

## THE DYNAMIC OF COLLOIDAL CdS INVESTIGATED BY SPECTRAL METHODS

Tatiana Oncescu \* and Lucia Meahcov

**abstract:** Prepared CdS particles have been characterized by their absorption and emission spectra. The band gap value  $E_g$  obtained from the absorption spectra permitted us to calculate a particle size of  $75 \pm 5$  Å. The fluorescence quenching of CdS with methylviologen led to a particle size of  $70 \pm 5$  Å in good agreement with the absorption measurements. In the absorption spectrum the band gap shifted toward the longer wavelengths with the particle size increasing put into evidence by a moderate aged colloid. The shifting of the fluorescence peaks toward the longer wavelength in the red spectral region, with the exciting wavelength shows a polydispersity CdS. These conclusions are in good agreement with the results obtained from temperature jump experiments, which put into evidence the dissociation as well as the aggregation processes of CdS particles.

### Introduction

CdS colloids have received considerable attention because of their photocatalytic activity under visible light irradiation [1-4]. A notable development in this area was to prepare small colloidal semiconductor particles and to observe optical effects due to size quantization. When the characteristic dimension of semiconductor nanocrystals is comparable to (or smaller than) their bulk exciton diameter, they exhibit size-dependent optoelectronic properties due to quantum confinement of electrons, the most well-known example of which is the shift in the absorption spectra to shorter wavelengths with decreasing particle size [5-7].

The determination of ionization energies and of chemical nature of the defects and impurities is one of the basic problems in semiconductor physics. The present paper deals with the fluorescence emission of colloidal CdS under various conditions. It is known that on irradiation with visible light characterized by energies higher than the energy gap ( $E_g$ ), the main radiative processes which take place are the following:



---

\* Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, Bd Elisabeta 4-12  
RO-030018, Bucharest

## Experimental

We prepared colloidal CdS ( $8.73 \times 10^{-4}$  M) using the recipe of Kalyanasundaram et al. [4] as well as the variant modified by us in a previous paper [8], by replacing  $(\text{NH}_4)_2\text{S}$  with  $\text{Na}_2\text{S}$  (Fluka) in  $2 \times 10^{-4}$  M concentration and bubbling Argon during the synthesis. One used a styrene-maleic anhydride 1:1 copolymer as stabilizer and methylviologen (Sigma) for fluorescence quenching measurements.

The colloidal CdS was characterized by its absorption spectrum using an Unicam  $\alpha$  Helyos spectrophotometer and by its fluorescence spectrum recorded with an Aminco-Bowman spectrofluorimeter .

For temperature jump experiments we used a T-jump transient Spectrometer, Studien Messanlagen - Gottingen.

## Results and Discussions

### I. Particle size determination

The first aim of our study was to determine the particle size of the colloidal CdS synthesized.

#### Spectrophotometric measurements

On this purpose we used the equation [9]:

$$\varepsilon h\nu = k (h\nu - E_g \times e)^{1/2} \quad (4)$$

in which we fitted the experimental values of  $\varepsilon$  ( molar absorption coefficient) and  $h\nu$  resulted from the first exciton band of its absorption spectrum between 370-500 nm. One obtained a value of 2.6 eV for  $E_g$  with which one calculated the particle size  $d_p$  with Brus's equation [10]:

$$E_g = E + \frac{h^2}{2d_p^2} e (1/m_e^* + 1/m_h^*) - 3.6 e / 4\pi D d_p \quad (5)$$

where:  $m_e^* = 0,19 m_e$ ;  $m_h^* = 0,8 m_e$  ( $m_e = 9.11 \times 10^{-31}$  kg)

$e = 1.602 \times 10^{-19}$  C and D the dielectric constant:

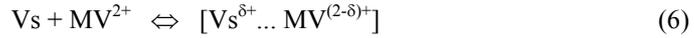
$$D = 5.7D_0, \quad D_0 = 8.854 \times 10^{-12} \text{ C}^2\text{J}^{-1} \text{ m}^{-1}$$

One obtained from equation (5) a particle diameter  $d_p$  around  $75 \pm 5$  Å.

#### Spectrofluorimetric measurements

By exciting the fluorescence emission with different wavelengths in the first exciton band of a fresh CdS colloid one observed a shifting toward the longer wavelength in the red region of the spectrum. We ascribed this behavior to the polydisperse CdS obtained from our synthesis in agreement with Lippens and Lannoo [12].

We determined the particle size also from the red fluorescence emission using a colloidal solution of  $1.75 \times 10^{-4}$  M CdS and methylviologen  $MV^{2+}$  as quencher. This emission is due to the sulfur vacancies Vs resulted from the synthesis in the CdS lattice. To evaluate the particle size applying Poisson statistics [11] one used  $MV^{2+}$  at very low concentration ( $10^{-8}$ - $10^{-9}$  M) so that practically it is total adsorbed onto particle surface. This interacts with sulfur vacancies forming a complex at the particle surface as follows:



which explains the red emission quenching as Fig. 1 shows.

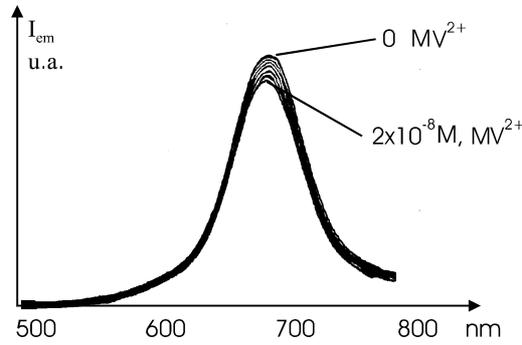


Fig. 1: The fluorescence quenching of CdS colloid by  $MV^{2+}$

Using equation (7):

$$r = \left( \frac{3MN}{4\pi\rho N_A} \right)^{1/3} \quad (7)$$

in which  $M$  is the molecular weight expressed in g,  $\rho$  sol density ( $0.99176 \text{ g/cm}^3$ ),  $N_A$  Avogadro's number,  $N$  the aggregations number (the number of CdS molecules per particle). From equation (8) one obtained  $N$ :

$$N = \frac{Q[\text{CdS}]}{[MV^{2+}]_{\text{ads}}} \quad (8)$$

where  $Q$  is the mean number of  $MV^{+2}$  molecules adsorbed per CdS particle. This parameter is correlated with the fluorescence quenching measurement by the equation:

$$I/I_0 = e^{-Q} \quad (9)$$

in which  $I$  and  $I_0$  are the fluorescence intensities in the presence and absence of  $MV^{+2}$ , respectively. This treatment lead to a number of 750 molecules/particle with a diameter of an average value  $70 \pm 5 \text{ \AA}$  for  $\lambda_{\text{ex}} = 380 \text{ nm}$  in good agreements with the value resulted from the absorption measurements taking into account the polydispersion of CdS sol.

## II. Kinetic determinations. T-jump experiments

Information on the dynamic of CdS particles we obtained by using the temperature jump method. This method changes suddenly the system temperature (few degrees) and follows the absorbance variation at  $\lambda = 436 \text{ nm}$  (in the absorption band of CdS).

Cizeron and Pileni (13) reported that they observed CdS nucleation by using stopped flow method, followed spectral too.

When the colloidal CdS is moderate aged (by keeping it of about 18 hours at  $60^\circ\text{C}$ ) the absorption band gap shifted toward longer wavelengths concomitant with the absorbance increasing on the whole spectral region (Fig. 2).

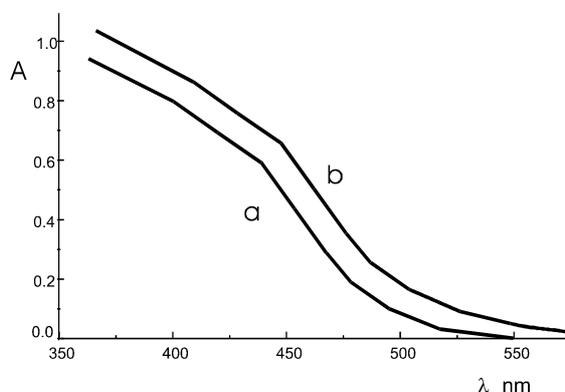


Fig. 2: The absorption spectra of colloidal CdS: a) fresh; b) moderate aged

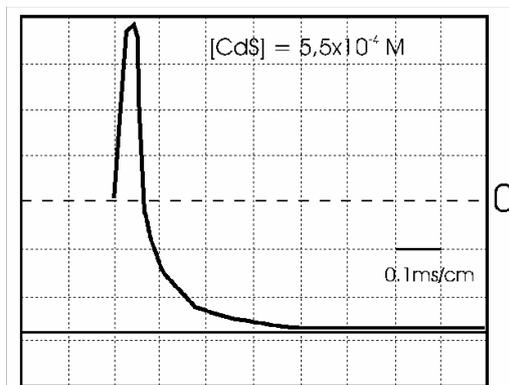
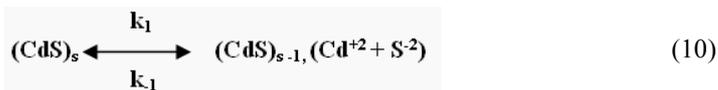


Fig. 3: T-jump relaxation curve of small CdS particles dissociation

In Fig. 2 the absorption spectrum of a moderate aged CdS positioned at higher absorption than the fresh one and with a band gap shifted to longer wavelengths suggests the growth of the particles. These spectral observations are in good agreement with our T-jump experiments.

The polydisperse CdS evidenced two types of processes in the time interval of  $60 \mu\text{s}$ - $60 \text{ ms}$ : fast processes as well as slower ones. We exemplified in Fig. 3 the fastest process.

We assigned the decrease of the absorbance in Fig. 3 (0.25 – 0.60 ms) to the fast process of the small particles dissociation according to the equilibrium:



where **s** is the molecule number in the **small** particles.

The slower processes contrary, present an increasing of the absorbance as Fig. 4 shows, in the time interval of 4.5 – 11.5 ms.

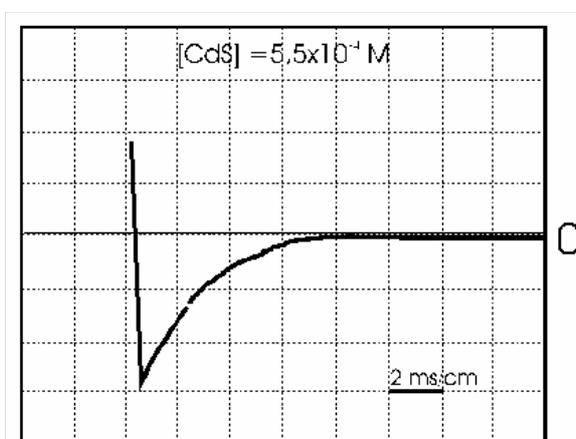
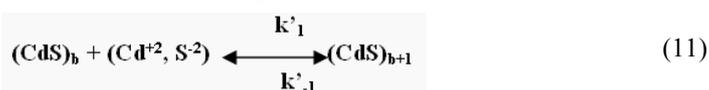


Fig. 4: *T*-jump relaxation curve of big CdS particles growth

We attributed this relaxation curve to the particle growth as follows:



where **b** is the molecule number in a **big** particle. These results suggest the growth of large particles at the expense of the smaller ones which dissociates.

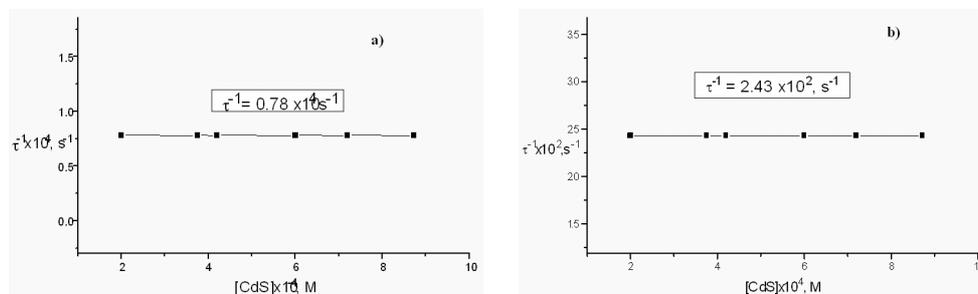
These two types of processes (10) and (11) assure the dynamic of CdS particles via Ostwald ripening [14].

Unfortunately, it was not possible to evaluate the rate constants of these processes because the reciprocal relaxation time  $\tau^{-1}$  was the same, independent to the initial CdS concentration as Fig. 5 a) and b) shows.

Such behavior is typical to an unimolecular process, characterized by the reciprocal value of the relaxation time  $\tau^{-1}$ :

$$\tau_s^{-1} = k_1 + k_{-1} \quad (12 \text{ a})$$

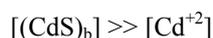
with a value  $\tau_s^{-1} = 0.78 \times 10^4 \text{ s}^{-1}$  for the dissociation process. This corresponds to the relaxation time of  $1.3 \times 10^{-4} \text{ s}$ .



**Fig. 5:** The variation of the relaxation time with CdS concentration:

a) for the fast dissociation process; b) for the slower growth process.

Although reaction (11) is a bimolecular one it proceeds as a pseudo first order kinetic due to our experimental conditions, namely:



In this case the relaxation time is:

$$\tau_b^{-1} = k'_{-1} + k'_{-1} \quad (12 \text{ b})$$

as Fig. 5 b) shows for the slowest aggregation process with  $\tau_b^{-1} = 2.43 \times 10^2 \text{ s}^{-1}$  corresponding to the relaxation time of  $4.1 \times 10^{-3} \text{ s}$ , three times lower than that of the dissociation process.

We consider that the results of T-jump experiments represent a confirmation of the growth and dissociation processes involved in the investigated system. It is for the first time when one used the temperature jump method on this aim in CdS colloidal system.

Temperature fluctuations are probably the most important factor influencing the stability of dispersions, according the classical Ostwald ripening (16).

## Conclusions

One synthesized colloidal CdS, which presents the following characteristics:

- an average diameter of around  $73 \pm 5 \text{ \AA}$  put into evidence by the fluorescence shifting to longer wavelengths with the exciting ones, suggesting a polydisperse colloid.
- the location of the aged colloidal CdS absorption spectrum above of the fresh one suggests the growth of the particles.
- T-jump experiments confirm the dynamic of colloidal CdS particles, by the increasing of the big particles on the expense of the small ones.

## REFERENCES

1. Bard, A.J. (1982) *J. Phys. Chem.* **86**, 172.
2. Henglein, A. (1986) *Ber. Bunsenges, Phys. Chem.* a) **86**, 241, b) **86**, 301.

3. Henglein, A. (1988) *Current Chemistry*, 143
4. Kalyanasundam, K., Borgarello, E., Dounghoug, D., Gratzel, M. (1981) *Angew. Chem.* **93**, 11,1012.
5. Brus, L.E. (1986) *J. Phys. Chem.* **90**, 2555.
6. Wang, Y., N. Herron, N. (1991) *J. Phys. Chem.* **95**, 525.
7. Brus, L.E. (1991) *Appl. Phys. A* **53**, 465.
8. Oncescu, T., Meahcov, L. (1999) *Int. J. of Photoenergy* **1**, 74.
9. Wang, Y., Suna, A., Mahler, W., Kasowski, R. (1987) *J. Chem. Phys.* **87**, 7315.
10. Brus, L.E. (1984) *J. Chem. Phys.* **80**, 4403.
11. Ramsden, J.J., Gratzel, M. (1984) *J. Chem. Soc., Faraday Trans.I* **80**, 919.
12. Lippens, P.E., Lannoo, M. (1989) *Phys. Rev. B*, **39**, 10935.
13. Henglein, A. (1988) Mechanism of Reactions on Colloidal Microelectrodes and Size Quantization Effects – *Current Chemistry* **143**, 170.
14. Cizeron, J., Pileni, M.P. (1995) *J. Phys. Chem.* **99**, 17410.
15. Fojtic, A., Weller, H., Hoch, U., Henglein, A. (1984) *Ber. Bunsenges. Phys. Chem.*, **88**, 969.
16. Wedlock, D.J. (1992) **Colloid and Surface Engineering Applications in the Process Industries**, Richard A. Williams, cap.3, 115.