

Cadmium sulphide nanoparticles embedded in polymeric matrices

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Semiconductor nanoparticles represent a very interesting research topic mainly for the optoelectronics applications. The semiconductor particles exhibit properties dependent on the crystallites size, such as the band gap width and the linear optical characteristics (transmission and fluorescence cut-off) besides the non-linear characteristics (refractive index, second and third harmonic generation, two photons absorption, etc). The paper presents the synthesis of CdS nanocrystals and their integration in polymeric matrix. The effect of some polymers with different electrical charges, like polyvinyl alcohol, polyvinyl pyrrolidone, or copolymers maleic anhydride/styrene, maleic anhydride/vinyl acetate upon the physico-chemical properties of nanocrystals generated in the aqueous phase was studied. The synthesized nanocrystals were dispersed in polymeric matrix and then were applied on glass support to form films. The properties of the prepared nanoparticles and also the deposited films were investigated by confocal laser scanning microscopy, UV-VIS and fluorescence spectroscopy. In this work we also deal with obtaining of thin films based on colloidal CdS imbedded in potassium silicate-based inorganic polymer. The starting solution was prepared by mixing CdS 10^{-4} M aqueous colloidal solution with SSK (potassium silicate solution) aqueous solution ($K_2O/SiO_2=1/5$). We prepared several precursor solutions with CdS/SSK=1/1; 2/1; 3/1; 1/2; 1/3 ratios. The films have been obtained by the deposition of the above-mentioned mixture on a silicate glass substrate, by means of a special aluminum device based on "dragging method". After heat treatment, the films have been characterized by fluorescence spectroscopy, which revealed emission peaks at 450 nm, 465 nm, 500 nm, 525 nm and 540 nm, depending on the size of CdS nanocrystals. The microstructure of the films was proved by TEM (transmission electronic microscopy) analysis which presented the relative homogeneous morphology of the films.

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1. Introduction

The semiconductor nanoparticles exhibit size dependent properties, size quantum effect such as a blue shift of absorption onset, a change of electrochemical potential band edge, and an enhancement of photocatalytic activities, with decreasing crystallite size [1] Cadmium sulphide, a direct gap material with E_g of 2.42 eV at room temperature, can be used for photoelectronic devices [2].

For the semiconductor crystallite, its electronic properties start to change if the diameter approaches to the Bohr diameter; this is the so-called quantum size effect, which can be observed as a blue shift in the optical bandgap. By incorporation of small semiconductor clusters into solid matrices such as polymers and glasses the problems associated with colloidal solutions are solved [3].

In the case of CdS, quantum size effect occurs as the crystallite diameter is comparable or below the exciton diameter of 5-6 nm. Many techniques have been explored to synthesize small clusters, mostly II-VI such as CdS, in

the nanometer size regime in a variety of media, such as micelles, polymers, glasses, solutions, thin films and zeolites [4-6].

The modification of CdS nanocrystals surface prevents their aggregation and sedimentation and improves the photoluminescence properties [2]. During the wet chemical synthesis of nanoparticles, organic stabilizers are usually used to prevent them from aggregation by capping their surfaces. In this purpose the use of polymers and copolymers is the optimal solution. The reason is that the polymer matrices provide for processability, solubility, and control of the growth and morphology of the nanoparticles [7]. In this paper we report a simple synthetic procedure of CdS nanoparticles that, besides formation, allows coating with different polymers to improve their physico-chemical properties. By dispersing the synthesized CdS nanocrystals in a polymeric matrix and also in potassium silicate matrix some films have been prepared. We investigated the growth and morphology of the nanoparticles and characterized the properties of deposited films by using confocal laser scanning

microscopy, UV-VIS spectroscopy and fluorescence spectroscopy.

2. Experimental

2.1. Materials

The reactants, cadmium nitrate tetra hydrate $\text{Cd}(\text{NO}_3)_2 \times 4\text{H}_2\text{O}$, from Aldrich, and sodium sulphide nona hydrate ($\text{Na}_2\text{S} \times 9\text{H}_2\text{O}$), from Fluka, were analytical grade purity. The polymers: polyvinyl pyrrolidone K60 (PVP) 45% water, polyvinyl alcohol (PVA) 89% hydrolyzed were supplied by Fluka, and were used without further purification. The copolymers, styrene/maleic anhydride 1:1 with $M = 60,500$ (CoSMA), vinyl acetate/maleic anhydride 1:1 with $M = 90,000$ (CoVAMA) were prepared as laboratory samples at Macromolecular Chemistry Institute - Iasi (Romania). The water used in the experiments was Millipore filtered.

2.2. Preparation of nanoparticles

Therefore two methods were used:

Method 1. A mixture formed by an aqueous solution of Na_2S with the concentration $2.4\text{-}5.0 \times 10^{-3}$ M and the polymer or copolymer in concentration of 0.2 % (weight) was prepared. Afterwards, this blend was mixed under rapid stirring (300 rpm) with a second aqueous solution of $\text{Cd}(\text{NO}_3)_2 \times 4\text{H}_2\text{O}$ of concentration 1×10^{-3} M, and nitrogen gas was bubbled throughout system.

Method 2. The cadmium ions in the solution were obtained from the solubilization in the purified water of salt as cadmium nitrate, and were mixed with a solution of reducing agent such as sulphide ions (Na_2S). Colloidal cadmium sulphide particles were prepared by mixing quickly (at 300 rpm) the two solutions, afterwards these were introduced in a 0.2% polymer solution; the system was purged with N_2 gas for 30 minutes to prevent the photocorrosion and the formation of the colloidal sulphur. The aqueous solutions containing $\text{Cd}(\text{NO}_3)_2$ and Na_2S were freshly prepared and were used over short period from their preparation. The used copolymer was dissolved in a solution alkalized with NaOH 0.1N and the pH of the Na_2S aqueous solution was in the range of 9.5-11.

2.3. Preparation of the films

The films have been obtained by mixing CdS colloidal solution with a polymer solution. The mixture was stirred for five minutes. The films have been obtained by the deposition of the above-mentioned mixture on a soda-lime-silicate glass substrate, by means of an aluminium device having an inner hole and an aperture at the bottom, with a slope angle of 15° . The films have been dried at $105\text{-}120^\circ\text{C}$, for 5-10 min. After cooling the samples to

the room temperature, the films have been protected with aluminium foil.

Another way to prepare films, in this case in inorganic solution, was: the synthesized CdS nanocrystals were dispersed in potassium silicate matrix (SSK) and then were applied on glass support when the water is evaporating to form films.

Several samples were prepared at different CdS/SSK ratios, namely: 1:1; 2:1; 3:1; 1:2 and 1:3.

2.4. Methods

The absorption spectra of CdS nanoparticles were obtained by using a VARIAN Cary 100 Bio UV-Vis spectrophotometer and the fluorescence spectra were made by using a FluoroMax-4 HORIBA spectrofluorometer. The samples for TEM observations were prepared as follows. The particles were redispersed in ethanol 60 seconds by ultrasonication with a Sonifire model 250 apparatus (Branson). A drop of this dispersion was put onto a copper mesh with microgrid (Nisshin EM type) and dried under vacuum. Transmission electron microscope (TEM) observations were made by using a JEX 200CX (JEOL) instrument. A confocal laser scanning microscope (CLSM) fitted with fluorescence device (Leica) was used for films measurements.

3. Results and discussion

It has been experimentally documented that the precipitated uniform particles are typically polycrystalline and that their formation involves two distinct dynamical stages [8]. In the first process nanosize crystalline precursors, primary particles, are nucleated in supersaturated solution, while in the second process, these primary particles aggregate into larger colloids, secondary particles [9].

Colloidal cadmium sulphide particles were prepared by mixing two solutions one containing metal ions (Cd^{+2}) and other sulphide ions (S^{-2}) into aqueous-polymer system (see Experimental part). The formation mechanism of these particles was described by Towey and co-workers [10]. The synthesis of cadmium sulphide nanoparticles involved three steps: the chemical reaction step, the nucleation step and the particle growth step. The Ostwald ripening may also occur but this process involves dissolution of the solid.

For determination of the cadmium sulphide particles size, some of their specific properties were used.

The studies of Weller et co-workers has tried to correlate the cadmium sulphide particle size with the absorption spectra. They showed the experimental correlation of threshold wavelength and the particle threshold diameter [11].

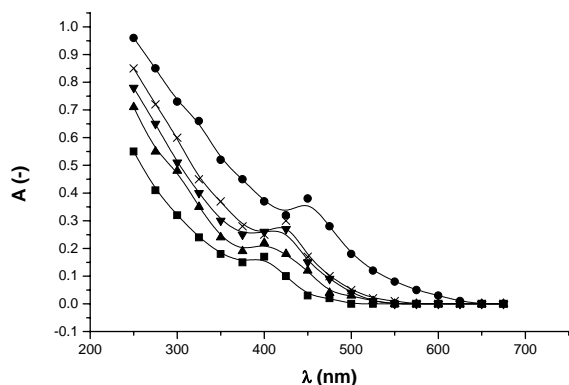


Fig. 1 - Absorption spectra of CdS nanoparticles: (■) without polymer; coated with: (●) PVA, (▲) PVP, (▼) CoVAMA, (×) CoSMA; $C_{[CdS]} = 1 \times 10^{-5} M$, 10 minutes after preparation

We can see from Fig.1 that the coated CdS samples present a displacement of the absorption peaks to the higher wavelengths and an increasing of the absorption intensities for the capped particles.

Excitation of the nanocrystals with energies above the bandgap leads to the promotion of an electron to the conduction band, leaving behind a hole in the valence band of the semiconductor. The electron and the hole can form a bound state called an exciton, and the characteristic size of this electron-hole bound state is often referred to as the Bohr radius. The Bohr radius a_B depends on the materials properties and it is given by [3]:

$$a_B = \frac{h^2 \varepsilon}{e^2} \left[\frac{1}{m_e} + \frac{1}{m_h} \right] \quad (1)$$

where h is Plank's constant, e is the elementary charge of an electron, ε is the bulk dielectric constant, and m_e and m_h are the effective masses of the electrons and holes, respectively. In the case of semiconductor particles, there is a correlation between the absorption spectrum and the energy of the band gap (E_g). The experimental correlation of threshold wavelength, λ_s , and the particle threshold diameter (d_p) is a function of the nanoparticle size [12].

The size of CdS nanoparticles was determined from the onset of light absorption, based on the previously published studies [13]. When decreasing the size of the nanocrystals below the Bohr radius, a three-dimensional confinement of the electrons and holes in the nanocrystals arises [14].

In consequence, the nanocrystals display modified optical and electronic properties, as compared to bulk materials. Most notably, the energy levels in the conduction and valence bands become discreet. These

properties vary as functions of the degree of confinement, and therefore as functions of the nanocrystals' size. As the confinement increases, so does the energy difference between the valence and conduction bands. According to Brus [15], the change in the bandgap width with respect to its bulk values as a function of the size of the nanoparticles can be expressed as:

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

where R is the nanoparticle radius and E^* is the effective Rydberg energy:

$$E^* = \frac{e^4}{2\varepsilon^2 h^2 (m_e^{-1} + m_h^{-1})} \quad (3)$$

The data from absorption spectra, presented in the Fig. 1, were fitted and estimated with the equation 2, obtaining the average diameters of bulk and capping CdS particles, which ranges within 5.9 and 9.6 nm. The sequence of the values of particle diameter (d_p), compared after 10 minutes mixing of two solutions, one containing metal ions and the other sulphide ions, was:

$$d_{p \text{ CdS-PVA}} > d_{p \text{ CdS-CoSMA}} > d_{p \text{ CdS-CoVAMA}} > d_{p \text{ CdS-PVP}} > d_{p \text{ CdS- without polymer}} \quad (4)$$

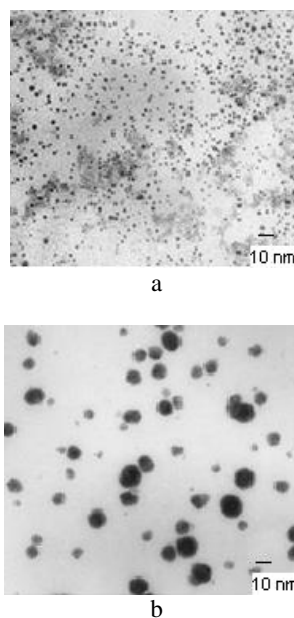


Fig. 2. TEM micrographs, a) CdS without polymer; b) almost spherical CdS particles, synthesized in presence of PVP.

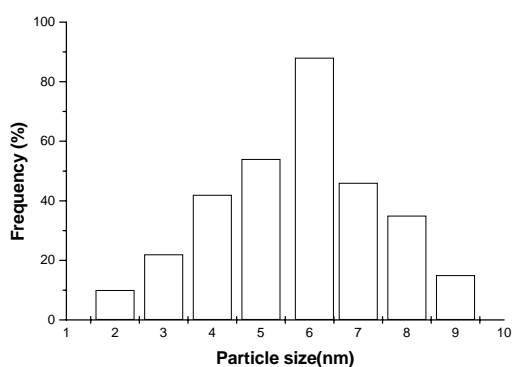
It could be observed that both the presence of the polymer and its nature influence the particle size diameter.

The shape of the particles is strongly dependent on the stabilizing polymers used. The shape of the particles coated with PVA and PVP, prepared in the present studies gave quasi-spherical particles.

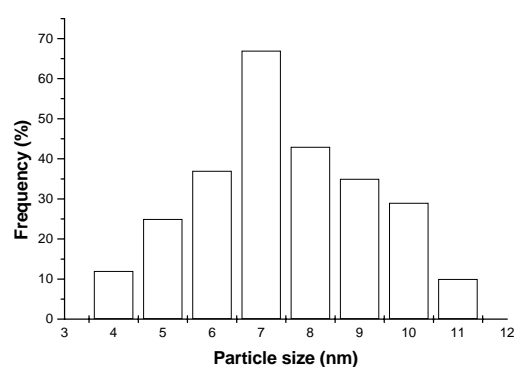
From TEM determinations we observe that the average diameter increases for the coated nanoparticles,

phenomenon that is more obvious in the presence of polymers like PVP, than in absence of the added polymers (see Fig. 2 b).

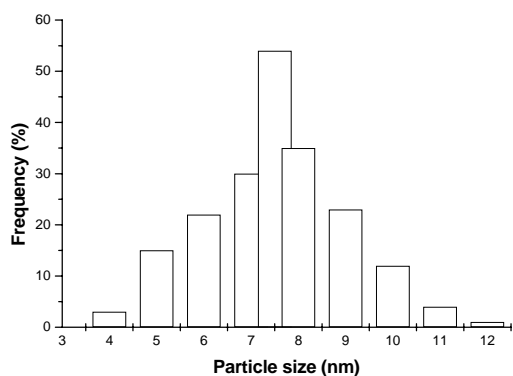
The Figures 3 a to e presents the results of the transmission electron microscopy determinations, which give information about the distribution of the particles average size.



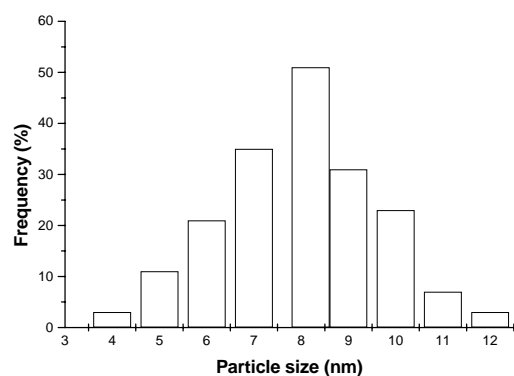
a)



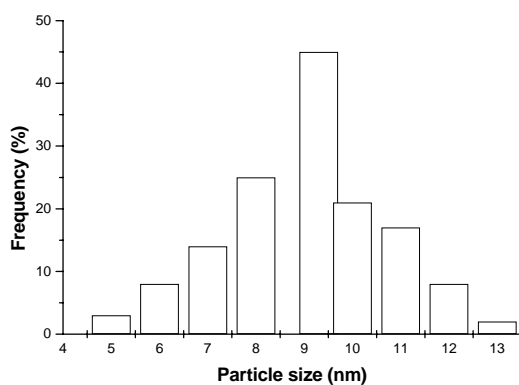
b)



c)



d)



e)

Fig. 3. Size distribution of nanoparticles: a) CdS without polymer; b) CdS coated with PVP; c) CdS coated with CoVAMA; d) CdS coated with CoSMA; e) CdS coated with PVA.

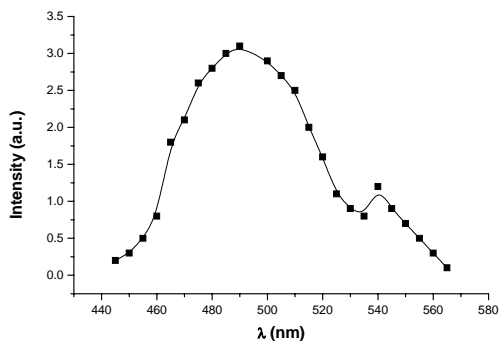
The frequency of the majority particles in the size distribution depends on the nature of the polymer and decreases if we add polymers in the system. In the growing stage, the size of coated crystals raise, the value of frequency decreases and the width of the distribution increases [9].

The synthesized nanoparticles were dispersed in polymeric matrix and then were applied on glass support to form films. The films are relatively homogeneous, have a nanostructured texture and a good adherence on support.

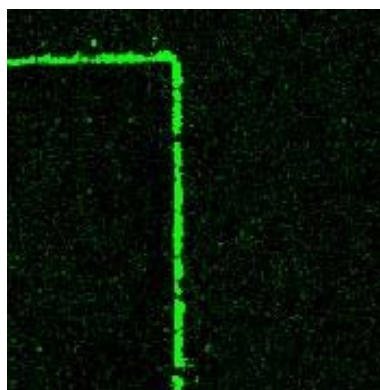
Fig. 4 b shows a microscopic image of the surface of PVA film with cadmium sulphide, made by confocal scanning laser microscope; can be observed as dispersed dots under a phase-contrast microscope, and the photoluminescence was detectable under fluorescence device (see the spectra from Fig. 4 a).

The film of sample CdS, which contains the copolymer styrene / maleic anhydride (CoSMA), presents for the emission spectrum a main maximum at 510 nm and some other peaks at 523 nm and 533 nm (see Fig. 5 a).

The micrograph of polymeric film in the Fig.5 b shows the existence of crystalline concentrations which contain the small particles relative spread in the polymeric matrices; it can be observed some clusters provided by the non-homogeneities of the film.



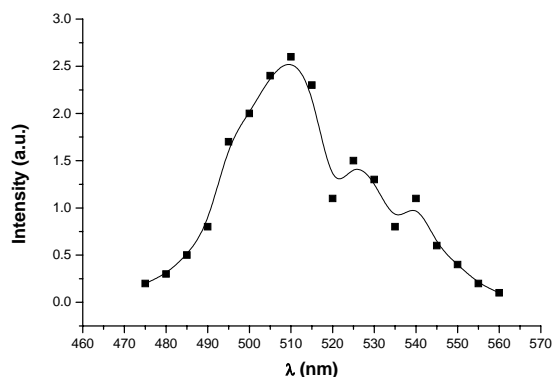
a



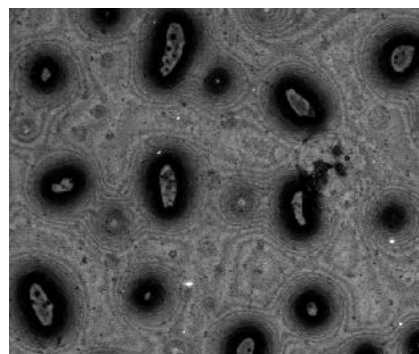
b

Fig. 4. a) Fluorescence of CdS nanoparticles in PVA film; b) surface of CdS - PVA film (in fluorescent light)

The extension of the spectral profile towards longer wavelengths (having higher intensity „tails”) and the photobleaching are the main problems concerning most organic fluorochromes. The narrow emission profile is the one that can enable several quantum dots conjugates to be simultaneously observed in multiple labeling experiments. The ability to stimulate multiple quantum dot sizes in the same specimen with a single excitation wavelength, obtaining several different fluorescent signals with a good signal to noise ratio is the reason to consider these artificial structures as excellent candidates for the multiple labeling experiments.



a

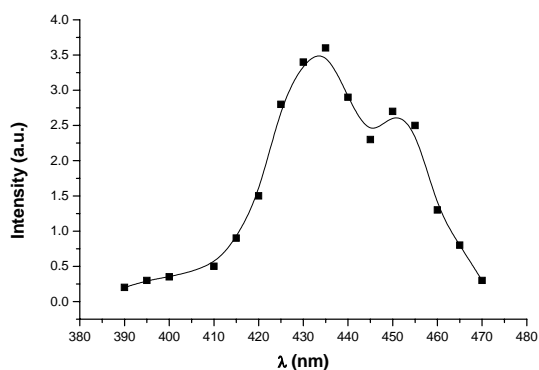


b

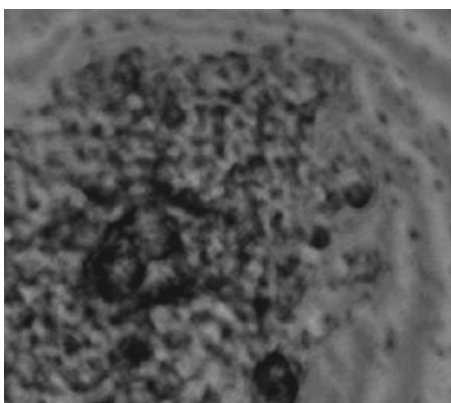
Fig. 5. a) Fluorescence of CdS nanoparticles in CoSMA film; b) surface of CdS - CoSMA film

The existence of CdS nanoparticles in the polymeric matrix can be confirmed by fluorescence spectroscopy of CLSM, because semiconductor particles exhibit light-emitting behaviour at a specific wavelength (Figs. 4a, 5a, 6a).

The emission has a strong dependence on the capping environment which could explain the change of the photoluminescence intensity quenching as polymer concentration is increased [16].



a



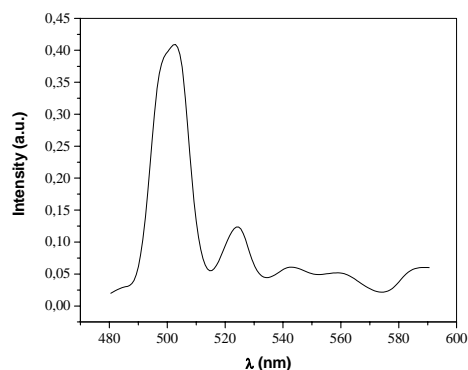
b

Fig. 6 a) Fluorescence of CdS nanoparticles in CoVAMA film; b) surface of CdS - CoVAMA film

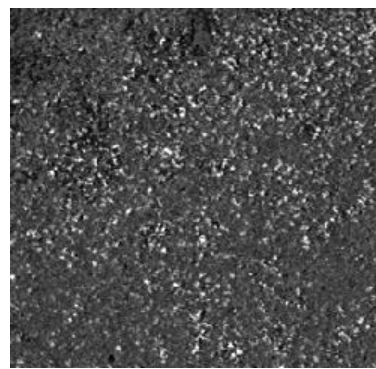
The results showed that the CdS-PVA, CdS-CoVAMA and CdS-CoSMA nanocomposite films have promising optical properties [17].

For the CdS nanocrystals dispersed in SSK, the best behavior presents the film containing CdS of 1×10^{-4} M concentration and the 1:1 CdS/SSK ratio, who is relatively homogeneous, have a nanostructured texture, a good adherence on support and stretch excellent on glass support.

Fig. 7 b shows a microscopic image of the surface of the deposited film made by confocal laser microscope, and cadmium sulphide can be observed as dispersed dots under a phase-contrast microscope, and some luminescence was detectable under fluorescence device (see Fig. 7 a). The determinations of fluorescence showed the fact that the film presents many spectral peaks positions, the main at 500 nm, and some secondary at 525 nm and 540 nm, which prove the formation of small semiconductor clusters.



a



b

Fig. 7 a) Fluorescence of CdS nanoparticles in SSK film
b) Micrograph of the surface SSK film containing CdS

4. Conclusions

It has been demonstrated that the properties of cadmium sulphide nanoparticles embedded with polymers are strongly influenced by the nature of polymer. The used polymers have an important role in the size control, the stability and like capping agent of the particles.

The size of cadmium sulphide nanoparticles can be determined by fitting the absorbance data with some specific equations from quantum dots' literature.

The fluorescence properties depend on the nature of capping polymer. The fluorescence intensity of CdS nanoparticle has an important increase in presence of polymeric film.

The flexible processing technique opens the possibility to obtain semiconductor particles into polymeric film for optical devices with various shapes.

The photoluminescence emission of cadmium sulphide nanocrystals with a functionalized surface is more efficient in combination with an inorganic film.

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