Cadmium Selenide Nanoparticles Synthesis in Water-Soluble Polymer System

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Water soluble cadmium selenide (CdSe) nanoparticles were chemically obtained by polymer assisted synthesis at 70 Celsius degree from aqueous solution, using $Cd(CH_3COO)_2{\cdot}2H_2O$ or $Cd(NO_3)_2{\cdot}4H_2O$ as cadmium source and H_2SeO_3 as selenium source. The clustering of CdSe nanoparticles synthesized in poly(amidehydroxyurethane) matrix was clearly revealed by X-ray diffraction and Atomic Force Microscopy films studies. The obtained CdSe nanocrystallites have hexagonal symmetry with an average dimension of 25 nm. The Fourier Transform Infrared spectra show the interaction between the nanoparticles and urethane carbonyl and C – O – C etheric groups of polymer. The dimension of CdSe – polymer entities in water solution was explored by Laser Diffraction method and confirmed the capping of CdSe nanoparticles by the polymer.

Keywords: CdSe, nanoparticles, polymer assisted synthesis, structural characterization

Semiconductor nanocrystals, exhibit strongly size dependent optical and electrical properties [1]. Chemical synthesis of high quality semiconductor nanocrystals has shown potential applications in thin film light-emitting devices [2], non-linear optical devices [3] and solar cells [4]. Luminescent semiconductor quantum dots can be used to tag biomolecules for bio-detection and bio-imaging [5]. Some efforts have been made to incorporate nanoparticles into polymer microbeads in order to render them water soluble, chemically stable, and biocompatible in physiological media [6]. CdSe nanoparticles are very promising for biological applications because they exhibit high sensitivity of absorption maxima to particle size. Studies have shown that nanoparticles toxicity is due to Cd^{2+} ions being released into cells [7]. This is exacerbated by oxygen, UV exposure and the large exposed nanoparticles surfaces. To avoid these problems, nanoparticles are coated traditionally with ZnS to create a more benign surface. Stable polymers can be used as well, but non-biocompatible polymers may affect the normal behaviour of cells [8-10].

Nanoparticles produced from high temperature organic solvent synthetic strategies are monodisperse with very wide emission color ranging from ultraviolet to near infrared, but they are insoluble in water. Hence, a challenge is how to make the hydrophobic nanoparticles soluble in water. Compared with organic phase synthesis, aqueous synthesis exhibits good reproducibility, low toxicity, and the products have excellent water-solubility, stability and biological compatibility [11-13].

In this paper we have investigated two synthesis routes of CdSe nanoparticles in the water - poly(amidehydroxyurethane) (PAmHU) biocompatible polymer system, by restricted reaction room method. In essence, for a size-controlled synthesis of nanoparticles it is necessary to control the size of the microcompartment. The ability to control the different micelles morphologies consist in the regulation of the hydrophilic/hydrophobic balance. Since loading of an inorganic precursor can change the size and shape of the micelles for each given system the solubilization process has to be taken into account.

Experimental part

PAmHU is a water-soluble polymer [14] which was also tested for biocompatibility [15] (fig. 1).

We tried to obtain CdSe nanoparticles by two routes. In the first case (route I) the Se source is Na_2SeSO_3 obtained by refluxing of Se powder with Na_2SO_3 aqueous solution for 30 min. Cadmium ions are introduced using $Cd(NO_3)_2{\cdot}4H_2O$ or $Cd(CH_3COO)_2{\cdot}2H_2O$ aqueous solutions. The CdSe particles are formed according to the following reactions:

$$Cd(CH_3COO)_{2(aq)} + Na_2SeSO_{3(aq)} + H_2O \longrightarrow \longrightarrow CdSe + Na_2SO_{4(aq)} + 2CH_3COOH_{(aq)}, \quad (1)$$

$$Cd(NO_3)_{2(aq)} + Na_2SeSO_{3(aq)} + H_2O \longrightarrow \longrightarrow CdSe + Na_2SO_{4(aq)} + 2HNO_{3(aq)}. \quad (2)$$

The overall chemical reaction can be represented in the following form:

$$Cd^{2+} + SeSO_3^{2-} + H_2O \longrightarrow CdSe + SO_4^{2-} + 2H^+. \quad (3)$$

Another source of Se is H_2SeO_3 obtained from SeO_2 and water. In this case we have used as reducing agent - $N_2H_4{\cdot}2HCl$. The chemical process involved in the route II is:

$$2Cd(CH_3COO)_{2(aq)} + 2H_2SeO_{3(aq)} + 3N_2H_{4(aq)} \longrightarrow \longrightarrow 2CdSe + 4CH_3COOH_{(aq)} + 3N_2 + 6H_2O, \quad (4)$$

$$2Cd(NO_3)_{2(aq)} + 2H_2SeO_{3(aq)} + 3N_2H_{4(aq)} \longrightarrow \longrightarrow 2CdSe + 4HNO_{3(aq)} + 3N_2 + 6H_2O, \quad (5)$$

with the following overall chemical reaction:

$$2Cd^{2+} + 2SeO_3^{2-} + 3N_2H_4 \longrightarrow 2CdSe + 3N_2 + 6H_2O. \quad (6)$$

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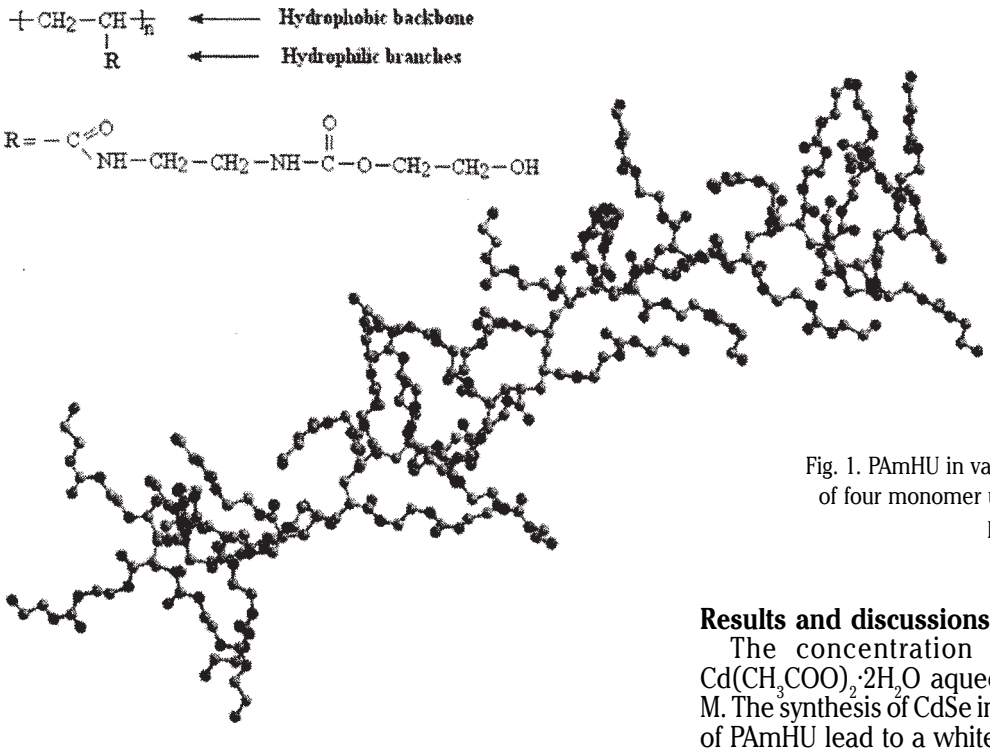


Fig. 1. PAmHU in vacuum optimised molecular structure of four monomer units. Inset - PAmHU monomer unit primary structure

In the route I case (Se source - Na_2SeSO_3) the reaction is very fast even at room temperature but the CdSe particles precipitates after one day at room temperature. When the second route (Se source - H_2SeO_3) is used the formation of CdSe is observed only after heating at 70°C and the particles are stable into solution for a very long time (more than 3 months).

Taking into account the stability in water of CdSe particles obtained by route II we focused our investigation efforts on the samples obtained from this synthesis route.

The advantage of the aqueous synthesis route is that the biocompatibility of the final system is not affected because the synthesis does not imply any organic solvent. Also, the reaction conditions are gentle (normal atmosphere, pressure and moderate temperature).

Thin film samples were obtained by deposition of the synthesized system onto glass substrates followed by evaporation.

The microphase structure was investigated by X-ray diffraction (XRD) performed on a DRON-2 diffractometer, provided with nickel-filtered Cu Kα radiation at 25 kV operational voltage. The particle size was determined, from X-ray diffractograms, according to Scherrer relationship [16]:

$$L = K\frac{\lambda}{\beta \cdot \cos\theta}, \qquad (7)$$

where L is the diameter of nanocrystals in angstroms, K is a constant (0.89), β is the half maximum line width, θ is the diffraction angle and λ is the X-ray wavelength (1.5418 Å). Atomic Force Microscopy (AFM) was done using a Solver PRO – M (NT – MDT) using a NSG 10 cantilever operated at 11.5 N/m force constant and 264.93 kHz, in semicontact mode. The Fourier Transform Infrared (FTIR) spectra were recorded on Jasco FTIR 410. The dimension of the particles coated with PAmHU polymer was determined by laser diffraction method (LD) with Shimadzu – SALD - 7001 Laser Diffraction Particle Size Analyzer.

Results and discussions

The concentration of the $Cd(NO_3)_2 \cdot 4H_2O$ and $Cd(CH_3COO)_2 \cdot 2H_2O$ aqueous stock solutions was $5 \cdot 10^{-2}$ M. The synthesis of CdSe in aqueous media in the absence of PAmHU lead to a white flocculated compound that in 24 h changed color progressively to yellow – orange – dark red (in the case of $Cd(CH_3COO)_2 \cdot 2H_2O$ precursor) and to green – yellow – orange – dark red (in the case of $Cd(NO_3)_2 \cdot 4H_2O$ precursor).

Good results were obtained for 2 mL PAmHU solution (~ 1 g/L) mixed with 1 mL $Cd(CH_3COO)_2 \cdot 4H_2O$ (10^{-2}M) or 1 mL $Cd(NO_3)_2$ (10^{-2}M), 1.5 mL $N_2H_4 \cdot 2HCl$ (10^{-2}M), and 1mL H_2SeO_3 (10^{-2}M).

The reactions were initiated by heating the precursor system at 70°C for 30 min under stirring at high speed and produced orange – red solutions. These results were compared with a reference sample of CdSe crystals obtained by PAmHU free synthesis.

The X-ray diffractograms from figure 2 show the existence of CdSe characteristic diffraction maxima superposed on the PAmHU amorphous envelope.

CdSe can crystallize in cubic or hexagonal structure. The cubic structure is known to be metastable, so the most common form is the hexagonal one (a = 4.30 Å and c = 7.01 Å). The XRD data recorded is in agreement with the reported values for the hexagonal unit cell (table I). From the X-ray diffractograms, using the Sherrer relation, we

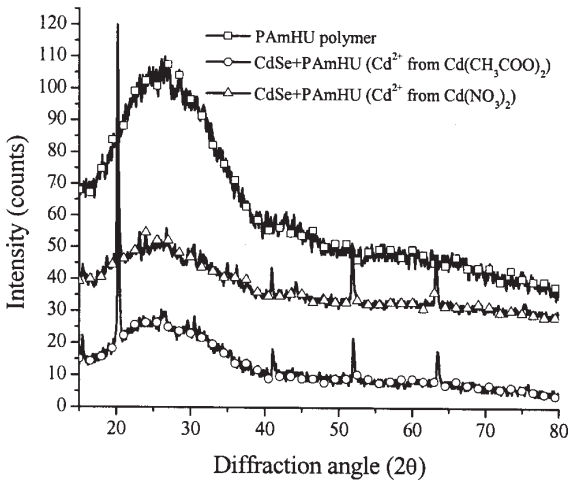


Fig. 2. X-ray diffractograms of PAmHU-CdSe systems, compared with PAmHU diffractogram

Table 1
LIST OF THE HKL, 2θ AND d VALUES OF CdSe FOR HEXAGONAL SYMMETRY FROM JCPDS FILE NO. 08-0459

No.	hkl	2θ(degree)	d(Å)
1.	100	23.8	3.730
2.	002	25.3	3.513
3.	101	27.0	3.294
4.	102	35.1	2.557
5.	110	41.9	2.153
6.	103	45.8	1.983
7.	200	48.8	1.865
8.	112	49.6	1.836
9.	201	50.8	1.803
10.	203	63.8	1.459

have obtained a 25 nm medium size of the CdSe nanoparticles. Both Cd^{2+} sources give nanoparticles with similar size. The type of anion (NO_3^- or CH_3COO^-) does not influence significantly the size of obtained nanoparticles.

In figures 3 and 4 are presented the 3D and 2D AFM film topologies of PAmHU polymer and PAmHU – CdSe nanoparticles systems respectively.

As can be seen from figure 3 the PAMHU films are morphological homogenous and self-aggregate systematically. On the other hand, from figure 4 it is obvious that the PAmHU – CdSe nanoparticles system is unhomogenous at the nanometric scale. The size of the CdSe particles obtained from AFM data ranges from 30 to 150 nm. This result and the morphologies of large CdSe particles suggest that the single crystalline 25 nm CdSe particles aggregate and form clusters up to 150 nm.

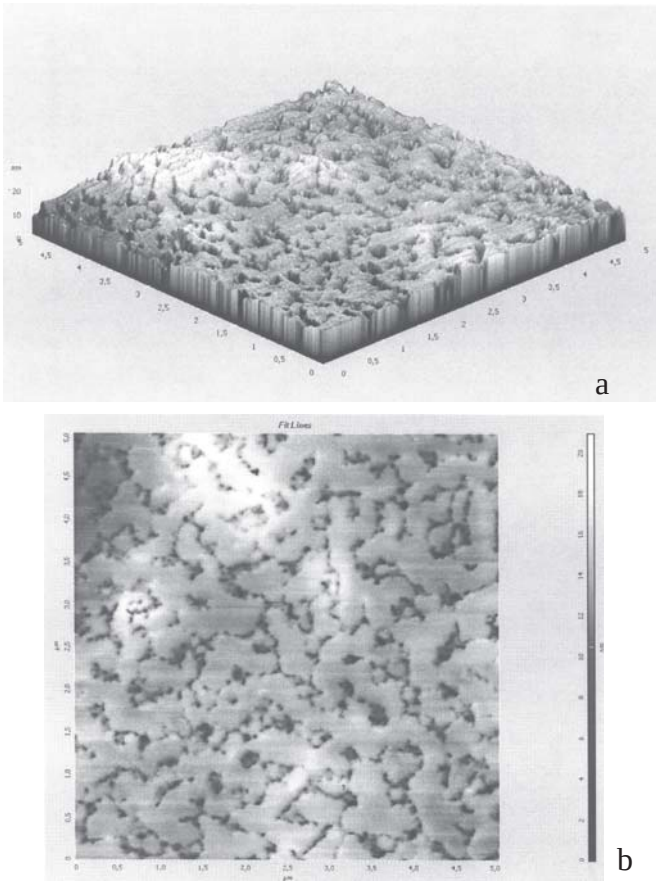


Fig. 3. 3D (a) and 2D (b) topographies of PAmHU films; the scale of square area is 5x5 μm²

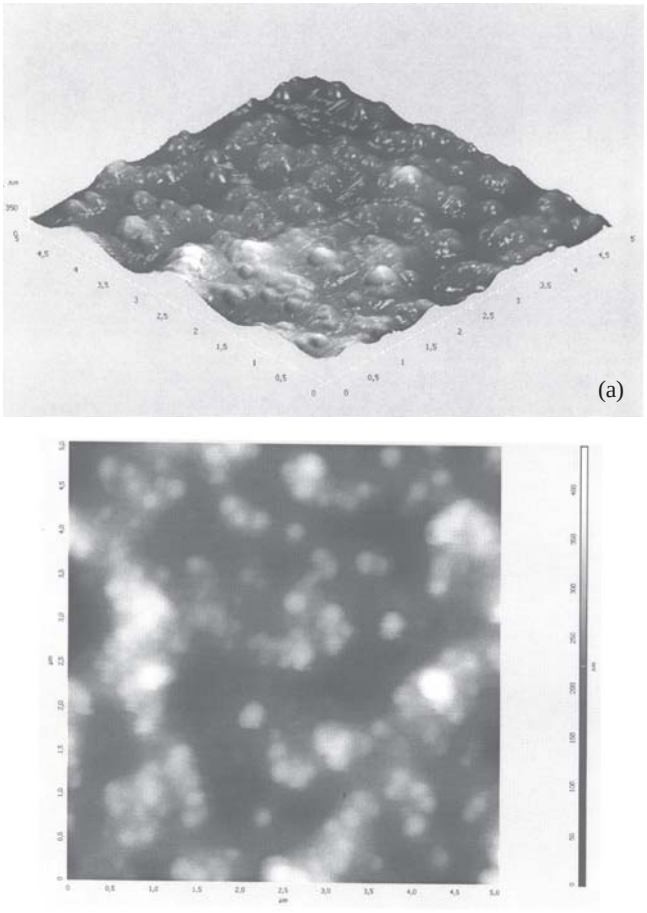
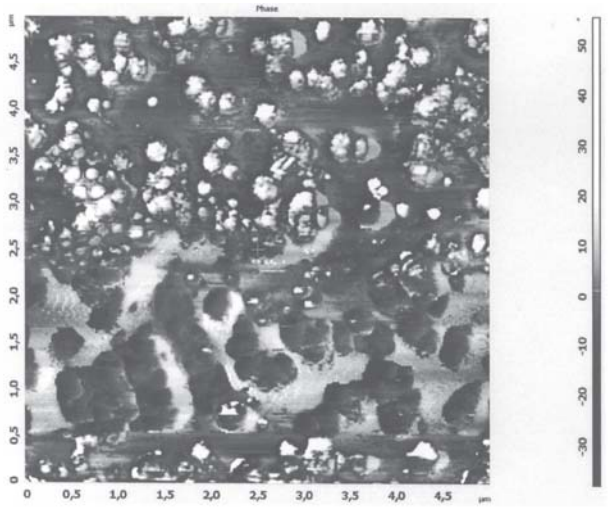


Fig. 4. (a) and (b)



(c)

Fig. 4. 3D (a) and 2D (b) topographies, and phase contrast (c) of films of PAmHU – CdSe (route II); the scale of square area is 5x5μm²

Comparing the CdSe-PAmHU FTIR spectra (fig. 5) with PAmHU FTIR spectrum noticeable differences both in the functional group region, 4000-1500 cm^{-1}, and fingerprint region, 1500-400 cm^{-1}, are observed. These differences are due to the interactions between CdSe nanoparticles and functional groups of PAmHU (carbonyl and C – O – C etheric groups). The PAmHU characteristic IR bands were discussed in [14]. The changes of the PAmHU IR spectra in the fingerprint region induced by the presence of CdSe nanoparticles demonstrate the existence of CdSe – polymer functional group interactions. Evidence of interactions between PAmHU and CdSe nanoparticles are assigned to 1,700 cm^{-1} hydrogen bonded urethane carbonyl band, and to the modes at 1,265 cm^{-1}, 1,158 cm^{-1} and 1,078 cm^{-1} bands of the C–O–C group. The C = O modes from acrylamide group are unmodified by the presence of CdSe nanoparticles.

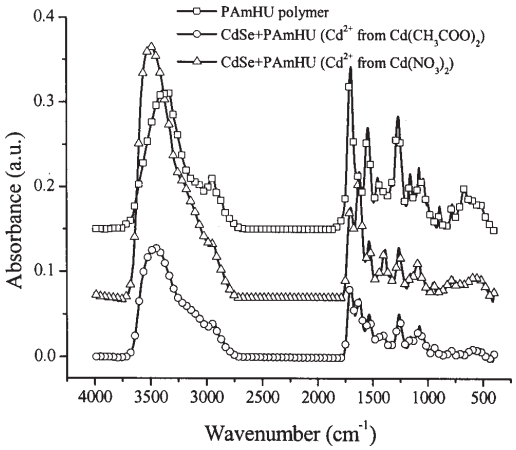


Fig. 5. FTIR spectra of CdSe-PAmHU samples

The nanoparticles dimension measured by LD confirms the existence of nanoparticles-polymer interactions. As it can be seen from figure 6, the nanoparticles are "seen" by the light as being bigger due to the capping of CdSe nanoparticles by polymer.

The solution of PAmHU polymer has a multimodal distribution of particles sizes. As a result of CdSe synthesis the ionic strength of the solutions increase and it seems to generate a *salting in* effect which is suggested by the absence of particles

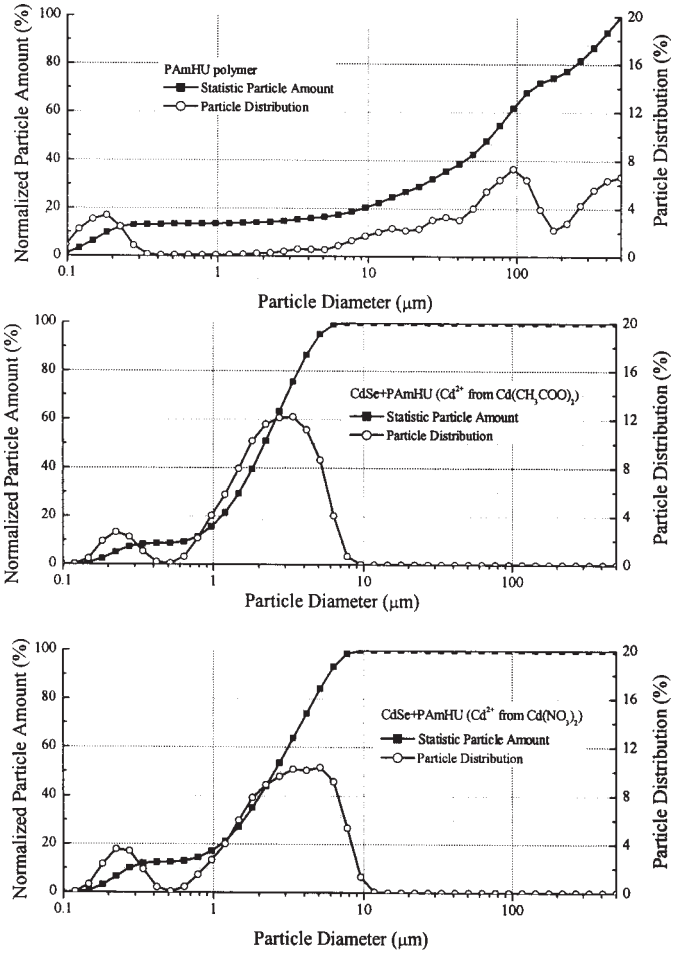


Fig. 6. Size distribution of PAmHU - CdSe particles

larger than 10 μm in the solutions which contains CdSe particles. The bimodal like distribution of CdSe – polymer nanoparticles dimension is due to the initial polymer multimodal size distribution and to the salting in effect mentioned before. The first generation of polymer particles (initial size centred at 180 nm) presents a size increase to a maximum at 250 nm due to the linkage with CdSe particles. The second generation observed in the CdSe containing solutions can be attributed to the clustering of multiple CdSe – polymer entities.

Conclusions

Cadmium selenide water soluble nanoparticles were chemically obtained by polymer assisted synthesis from aqueous media.

The average size of the CdSe nanoparticles obtained from X-ray diffractograms is 25 nm.

The size of CdSe particles, obtained from AFM data, ranges from 30 to 150 nm.

A comparative view of the CdSe-PAmHU and PAmHU FTIR spectra suggests the existence of CdSe – polymer functional groups interactions.

The capping of CdSe nanoparticles by PAmHU was shown by LD studies.

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