that leave the sample in the backward direction after the computational cycle, or are absorbed at the absolutely black coating of the cuvette (in this way a semi-infiniteness of a biological medium in the direction, normal to its surface, was simulated) do not excite the luminescence of nanoparticles. If the excitation photon is absorbed at a certain point of the sample with the coordinates $x$ $y$, $z$, then this point becomes a centre of luminescence, i.e., a source of secondary photons. In the case of nanoparticles the secondary photons are emitted in arbitrary directions in all the spectral range under study.

At the second stage we modelled the propagation of secondary photons from the sources, distributed over the sample volume, by means of the same Monte Carlo procedure. The number of secondary photons at a given point was assumed to be proportional to the number of excitation photons, absorbed in this point. The optical scheme of the excitation and detection of the luminescence spectra is presented in Fig. 2.
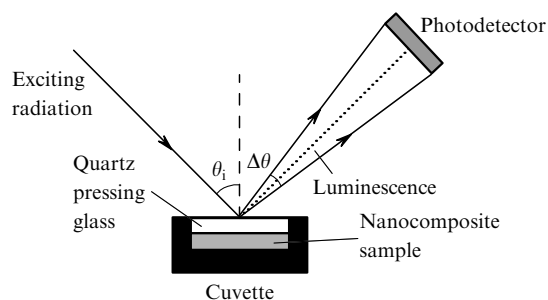


**Figure 2.** Geometry of luminescence registration experiment.

Thus for each luminescence wavelength the propagation of $M$ luminescence photons was modelled using the corresponding spectral characteristics of the medium. Each luminescence photon has the statistical weight $\omega(\lambda) = 1/(N + M + S)$, where $S$ is the number of spectral components in the luminescence spectrum, i.e. the number of wavelengths $\lambda$. The computation cycle is finished either by the absorption of the photon in the medium, or by its exit through the back hemisphere of the sample. The calculation was carried out subsequently for all points of the sample with nonzero number of the absorbed photons of the exciting radiation. Up to the luminescence quantum yield, the desired correction curve results from summation of all luminescence photons that exit within the solid angle with the vertex at the point of exit on the front surface of the sample, subtended by the photodetector surface. This curve can be used to obtain the spectrum of luminescence as it looks at the emission site inside the object.

The present method is proposed by us instead of the standard methods of solving the inverse problem by modelling the luminescence transport for the source, distributed in the sample, using the experimental luminescence spectrum as initial data and subsequent minimisation of the residual function of the model and experimental spectra under the variation of the luminescence quantum yield [20–24]. The advantages of our method include the reduction of the calculation time, the possibility to obtain the data with small error for very high densities of the exciting radiation and weak signals.

## 4. Results and their discussion

Figures 3 and 4 present the experimental spectra of the total reflection $R$ and total transmission $T$, and also the calculated spectral dependences of the scattering $\mu_s'$ and absorption $\mu_a$ coefficients of CdS nanoparticles, synthesised in the high-pressure polyethylene matrix (HPPM) and in orthoxylene. From these dependences it follows that although in the visible region the coefficients of absorption and scattering are comparable, their behaviour is different. The edge of the absorption band (determined by the bending point) is found at the wavelength 500 nm for HPPM samples and at 320 nm for nanoparticles in orthoxylene. Our studies have shown that the nanoparticles in the samples of both types are characterised by a hexagonal structure [12], and, therefore, the different position of the absorption band edge may be caused
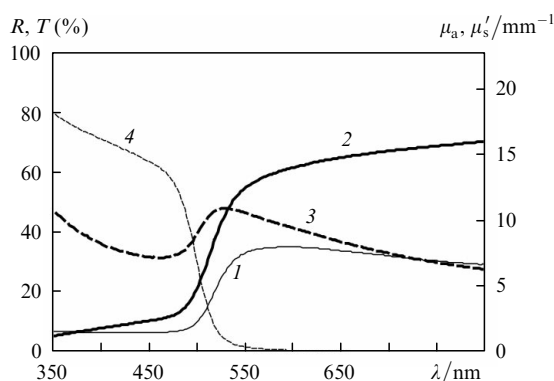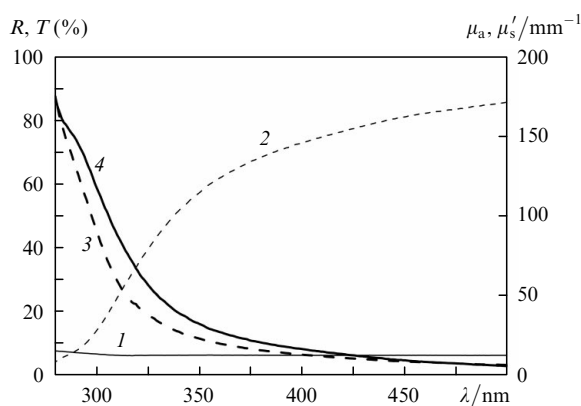


**Figure 3.** Spectra of the total reflection $R$ ($1$), total transmission $T$ ($2$), coefficients of scattering ($\mu_s'$; $3$) and absorption ($\mu_a$; $4$) for the 105-μm-thick sample containing 30 wt.% of CdS nanoparticles, synthesised in HPPM.
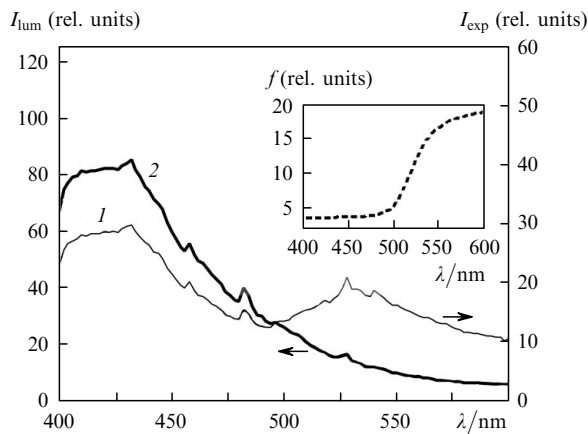


**Figure 4.** Spectra of the total reflection $R$ ($1$), total transmission $T$ ($2$), coefficients of scattering ($\mu_s'$; $3$) and absorption ($\mu_a$; $4$) for CdS nanoparticles, synthesised in orthoxylene during 180 min.

only by the difference in the size of nanoparticles, which is 4–6 nm in the HPPM [25] and 2–3 nm in the orthoxylene [12].
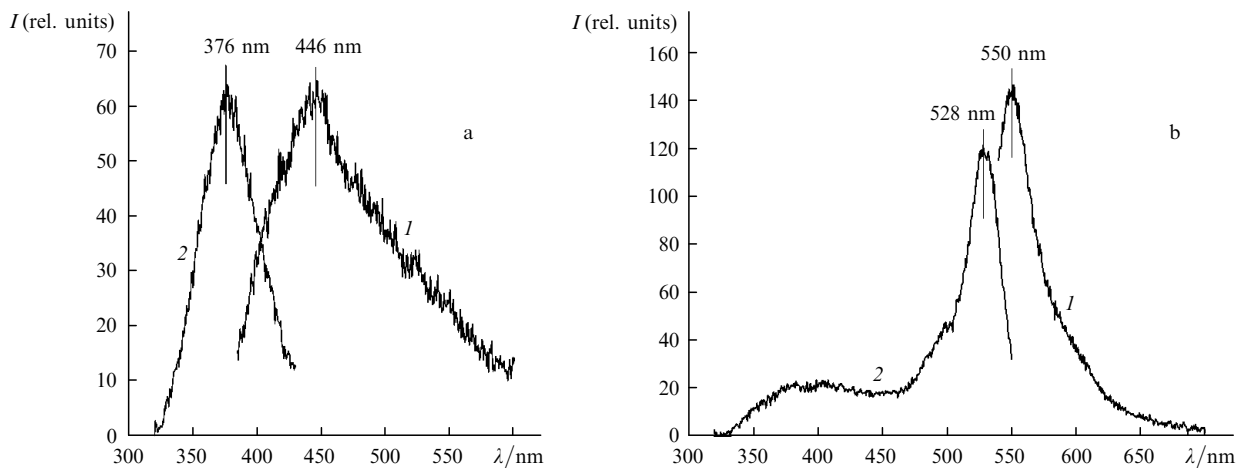
The experimental and corrected spectra of luminescence of CdS nanoparticles, synthesized in HPPM and orthoxylene, are presented in Figs 5–7. In the experimental spectra



**Figure 5.** Experimental ( *1* ) and corrected ( *2* ) luminescence spectra of the 105-μm-thick sample, containing 30 wt. % of CdS nanoparticles, synthesised in HPPM. In the inset the correction curve used in the spectra correction is shown.

of HPPM samples two broad bands are observed with the maxima at 420 and 530 nm. The comparison of absorption and luminescence spectra shows that both luminescence bands appear in the region of strong absorption and scattering. Therefore, one should expect large difference between the experimental spectra measured outside and those of the local volumes inside the sample. This is confirmed by the correction curve, calculated by us (inset in Fig. 5). In the corrected luminescence spectrum (Fig. 5) the band at 530 nm is absent, i.e., its presence in the experimental spectrum is caused by the strong change of absorption in the range 500–530 nm. Therefore, the overlapping of the broad luminescence band and the edge of the absorption band of nanoparticles, together with the significant scattering, leads to the formation of a ghost band.

For the nanoparticles in orthoxylene solution two luminescence bands are observed with the maxima at 446 and 550 m (Fig. 6). Both bands are far from the edge of the absorption band, so one may expect insignificant distortion of the luminescence bands measured outside in comparison with those of the local volumes inside the sample. At the same time the shorter-wavelength luminescence band is closer to the edge of the absorption band, and, hence, for this band greater distortions should be expected because of greater slope of the absorption coefficient spectral curve. This is observed in the corrected spectra, namely, at small



**Figure 6.** Experimental spectra of luminescence ( *1* ) and excitation ( *2* ) of the sample with CdS nanoparticles, synthesised in orthoxylene during 180 min. The luminescence was excited using the radiation with the wavelengths 376 (a) and 528 nm (b).
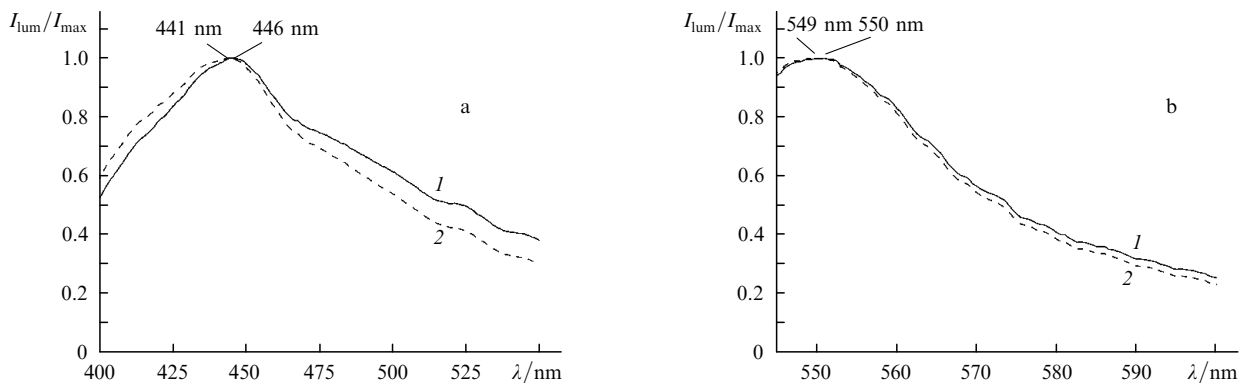


**Figure 7.** Experimental ( *1* ) and corrected ( *2* ) spectra of luminescence of CdS nanoparticles, synthesised in the orthoxylene during 180 min, normalised to the maximal intensity. The luminescence was excited by the radiation with the wavelengths 376 (a) and 528 nm (b).

absorption and scattering (at 550 nm) the shift of the band maximum is only 1 nm, i.e., the distortion is practically absent (Fig. 7b), while at greater absorption and scattering (at 446 nm) the shift of the maximum reaches 5 nm (Fig. 7a), and the difference of the spectra becomes more evident.

## 5. Conclusions

Thus, we can conclude that the developed algorithm and program for calculating the luminescence intensity of absorbing/scattering samples, including those containing nanoparticles, allow the reconstruction of the luminescence spectrum, emitted by local volumes inside the sample. The increase in the absorption and scattering coefficients of the environment, surrounding the luminescent particles, leads to greater distortion of their observed luminescence spectra. The application of the present method may play essential role in the analysis of the conditions for measuring the experimental luminescence spectra and the reasons why they appear different from the true ones.

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