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Mathematical Equation of Fluorescence Intensity for Polydisperse Sols

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This paper describes the aging phenomena of colloidal CdS, using fluorescence emission results. It is known that particles of different sizes have not only different absorption spectra but also different fluorescence spectra. This effect is not surprising, because excitation at different wavelengths leads to the excitation of different size particles that do not have the same fluorescence intensity at the wavelength where the fluorescence is recorded.

KEY WORDS: Colloidal CdS; nanoparticles; fluorescence; aging phenomena; computer modeling.

INTRODUCTION

Colloidal semiconductor nanoparticles are of particular interest because of their size-dependent photophysical, photochemical, and non-linear optical properties [1]. Recently, there has been a surge of interest in the use of colloidal semiconductor particles as models for fundamental studies of luminescence phenomena and charge-transfer processes at the semiconductor-solution interface [2]. In the case of CdS colloids, the fluorescence emission is controlled by surface processes, and thus can be used to monitor surface kinetics, in much the same way that molecular luminescence is used to follow excited-state molecular reactions [3].

EXPERIMENTAL

Colloidal CdS (8.73×10^{-4} M) was prepared using Kalyanasundaram's method [4] by replacing $(NH_4)_2S$ with Na_2S (Fluka) in an excess of 2×10^{-4} M, bubbling argon during the synthesis. A styrene-maleic anhydride (1/1) copolymer was used as a stabilizer.

Colloidal CdS was characterized by its absorption spectrum using a Unicam α Helyos spectrophotometer and by its fluorescence spectrum recorded with a Aminco-Bowman spectrofluorimeter. We determined the particle size from the absorption spectrum [5,6] and emission spectrum [7] and obtained an average value $d_p = 70$ A for the larger particles.

By exciting with the wavelengths in the domain of 260–390 nm, the emission spectra are positioned between 500 and 790 nm. The measurements where taken at: 1, 2, 6, and 14 days from when the colloidal CdS was prepared (colloidal CdS was kept in dark between these measurements). Table I shows the differences between emission intensities for a fresh and an aged CdS sol.

RESULTS AND DISCUSSION

For a fluorescent colloidal monodisperse solution, the emission intensity, I_{em}, is a Gaussian function and has its maximum value at the same $\lambda_{0\ em}$ independent of λ_{ex}. Only its intensity depends on λ_{ex} (Fig. 1).

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Table 1. Fluorescence Emission Intensity for a Fresh Colloidal CdS and for an Aged One (After 1 Day at T = 60°C)

Nr.	λ_{ex} (nm)	I_{em} fresh colloid (cm)	I_{em} aged colloid (cm)
1	260	4	1.5
2	270	5.5	3.5
3	280	7.6	9
4	290	10.8	12
5	300	13	14.9
6	310	15.1	16
7	320	16	17
8	330	15.5	16.7
9	340	15	15.6
1	350	11.9	14.5
11	360	10.1	11.8
12	370	8	10
13	380	6	7
14	390	2.5	6
15	400	1	4

$$I_{em} = Q\cdot\exp[-a\cdot(\lambda_{em} - \lambda_{0\,em})^2] \quad (1)$$

where: $a > 0$ is a material parameter and Q is the maximum value of fluorescence emission.

In conformity with Parker [8],

$$Q = \phi\cdot I_A, \quad (2)$$

where: I_A is the absorbed radiation intensity, and ϕ is the quantum yield of fluorescence. Then Eq. (1) becomes:

$$I_{em} = \phi\cdot I_A\cdot\exp[-a\cdot(\lambda_{em} - \lambda_{0\,em})^2] \quad (3)$$

with:

$$I_A = I_0\cdot[1 - \exp(-kcl)] \quad (4)$$

Combining all these equations results in the general equation for monodisperse sols:

$$I_{em} = \phi I_0\cdot[1 - \exp(-kcl)]\cdot\exp[-a\cdot(\lambda_{em} - \lambda_{0\,em})^2] \quad (5)$$

If the colloidal solution is polydisperse, the maximum value of fluorescence emission intensity depends by λ_{ex}, as Eq. (6) shows (Fig. 2):

$$I_{em} = \phi I_0[1 - \exp(-kcl)]\cdot\exp[-a\cdot(\lambda_{em} - f(\lambda_{ex}))^2] \quad (6)$$

For a colloidal CdS $f(\lambda_{ex}) = A + B\cdot\lambda_{ex}$, where *A* and *B* are fitting parameters ($\lambda_{em} = f(\lambda_{ex})$) for which I_{em} is the maximum intensity value. In particular, for our colloidal CdS $\lambda_{ex} = 320$ n*m*, it was result:

$$I_{em} = \phi I_0[1 - \exp(-kcl)]\cdot\exp[-a\cdot(\lambda_{em} - 2\cdot\lambda_{ex} + 30)^2] \quad (7)$$

The aging of colloidal CdS is a dynamic process that made the size of these particles vary in time. Using a mathematical extrapolation, we give to the aging phenomena an equation form. In this case, if we note:

$$P = \phi I_0[1 - \exp(-kcl)] \quad (8)$$

P becomes a function depending on time, $P(t)$. We obtain from processing experimental data a Pulls time dependence (Fig. 4), which obeys the next equation.

$$P(t) = a_0 + a_1\cdot[1 - \exp(-(t - t_0)/a_2)]\cdot\exp(-(t - t_0)/a_3) \quad (9)$$

a_i, i = 0 . . . 3, real constants and t = 0 at the moment that the nucleation process is finished.

By plotting P = P(t), we can see that λ_{ex} and t are independent variables:

$$I_{em}(\lambda_{ex}, t) = P(t)\cdot f(\lambda_{ex}) \quad (10)$$

Using equations (8), (9), and (10) we can rewrite the equation (7) for our CdS colloidal:

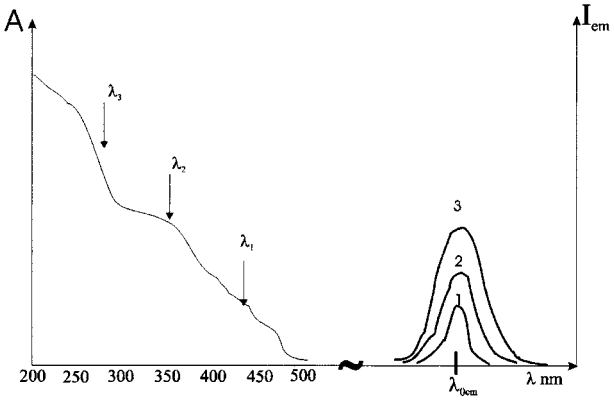


Fig. 1. Absorption and emission intensity for a monodisperse colloid.

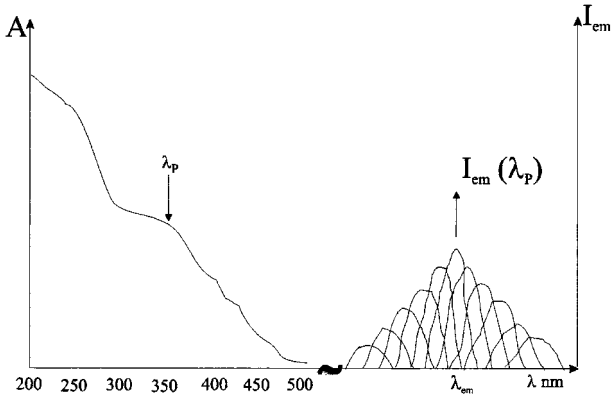


Fig. 2. Absorption and emission intensity for a polidisperse colloid.

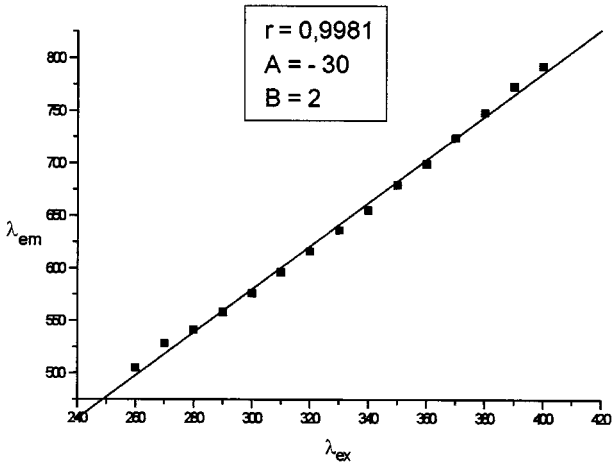
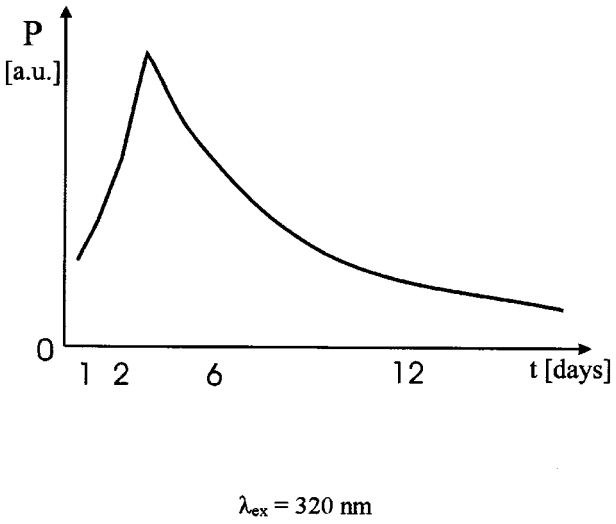


Fig. 3. λ_{em} of the maximum intensity emission vs. λ_{ex} for our colloidal CdS.



$\lambda_{ex} = 320$ nm

Fig. 4. Maximum emission intensity, time dependence.

$$I_{em} = \{a_0 + a_1 \cdot [1 - \exp(-(t - t_0)/a_2)] \cdot \exp(-(t - t_0)/a_3)\} \cdot \phi I_0 \cdot [1 - \exp(-kcl)] \cdot \exp[-a \cdot (\lambda_{em} - 2 \cdot \lambda_{ex} + 30)^2] \quad (11)$$

If we consider the maximum value of emission intensity as being proportional to the number of colloidal particles, $N_d(t)$,that are emitting at $\lambda_{0\ em}$ and having a diameter d, using a known dependence [3] $d \sim 1/\lambda_{0\ em}$, we can write:

$$N_d(t) = \{a_0 + a_1 \cdot [1 - \exp \cdot (-(t - t_0) / a_2)] \cdot \exp(-(t - t_0)/a_3)\} \cdot f(\lambda_{ex}) \quad (12)$$

For $\lambda_{ex} = \lambda_p$, where λ_p is the excitation wavelength for which the most probable colloidal particles emit, and for a weak dispersion $N_d \approx N$, results:
For $t = 0$

$$N(t) \sim \{a_0 + a_1 \cdot [1 - \exp(-(t - t_0)/a_2)] \cdot \exp(-(t - t_0)/a_3)\} \cdot f(\lambda_p) \quad (13)$$

$$N(t) = N_0 = \{a_0 + a_1 \cdot [1 - \exp(t_0/a_2)] \cdot \exp(t_0/a_3)\} \cdot f(\lambda_p) \quad (14)$$

N_0 is the initial number of the most probable particles when the nucleation is finished. For $t \to \infty$

$$N(t) = N_\infty \to (a_0 + a_1) \cdot f(\lambda_p) \quad (15)$$

N_∞ is the number of the most probable colloidal particles when the equilibrium is reached.

CONCLUSIONS

It is obvious that physics phenomena need a mathematical form to be described, to be able to realize a good image of them and find all parameters which influenced them. We found an equation form of emission intensity for a polydisperse colloid and particularized it to our colloidal CdS, Eq. (6).

To describe aging phenomena, we found time dependence of emission intensity, Eq. (11) and time dependence of colloidal particle number, Eq. (13). We define also two parameters, N_0 and N_∞, from Eqs. (14) and (15), which are the initial and equilibrium number of the most probable colloidal particles and are important parameters in describing the aging phenomena in time.

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