Behavior of Semiconductor Nanoparticles in Polymer Matrices

Sandu Peretz, George A. Stanciu[a], Mihail Elisa[b] and Eugenia Teodor[c]

Institute of Physical Chemistry "I. Murgulescu", Department of Colloids, 202 Spl. Independentei, 060021, Bucharest, Romania, e-mail: peretz@icf.ro

[a] Center for Microscopy-Microanalysis and Information Processing, University "Politehnica" Bucharest, 313 Spl. Independentei, 060032, Bucharest, Romania

[b] National Institute of Research and Development Optoelectronics - INOE 2000, 1 Atomistilor St., 77125, Magurele, Romania

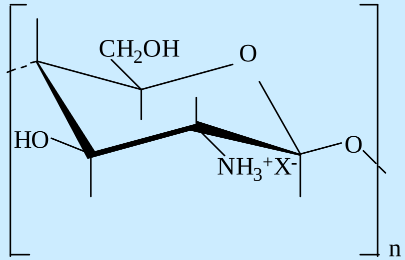
[c] National Institute of Research and Development for Biological Sciences, Centre of Bioanalysis, 296 Spl. Independentei, 060031, Bucharest, Romania

OBJECTIVES

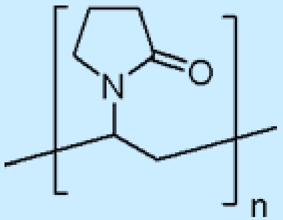
- To study the effect of some polymers with different electrical charges, like chitosan, alginate, carragennan, polyvinyl pyrrolidone or copolymer maleic anhidride/styrene, upon physico-chemical properties of nanoparticles generated in the polymeric phase.
- To calculate the size of nanoparticles by fitting the absorbance data with some specific equations from literature.
- To investigate the kinetic growth of nanoparticles with UV-Vis method.
- To study the fluorescence properties of the nanoparticles which depend on the nature of capping polymer.
- To synthesize films by dispersing nanoparticles in a polymeric matrix.
- To study the influence of nanoparticles coated with polymers on cultures of Vero cells.

POLYMERS

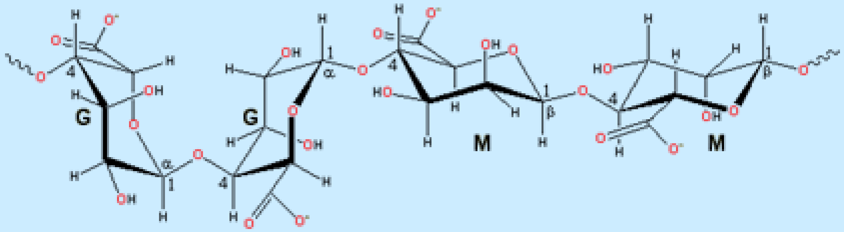
Chitosan



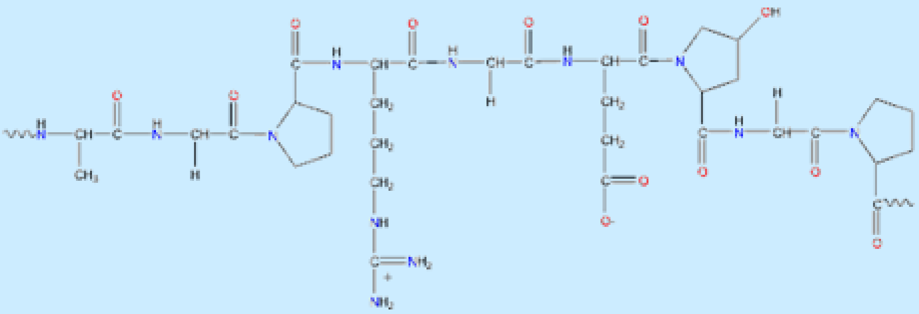
PVP



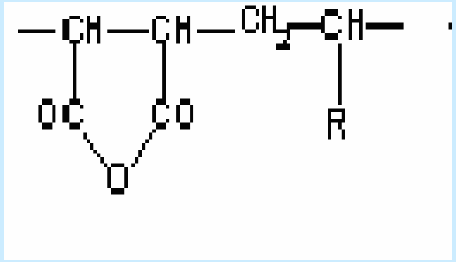
Alginate



k-Carrageenan



Copolymer maleic anhidride/stirene



$R=C_6H_5$

EXPERIMENTAL

Methods

- Confocal laser scanning microscopy (Leica TCS)
- UV-Vis spectroscopy (VARIAN Cary 100 Bio)
- Fluorescence spectroscopy (FluoroMax-4 HORIBA)
- TEM (JEX 200CX – JEOL)

NANOPARTICLES PREPARATION

$$Cd(NO_3)_2 + Na_2S \rightarrow CdS + 2NaNO_3 \quad (1)$$

Mechanism

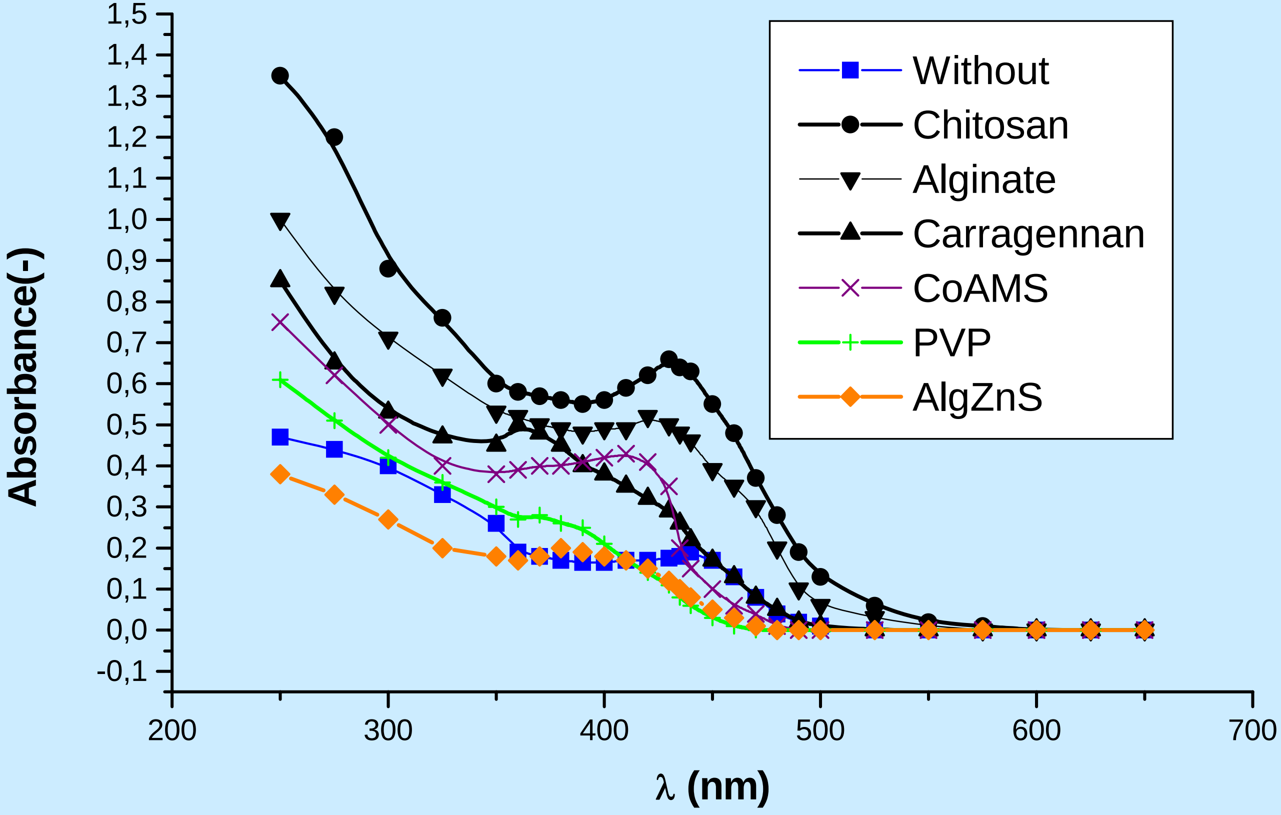
1. Formation of the CdS species: $Cd^{2+} + S^{2-} \rightarrow (CdS)_1$ (2)
2. Formation of aggregates: $(CdS)_m + (CdS)_n \rightarrow (CdS)_{n+m}$ $(m,n \geq 1)$ (3)
3. Growing of particles by addition of Cd^{2+} and S^{2-} ions:

   $(CdS)_n + S^{2-} \rightarrow (Cd_n S_{n+1})^{2-}$ (4)

   $(CdS)_n + Cd^{2+} \rightarrow (Cd_{n+1} S_n)^{2+}$ (5)
4. Termination will occur when the particle size becomes comparable to the droplet size.

$$ZnCl_2 + Na_2S \rightarrow ZnS + 2NaCl_2 \quad (6)$$

UV-Vis Spectroscopy



DETERMINATION OF PARTICLE SIZE

Determining the energy of the direct band gap (E_g) [1]

$$\frac{h\nu(A^2 - \sigma^2 h\nu)}{A^2} = E_g$$

Diameter of CdS nanoparticles (d_p) [2]

$$E_g - E_{g,bulk} = \frac{h^2}{2d_p^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) - \frac{3.6e^2}{4\pi\varepsilon d_p}$$

[1] Y. Wang and N. Herron, *J. Phys. Chem.*, **1991**, *95*, 525-532
[2] L.E. Brus , *J. Chem .Phys*, **1984,** *80*, 4403-4409

RESULTS

$\lambda_{\text{threshold CdS without}}$ = 480 nm $\quad$ $d_{P\ \text{calculated}}$ = 6.65 nm

$\lambda_{\text{threshold PVP}}$ = 490 nm $\quad$ $d_{P\ \text{calculated}}$ = 7.46 nm

$\lambda_{\text{threshold Carragennan}}$ = 495 nm $\quad$ $d_{P\ \text{calculated}}$ = 7.92 nm

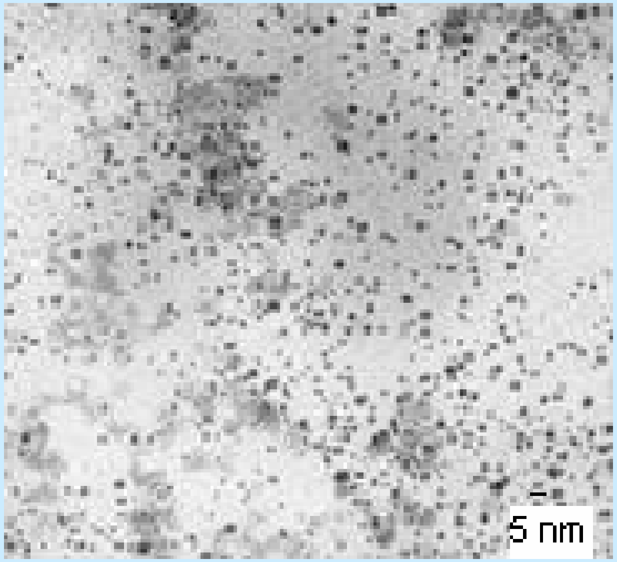
$\lambda_{\text{threshold CoAMS}}$ = 500 nm $\quad$ $d_{P\ \text{calculated}}$ = 8.41 nm

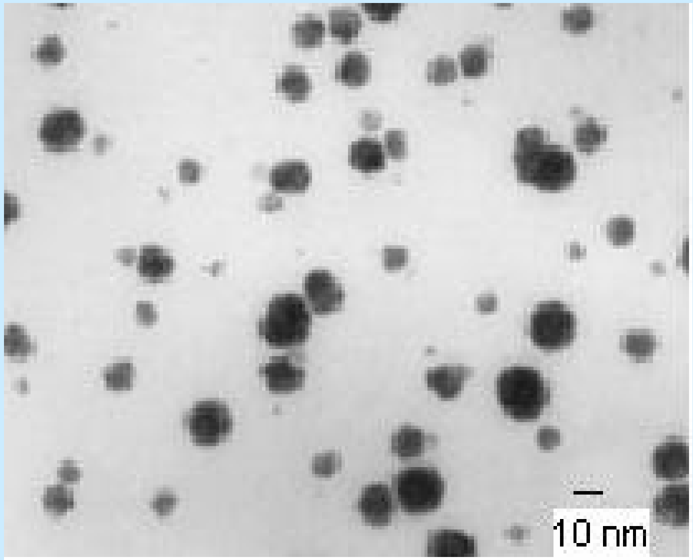
$\lambda_{\text{threshold Alginate}}$ = 505 nm $\quad$ $d_{P\ \text{calculated}}$ = 8.92 nm

$\lambda_{\text{threshold Chitosan}}$ = 520 nm $\quad$ $d_{P\ \text{calculated}}$ = 10.6 nm

$\lambda_{\text{threshold Alginate\_ZnS}}$ = 485 nm $\quad$ $d_{P\ \text{calculated}}$ = 7.01 nm

TEM MICROGRAPHS

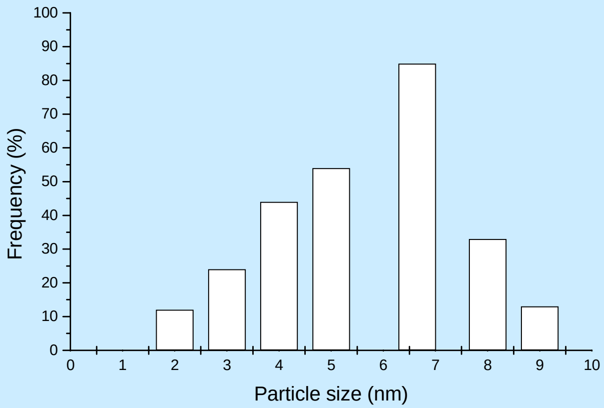




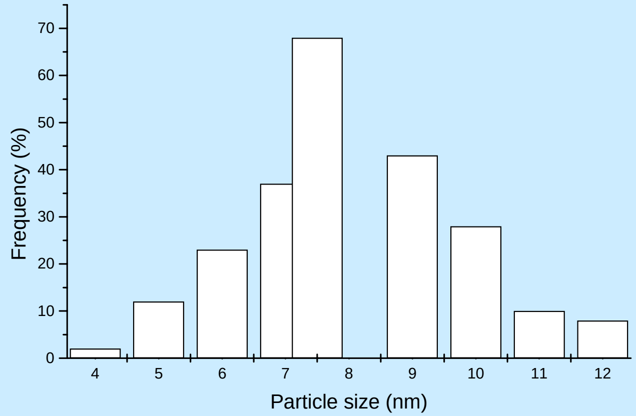
CdS without polymer

CdS coated with Chitosan

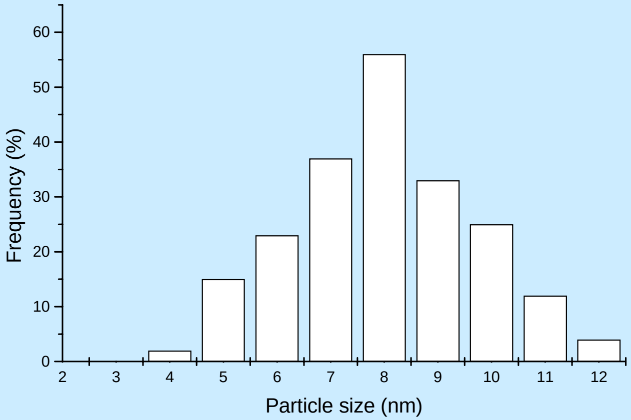
Computed size histograms



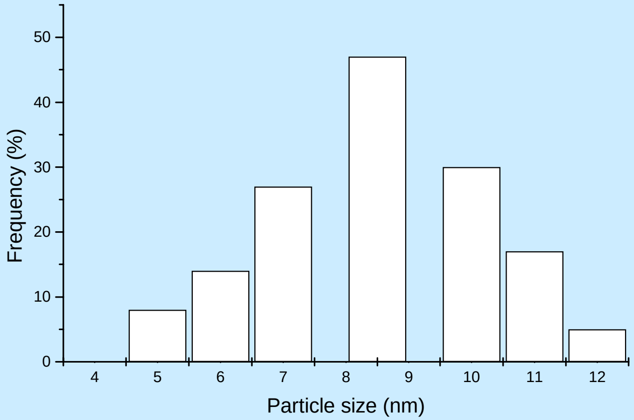
CdS without polymer



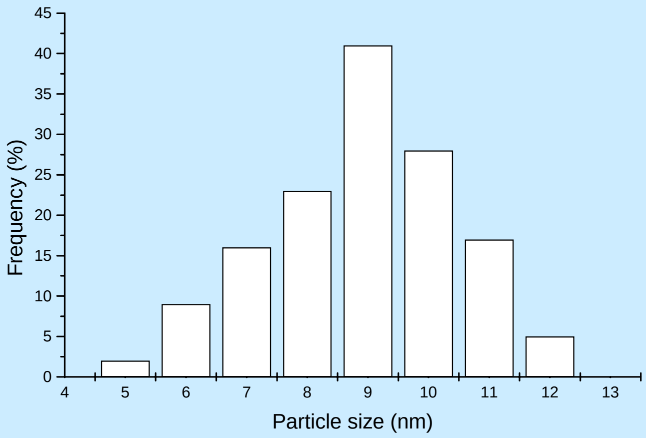
CdS coated with PVP



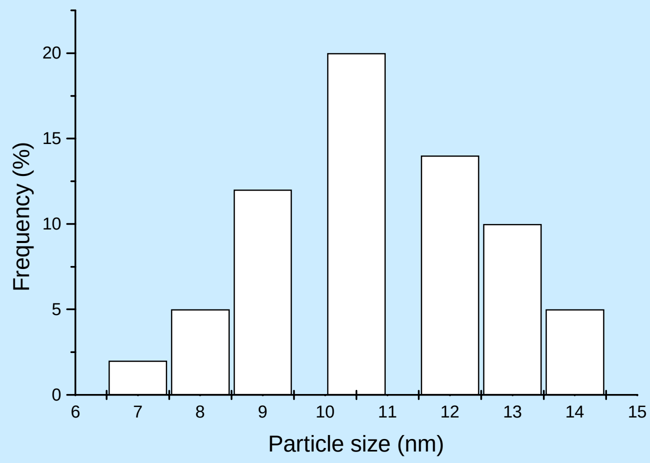
CdS coated with Carragennan



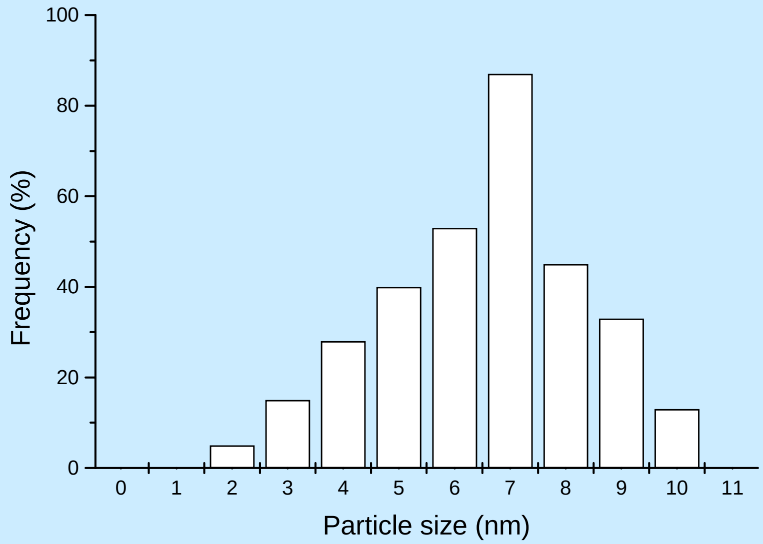
CdS coated with CoAMS



CdS coated with Alginate

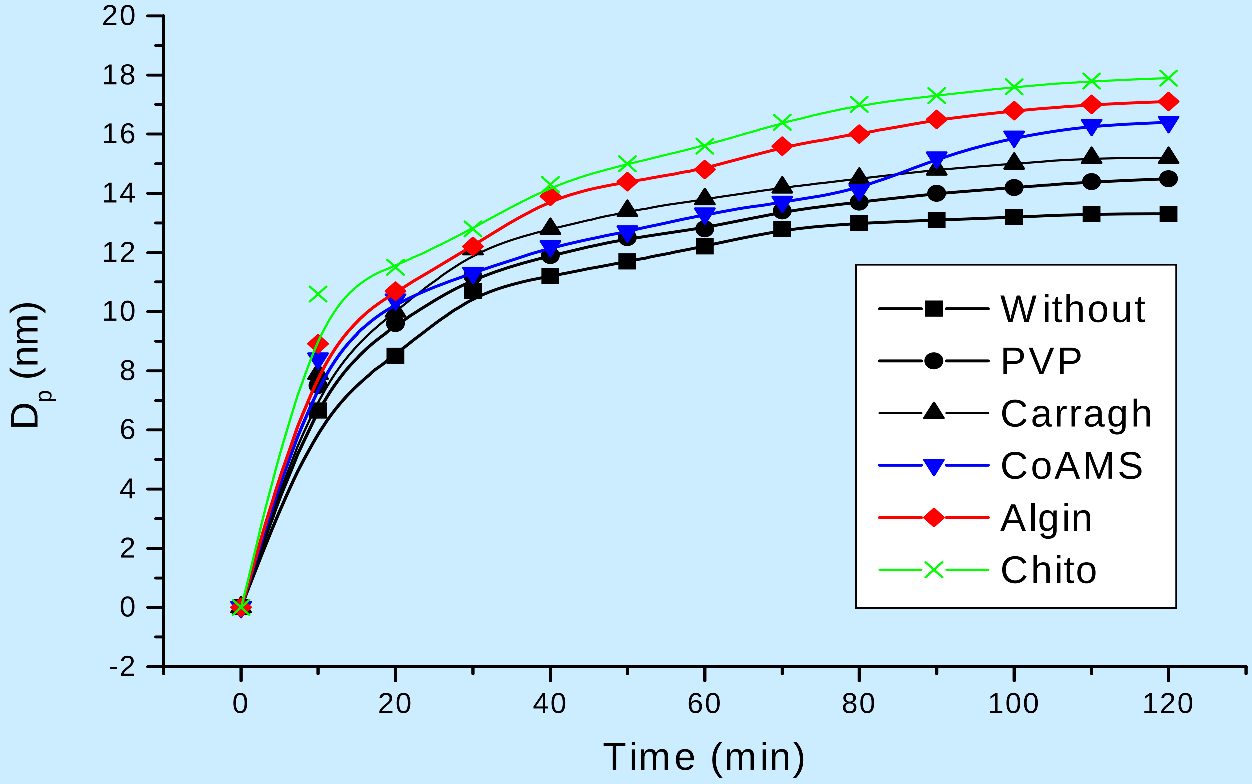


CdS coated with Chitosan

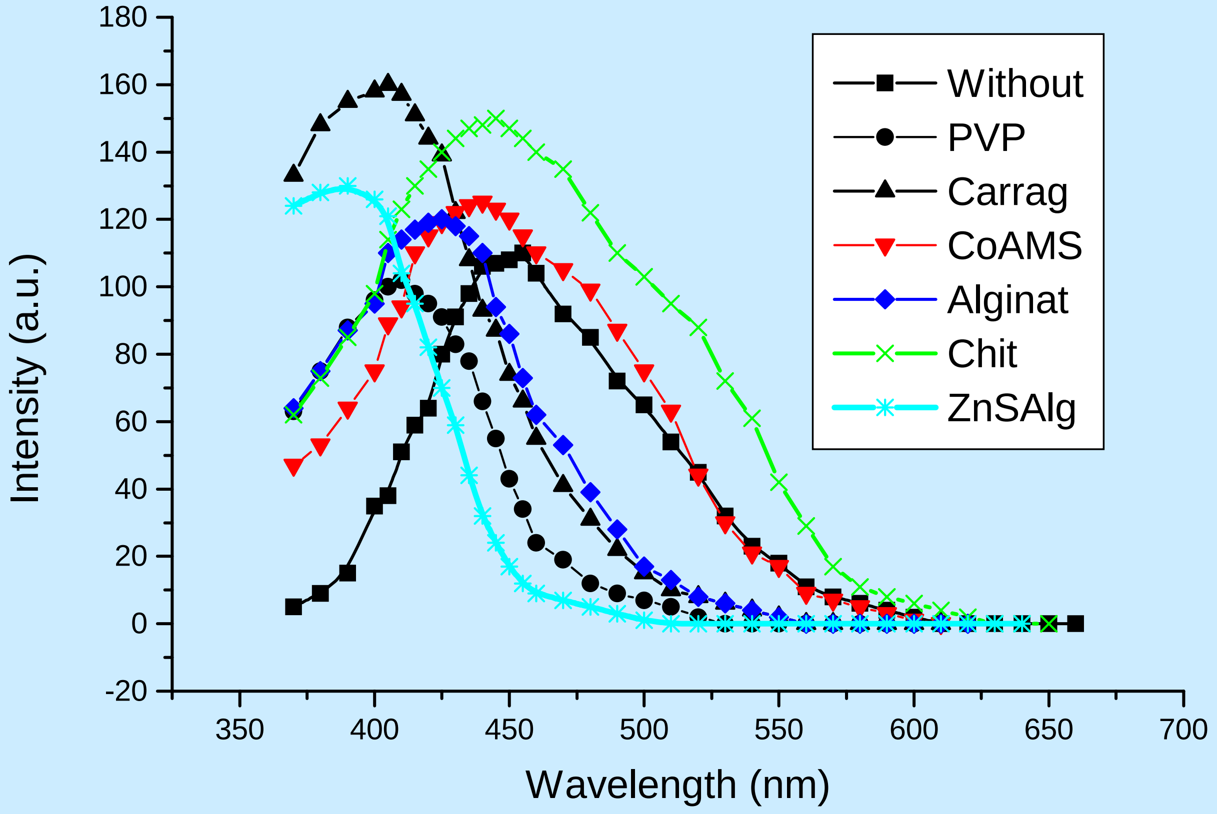


ZnS coated with Alginate

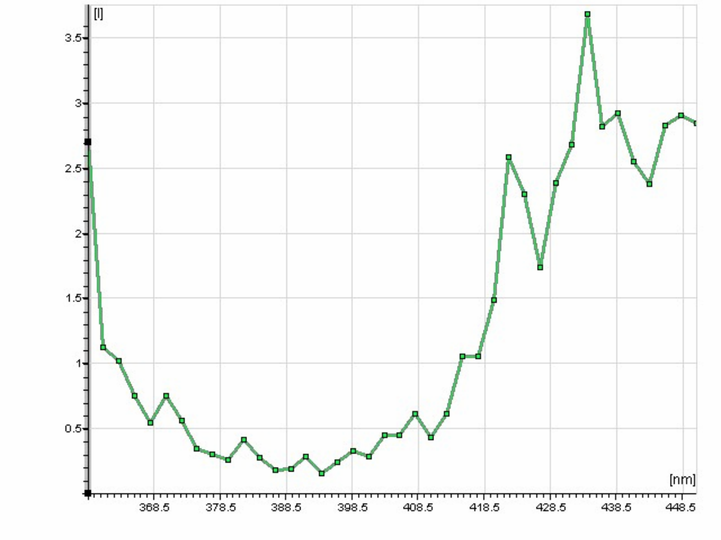
Kinetics of growth for CdS nanoparticles

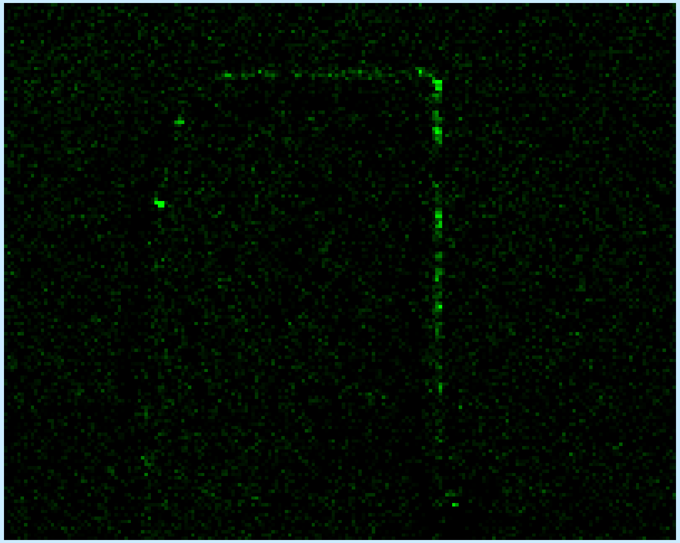


Fluorescence of the nanoparticles

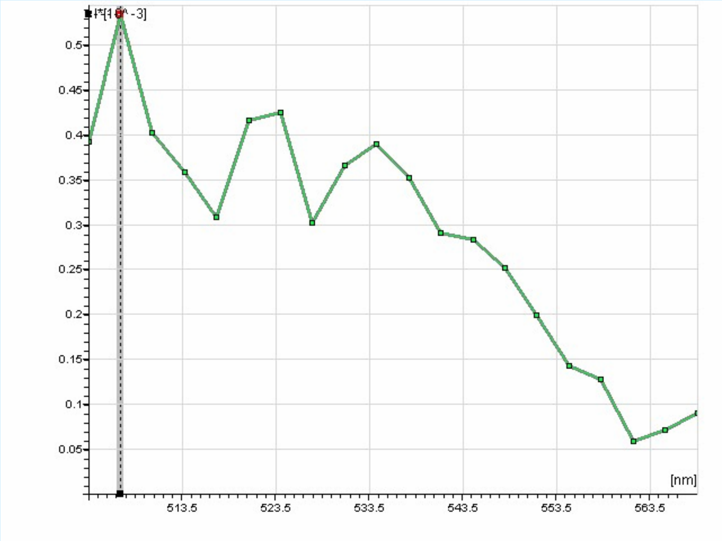


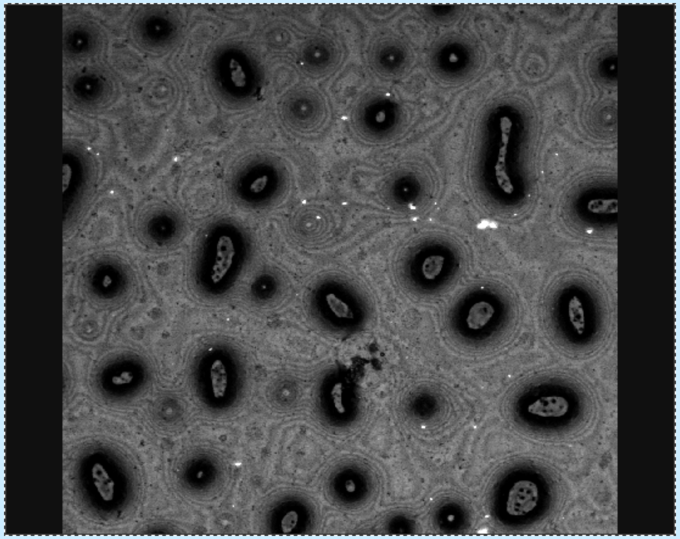
NANOSTRUCTURED FILMS



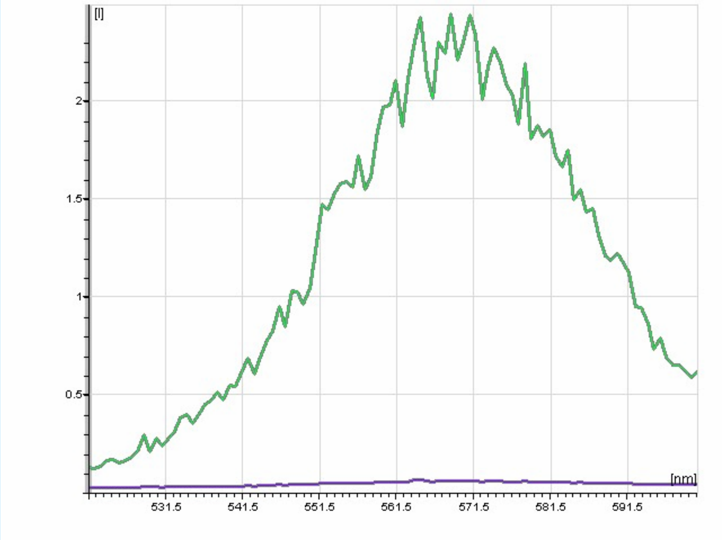


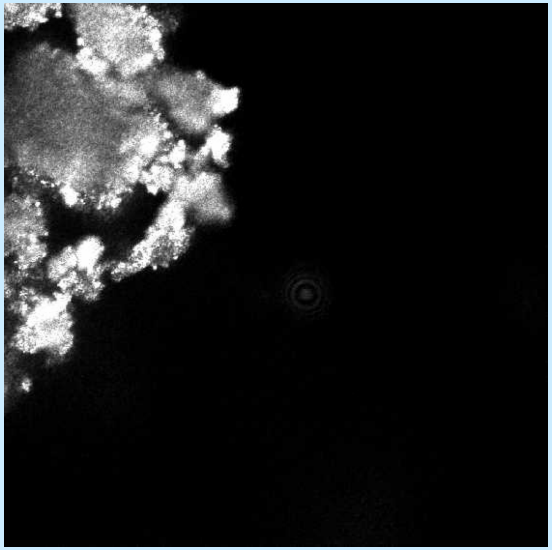
CdS in Chitosan polymeric film



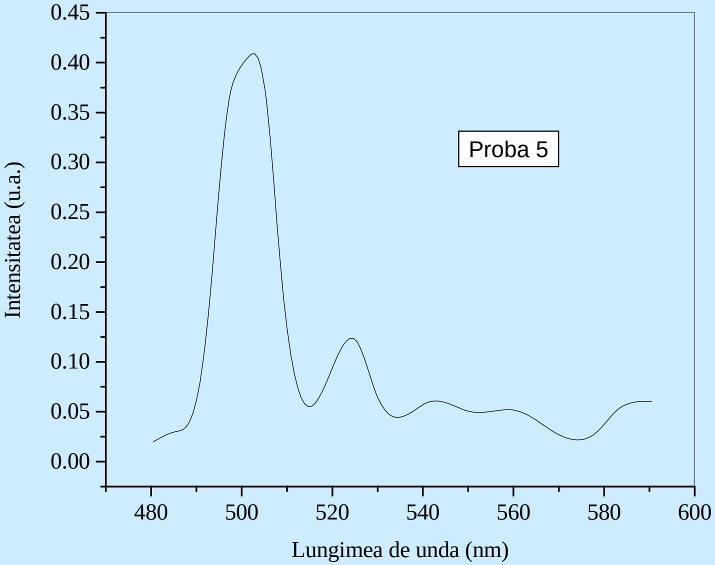


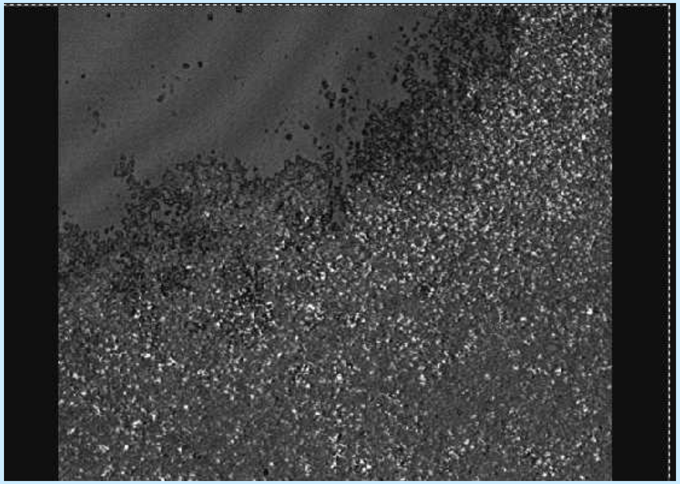
CdS in CoAMS polymeric film





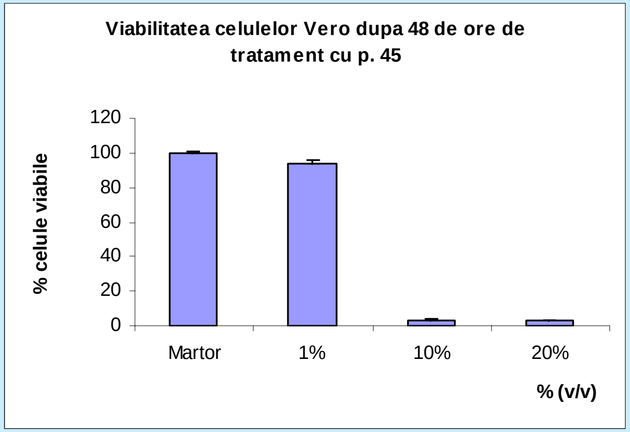
CdS powder in Carragennan polymeric film



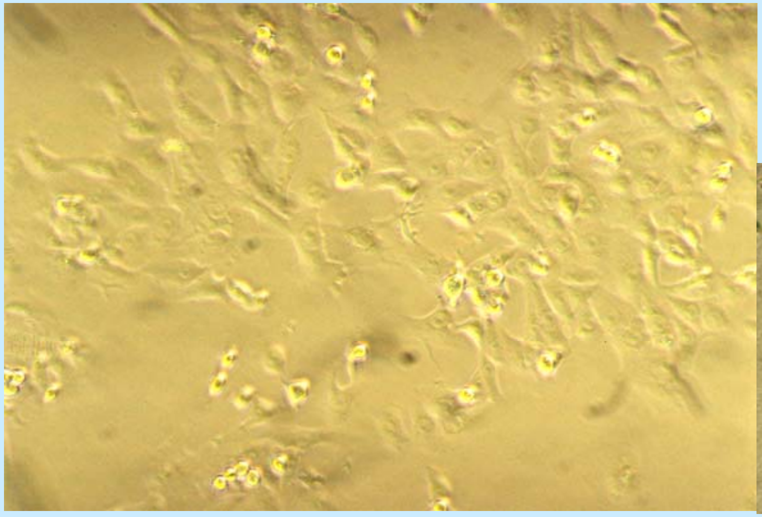


CdS in potassium silicate film

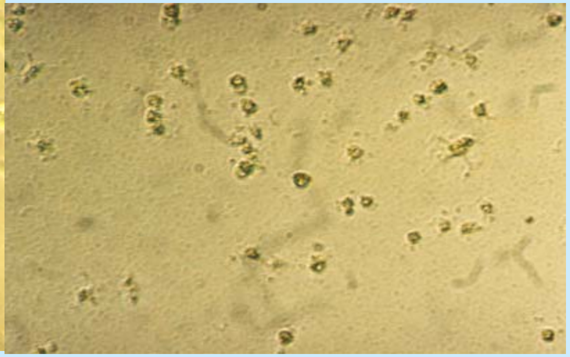
Behavior of Vero cells in presence of the nanoparticles



CdS-CoAMS

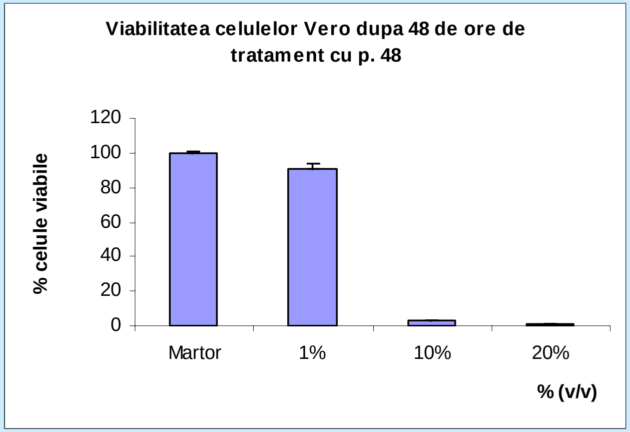


a

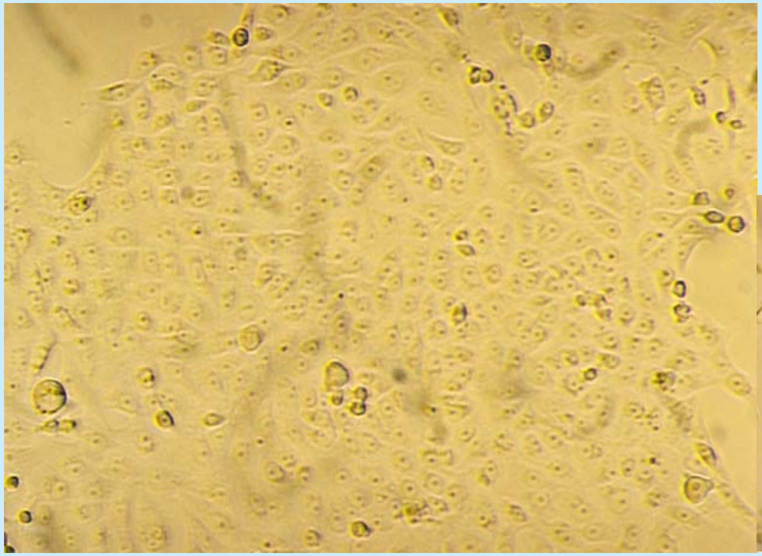


b

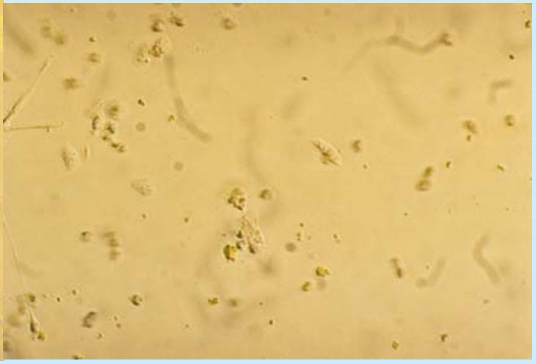
a) Vero Cells treated with 1% (w/w) sample containing CdS (CoAMS)
b) Vero Cells treated with 10% (w/w) sample containing CdS (CoAMS)



CdS-Alginate



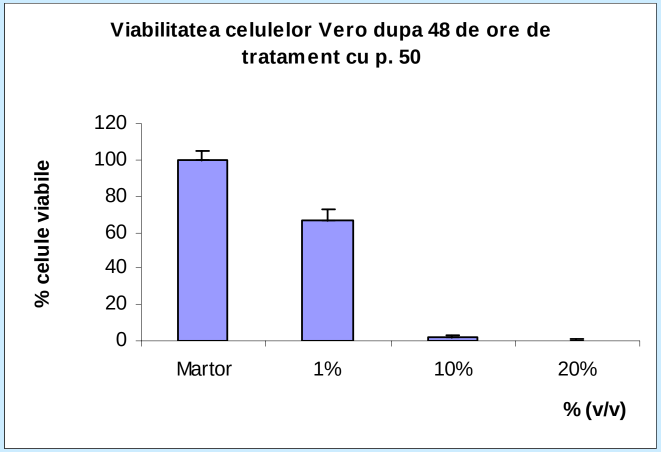
a



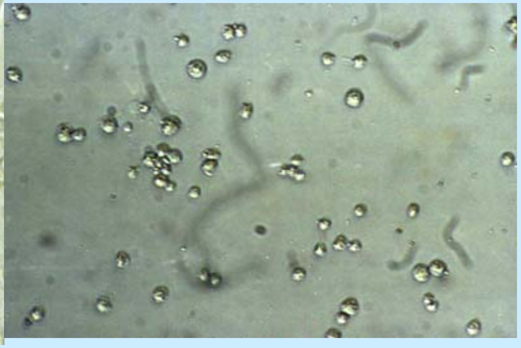
b

a) Vero Cells treated with 1% (w/w) sample containing CdS (Alginate)
b) Vero Cells treated with 10% (w/w) sample containing CdS (Alginate)

CdS-PVP



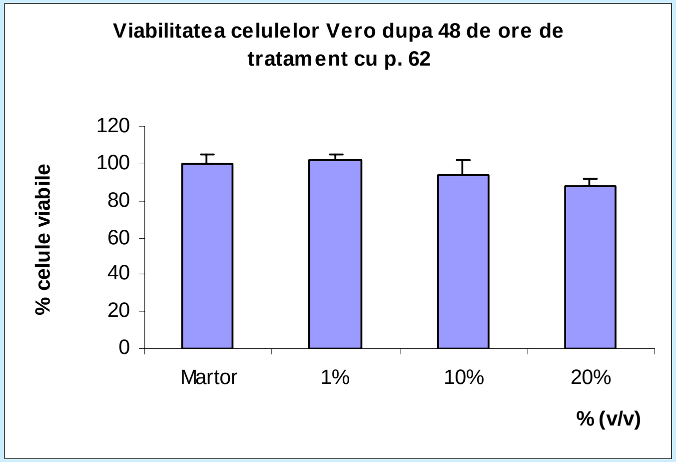
a

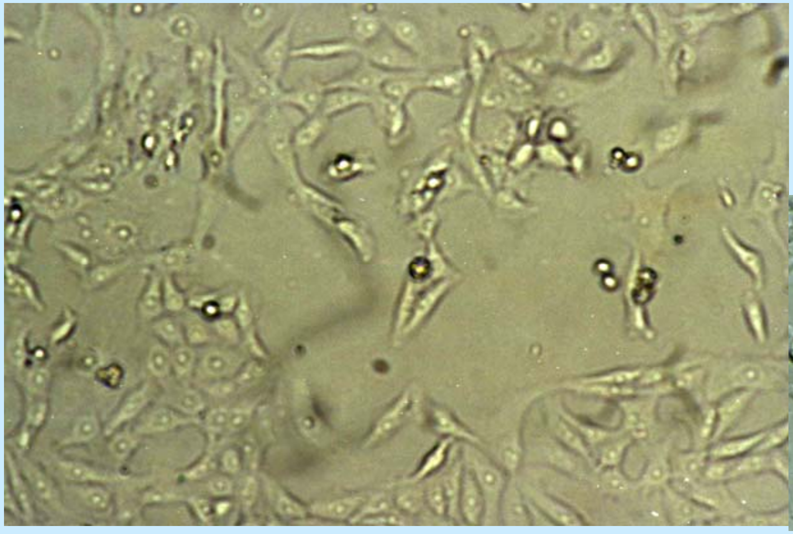


b

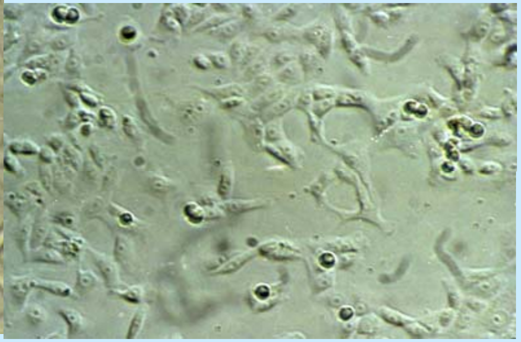
a) Vero Cells treated with 1% (w/w) sample containing CdS (PVP)
b) Vero Cells treated with 10% (w/w) sample containing CdS (PVP)

ZnS-Alginate





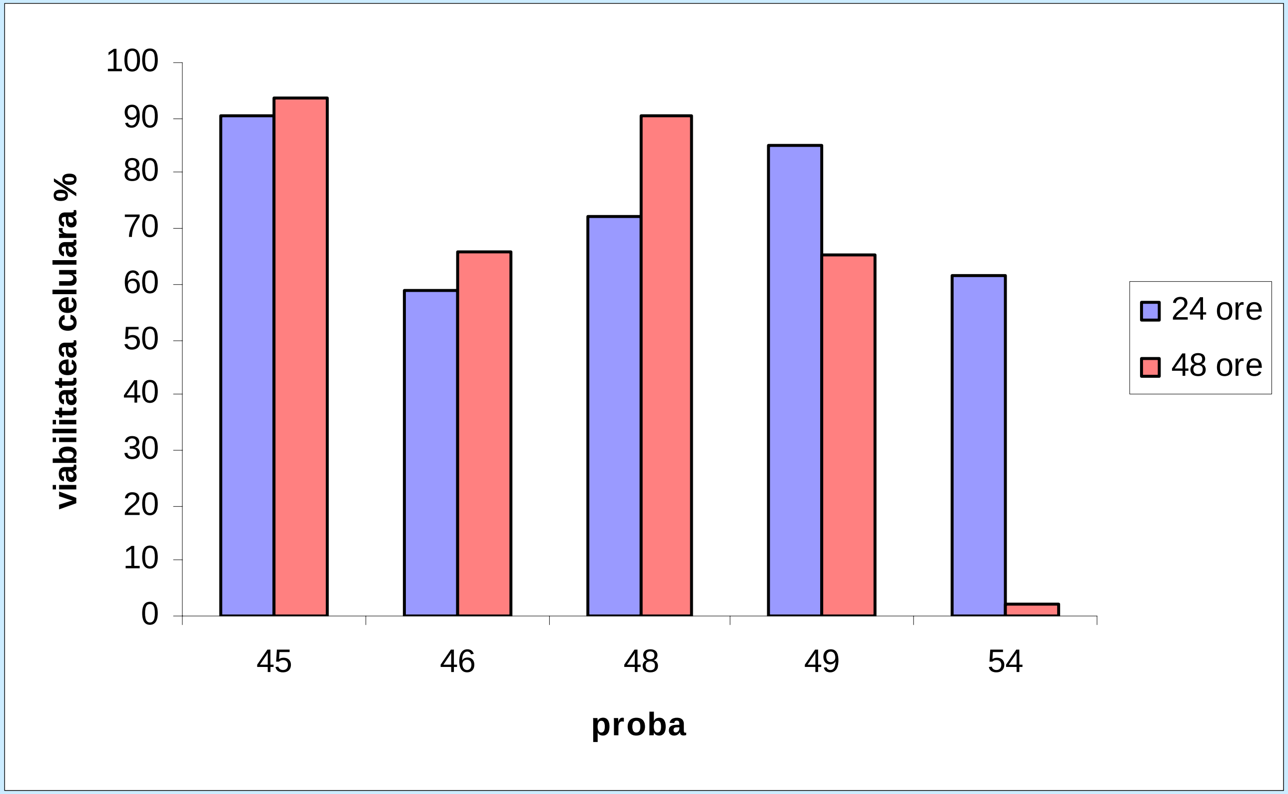
a



b

a) Vero Cells treated with 1% (w/w) sample containing ZnS (Alginate)
b) Vero Cells treated with 10% (w/w) sample containing ZnS (Alginate)

Vero cells cytotoxicity presented comparatively in 24 and 48 hours, concentration 10 μM



CONCLUSIONS

- We have elaborated a simple and efficient method for the obtaining semiconductor nanoparticles in polymers solution. The used polymers have an important role in the size control, the stability and like capping agent of the particles.

- The nanoparticles can exist long time in polymers solution and they can be used for the obtaining of films on glass support. The size of nanoparticles was determined by fitting the absorbance data with some specific equations from literature.

- The kinetic data from UV-Vis spectra show that the nanoparticles present an initial rapid formation, followed by a very slow growth process. The fluorescence properties depend on the nature of capping polymer.

- The samples containing CdS- CoAMS, CdS-Alginate, CdS-PVP, and ZnS-Alginate have the best behavior and the lower toxicity accountable to Vero cells.

- The toxicity diminishes up to 10 times by covering with polymer the semiconductor nanoparticles, and for the samples containing CdS-CoAMS, CdS-Alginate and especially ZnS-Alginate in concentrations of $1x10^{-5}$ M, the cell culture resists more than 24 hours; all these facts are the good premise for imagistic studies.

ACKNOWLEDGMENTS

This work was supported by funding from the National Authority for Scientific Research of Romania in the 51/2005 Excellence Research Project

VA MULTUMIM!