INSTITUTE OF PHYSICAL CHEMISTRY "I. MURGULESCU"
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SYNTHESIS, SIZE CONTROL AND STABILITY OF CdS NANOPARTICLES IN WATER/OIL MICROEMULSIONS CONTAINING POLYMERS

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ABSTRACT

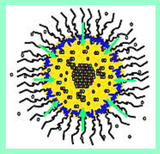
Cadmium sulfide nanoparticles have been synthesized by using a simple method in sodium bis(2-ethylhexyl) sulfosuccinate/ water/heptane system. The effect of some polymers and copolymers with different electrical charges, like alginate, chitosan, styrene/maleic anhydride (CoMAS) and vinyl acetate/maleic anhydride (CoMAVA), upon physico-chemical properties of cadmium sulfide nanoparticles generated in water/oil microemulsion was studied. The size of the cadmium sulfide particles was determined by fitting the absorbance data with some equations from quantum dots' literature, and the results were confirmed by using transmission electron microscopy method. The data of UV-Vis spectra recorded at various times shows that a very slow growth process follows an initial rapid formation of cadmium sulfide nanoparticles. The size of particle was controlled by changing the microemulsion molar ratio, water to surfactant, w_0 = [H2O]/[AOT]. The diameter of CdS nanoparticle increases with the increasing of the w_0 molar ratio; the growth of the particle size is more evident if polymers were added into the system. The used polymers have an important role in the size control and for stability of the cadmium sulfide semiconductor nanoparticles. The absorbance properties and the diameter of particles increases with the increasing concentration of cadmium ions, phenomenon that is more obvious in the presence of copolymers like vinyl acetate/ maleic anhydride, than in absence of the polymers. The influence of the added polymers on the fluorescence of CdS nanoparticles was investigated in order to prepare water-dispersible polymer stabilized quantum dots with high fluorescence. These nanoparticles coated with polymers present low toxicity against cultures of Vero cells for a determined period of time, and this behavior opens the possibility of imagistic investigations in the diagnosis.

The measurements were made during 2008-2009 at ICF, University and NIRDBS Bucharest.

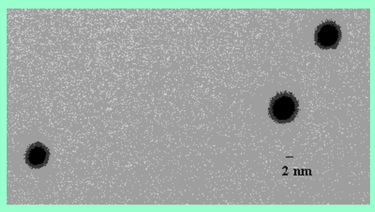
Formation of CdS

$$C_2H_5NS \rightarrow S^{2-} + \text{byproducts} \quad (1)$$
$$Cd^{2+} + S^{2-} \rightarrow (CdS)_1 \quad (2)$$
$$(CdS)_m + (CdS)_n \rightarrow (CdS)_{n+m}\ (m,n \geq 1) \quad (3)$$
$$(CdS)_n + S^{2-} \rightarrow (Cd_n S_{n+1})^{2-} \quad (4)$$
$$(CdS)_n + Cd^{2+} \rightarrow (Cd_{n+1} S_n)^{2+} \quad (5)$$

CdS nanoparticle inside of microemulsion droplets



TEM Image



CdS particles synthesized in presence of CoMAVA copolymer

The sequence of the diameter values of nanoparticles

$$d_{pChitosan} > d_{pAlginate} > d_{pCoMAVA} > d_{pCoMAS} > d_{pWithout\ polymer}$$

Determination of the particle size

Exciton energy of small particles

$$\Delta E = \frac{h^2\pi^2}{2R^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right] - \frac{1.786e^2}{\varepsilon R} - 0.248E^* \quad (6)$$

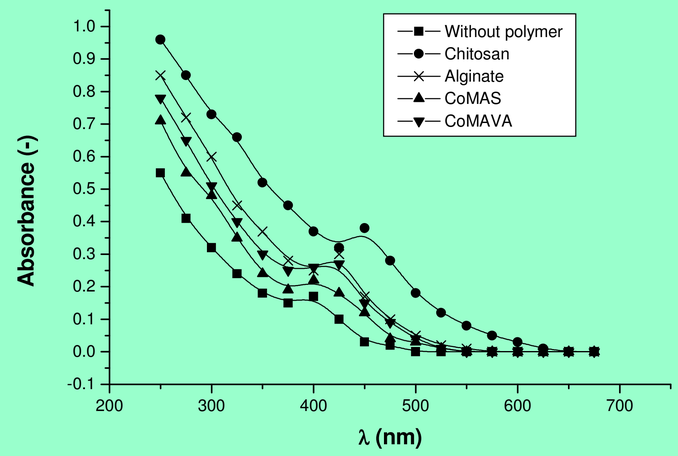
Threshold wavelength (λs) values from UV-Vis spectrum

$$\left(\frac{A}{\lambda}\right)^2 = K\left(\frac{1}{\lambda} - \frac{1}{\lambda_s}\right) \quad (7)$$

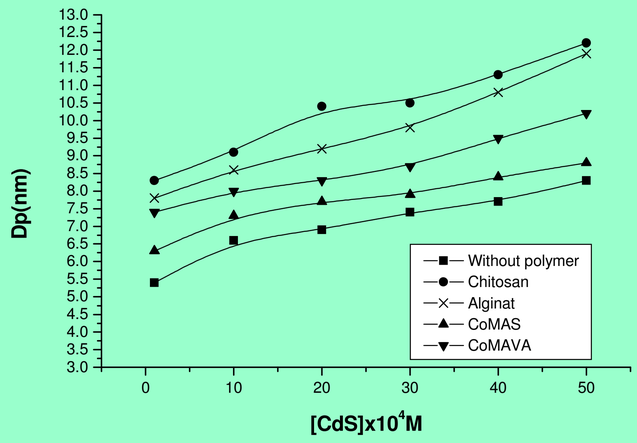
λs was used for estimation of the particle diameter

$$\lambda_s = 237.4 \cdot d_p^{0.168} \quad (8)$$

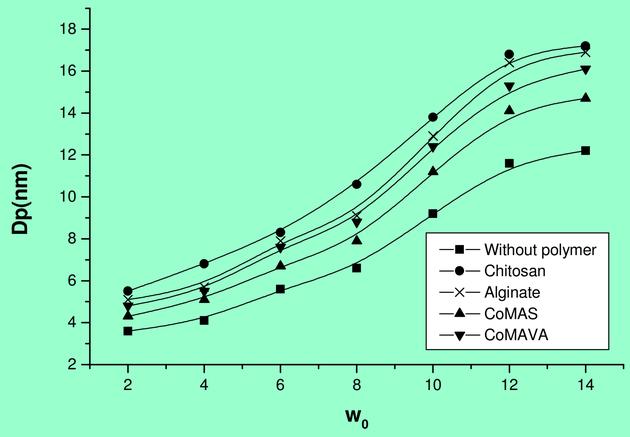
CdS absorption spectrum function the type of polymer



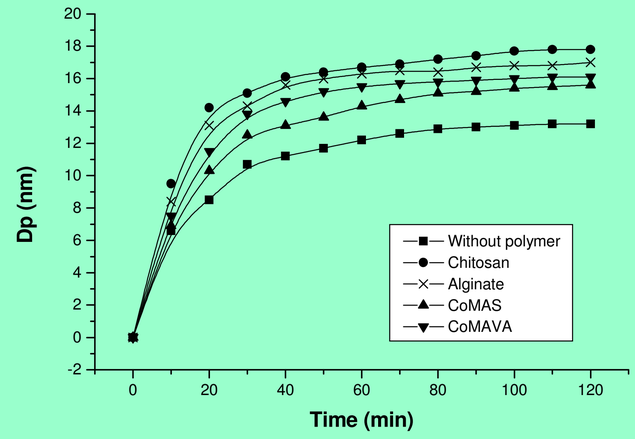
Effect of w_0 ratio on diameter of CdS particles



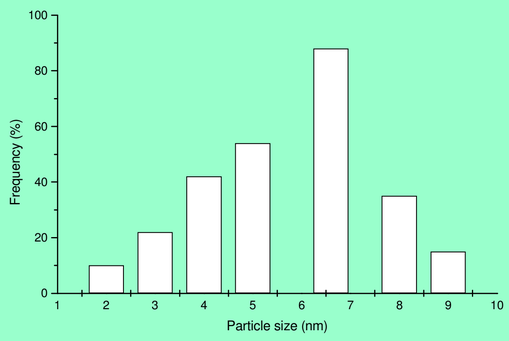
Effect of CdS concentration on the diameter of nanoparticles



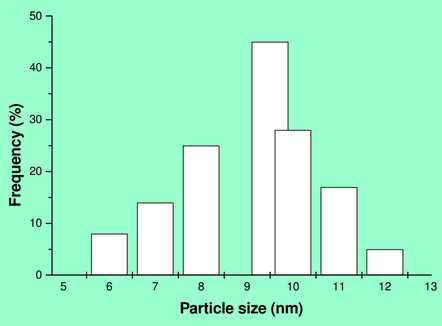
Kinetics experiments



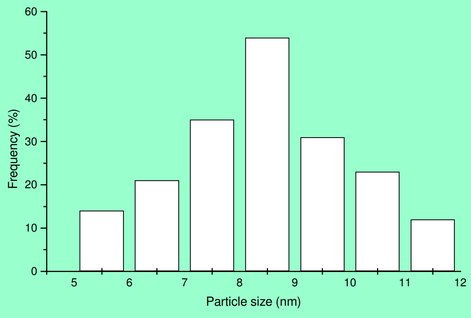
Size histogram of CdS nanoparticles



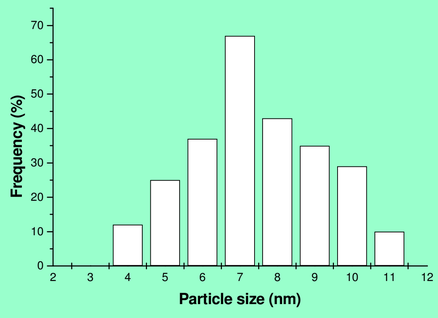
CdS without polymer



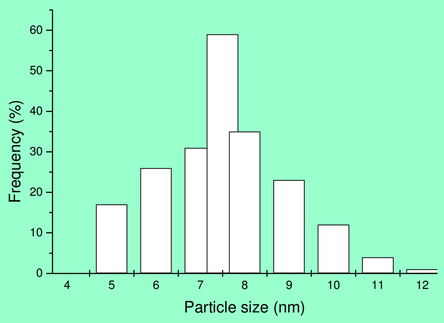
CdS with chitosan



CdS with alginate

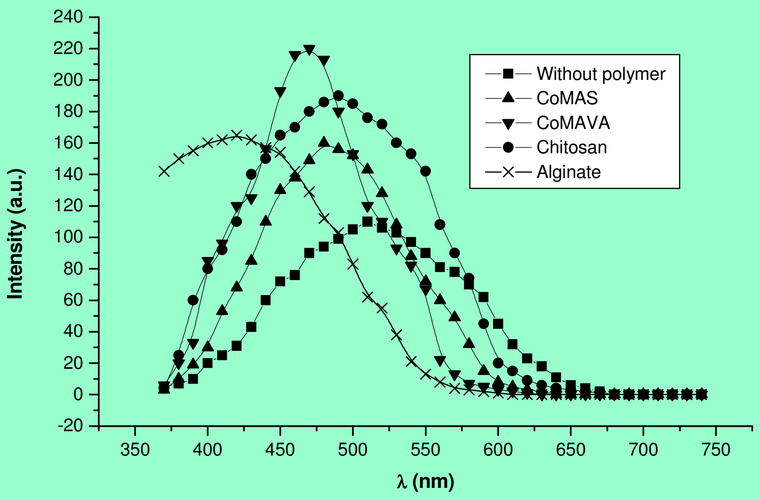


CdS with CoMAS

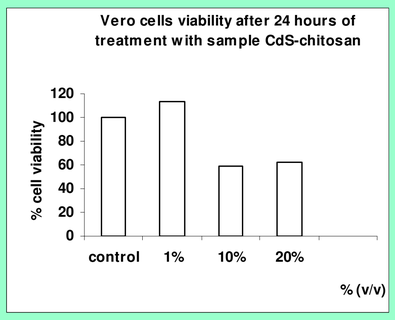


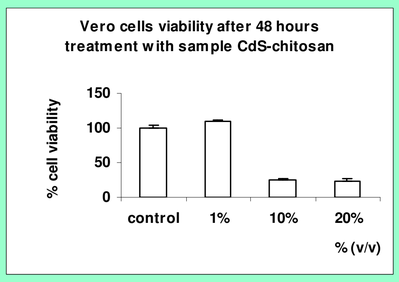
CdS with CoMAVA

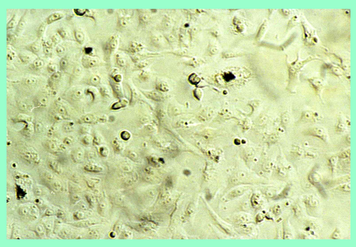
Fluorescence of CdS nanoparticles



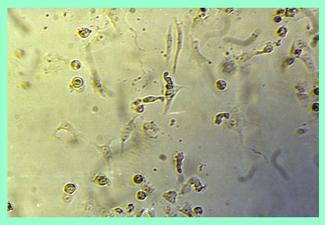
Effect of CdS nanoparticles on behavior of Vero cells







Vero Cells treated with 1% (w/w) sample containing CdS-Chitosan



Vero Cells treated with 10% (w/w) sample containing CdS-Chitosan

CONCLUSIONS

- Cadmium sulfide nanoparticles were prepared in water/oil microemulsions by two methods, in the presence and absence of polymers. The used polymers have an important role in the size control, the stability and like capping agent of the particles.
- The size of the cadmium sulfide particles was determined by fitting the absorbance data with equations quantum dots' literature, and the results were confirmed by using transmission electron microscopy method.
- The molecular chain and the electrostatic repulsion of the added polymer in the system could prevent the aggregation of the nanoparticles during their growth.
- The diameter of the particles increases with the increasing concentration of cadmium ions, phenomenon that is more obvious in the presence of copolymers like vinyl acetate/ maleic anhydride, than in absence of the polymers.
- The fluorescence of CdS nanoparticles depends on the nature of additive. The fluorescence intensity of CdS has an important increase in presence of vinyl acetate/maleic anhydride copolymer.
- These nanoparticles coated with polymers present low toxicity against cultures of Vero cells for 24 hours, and this behavior opens the possibility of imagistic investigations in the diagnosis.

REFERENCES

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