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LOW-TEMPERATURE SYNTHESIS OF CdS AND ZnS NANOPARTICLES BY SOLUTION METHOD USING AN ANIONIC SURFACTANT

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In this work, we present a novel and simple solution method to synthesize cadmium sulfide (CdS) and zinc sulfide (ZnS) nanoparticles (Nps). The solution-based processes for CdS and ZnS were carried out at room temperature (27 °C) using sodium dodecyl sulfate (SDS) as anionic surfactant for both chalcogenide systems. Thioacetamide (C_2H_5NS) was used as anionic precursor, and as the metal precursor cadmium chloride ($CdCl_2$) and zinc acetate ($C_4H_6O_4Zn.\ 2H_2O$) for CdS and ZnS Nps respectively. The pH for the solution of nanoparticles was 2.2 for CdS and 5.7 for ZnS. The conductivity for chalcogenide solution was also determinate. Optical properties of CdS and ZnS nanoparticles were analyzed by Ultraviolet-Visible (UV-Vis) spectroscopy; functional groups were identified by Fourier transform infrared spectroscopy (FTIR), the surface morphology by scanning electron microscopy (SEM) and the crystalline structure by X-Ray diffraction (XRD). The distribution size for nanoparticles were less than 100 nm for CdS and ZnS Nps.

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1. Introduction

Nanoparticle is a small solid whose diameter lies in the range of 1–100 nanometers, the advantages of its use are related to the size of these, because the properties of a material are related to the behavior of its electrons or how the atoms are ordered, therefore at the time of making a material at nanoscale these properties are modified [1]. Each nanoparticle develops different properties according to the material, size and shape given according to the method of synthesis used to make it.

There are different processes used to synthesize nanoparticles, like hydrothermal or solvothermal, sol–gel techniques, microwave approaches, and chemical vapor deposition techniques, these treatments are expensive, extensive, toxic and consume a lot of energy. [2 - 7]. However, there are methods at room temperature at low cost such as the solution or precipitation process and suspension colloidal synthesis routes [2,4].

One of the most important goals of materials synthesis, is the control of size and nanoparticles stability. Since the nanoparticles are thermodynamically unstable, an agglomeration

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effect and then a consequent crystal growth are usually observed. To avoid these phenomena, the nanoparticles are stabilized with organic systems that enveloped them and obstruct their agglomeration and the consequent growth [2, 4-7].

Chalcogenide nanoparticles have attracted much attention of many scientists over the past few years due to their properties which originate from quantum confinement effect [4-5]. CdS and ZnS nanoparticles which belong to II−VI group semiconductor compounds are materials having various applications [2-5].

CdS is an II−VI group semiconductor compound with direct band gap of 2.42 eV and has interesting optical and electrical properties; also is one of the most studied materials because it has a well-established relationship between the optical absorption and the size of the particle and has many applications in photoelectric conversion in solar cell, thin film transistor (TFT), nonlinear optics, semiconductor laser, flat panel display, photodiodes and sensors [2-4, 6].

ZnS belongs to II−IV group material, is a promising opto-electronic device material due to its wide direct band gap 3.72 to 3.77 eV, has been attracted considerable attention on its application in catalysis fields, optical devices, as an antireflection coating for hetero-junction solar cells [7], for light emitting diode [8], transistors, sensors and lasers, due to its excellent photoelectric conversion characteristics and luminescent properties (4-5, 8).

In this work we report the synthesis of nanoparticles of CdS and ZnS by solution method at room temperature, this brings us advantage as it reduces costs and can be industrially scaled [2-8].

2. Materials and methods

2.1 Materials

Thioacetamide (C_2H_5NS, ACS Reagent Grade, Aldrich, ≥99.0%) was used as anionic precursor, and as surfactant was used sodium dodecyl sulfate (SDS, J.T. Baker, 95%), for both chalcogenides. Surfactants can be classifieds according to the charge present in the hydrophilic portion of the molecule after dissociation in aqueous solution, in the case of SDS can be categorized as anionic surfactant according its dissociation [9-10].

Zinc acetate ($C_4H_6O_4Zn.\ 2H_2O$, ACS Reagent Grade, Aldrich, 99.0%) was used in the zinc sulfide nanoparticles as the metal precursor, and cadmium chloride ($CdCl_2$, ACS Reagent Grade ≥99%), was used in the nanoparticles of cadmium sulfide.

2.2 Nanoparticles synthesis

2.2.1 CdS

The synthesis of CdS Nps was prepared at room temperature in different concentrations of SDS (0.0025M, 0.005M or 0.01M) stirring for 5 min, then the $CdCl_2$ solution at 0.25 M was added dropwise continuing to stir 10 more min, finally thioacetamide 0.25 M solution was added dropwise allowing to stir 30 min later.

2.2.2 ZnS

The synthesis of ZnS Nps was prepared at room temperature in different concentrations of SDS (0.001M, 0.002M or 0.004M) stirring for 5 min, then the $Zn(CH_3COO)_2$ solution at 0.05 M was added dropwise continuing to stir 10 more min, finally thioacetamide 0.05 M solution was added dropwise allowing to stir 30 min later.

2.3 Characterization

The nanoparticles solutions were aged for a month; in this time the final pH was stabilized. The pH and the electrical conductivity for the Nps solutions were measurement using an HI 2550 Multiparameter pH/ ORP/°C/EC/TDS/NaCl Bench Meter.

Optical absorption measurements were performed using a Jeneway 6850 UV/visible spectrophotometer in the range from 300 to 1100 nm. The Infrared absorption spectra, was recorded by Thermo scientific Nicolet 6700 FT-IR Spectrometer. The morphology and nanoparticle size were characterized by Scanning Electron Microscopy (SEM) on JEOL, JSM

7000f microscope and the crystalline structure was analyzed by X-ray diffraction on Bruker D8 Advance.

3. Results and discussion

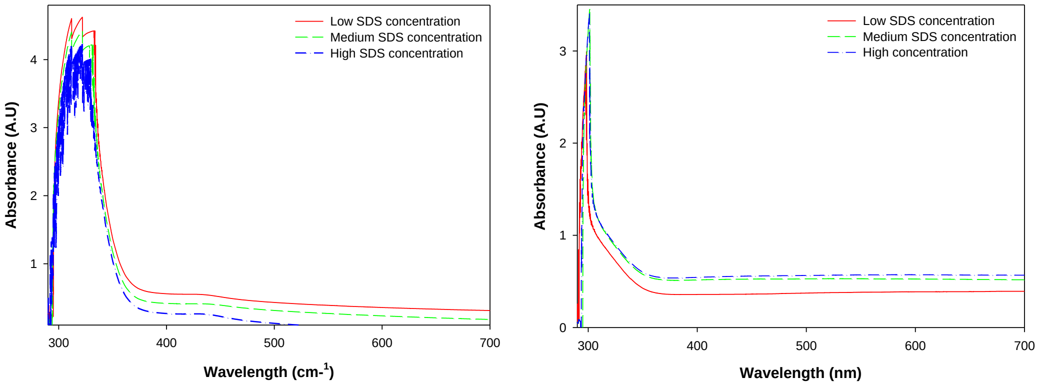
In our experimental conditions the pH nanoparticles solutions were stabilized at room temperature (27 °C) after one month, 5.4 to 2.2 for CdS and 6.2 to 5.7 for ZnS nanoparticles. SDS concentration do not have effect in the final pH for both systems, however the electrical conductivity for CdS Nps increased proportionality with SDS concentration and for ZnS nanoparticles practically it remains with the variation of SDS concentration (Table 1).

Table 1. pH values and electrical conductivity determinates at room temperature (27 °C) for CdS and ZnS nanoparticles.

CdS SDS concentration	*Electrical conductivity*	*pH*	*ZnS SDS concentration*	*Electrical conductivity*	*pH*
0.0025M	*6670 µS*	*2.18*	*0.001M*	*1230 µS*	*5.66*
0.005M	*6840 µS*	*2.20*	*0.002M*	*1183 µS*	*5.64*
0.01M	*7165 µS*	*2.13*	*0.004M*	*1229 µS*	*5.65*

The UV-Visible absorption spectra of CdS samples prepared under different concentration of SDS are shown in Fig. 1a. The absorption maxima for CdS samples are located at 391 nm; the CdS samples show a hyperchromic effect when SDS concentration decrease. The maximum absorption for CdS as a bulk material is around 460 nm. A blue shift it is observed between absorption edge of Nps respect to bulk CdS absorption band, this is may be due to quantum confinement effects [2-3, 6, 11-13, 15].

For ZnS Nps absorption maxima is observed at wavelengths in the range from 280 nm to 380 nm (Fig. 1b), the absorbance increased when the SDS increased in the ZnS Nps preparation. Blue shift is observed for ZnS nanoparticles when the SDS concentration decreased, this behavior was observed by others showing the stabilizer agent effect preventing the agglomeration [5, 7-8].



(a) *(b)*

Fig. 1. UV-Vis Absorption spectra for a) CdS Nps and b) ZnS nanoparticles synthesized at different SDS concentration.

The band gap of the nanoparticles was determined from the relation $\alpha(hv) = A(hv - \Delta Eg)m/2$, where A is a constant, ΔEg is the band gap of the material and α is the absorption coefficient, *hv* is the photon energy and m = 1 for a direct transition between bands (valence and conduction band).

As seen in Fig. 2 for CdS Nps the band gap decreases with increase of SDS concentration and in each absorption spectra the optical band gap values calculated are from 3 to 2.75 eV, these values are agreeing with the previously reported by others [2-3, 6, 11-13].

The band gap values calculated for ZnS Nps at different SDS concentrations are 3.41 eV, 3,38 V and 3.8, the range of band gap is in agreement with the values obtained for [7-8, 14] in each SDS concentration used in the Nps preparation (Fig. 2).

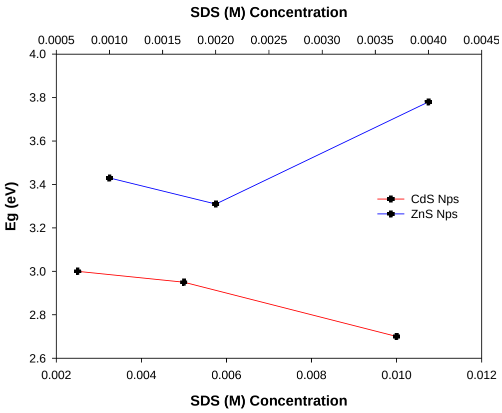
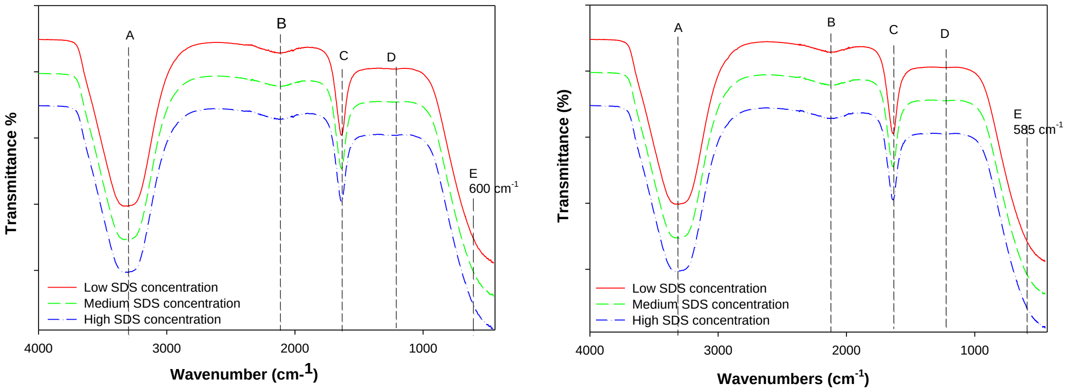


Fig. 2. Estimated band gap from optical absorption spectrum for CdS and ZnS nanoparticles synthesized at different SDS concentration.

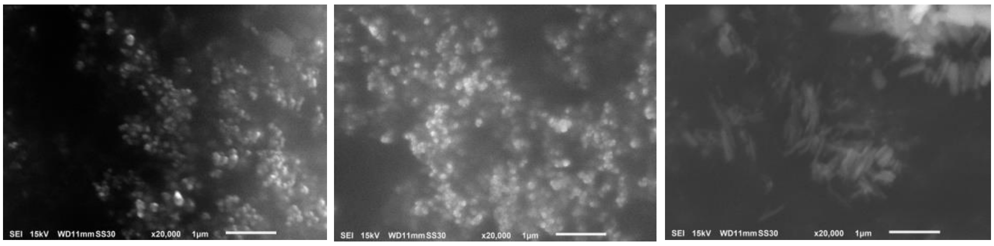
The FTIR spectrum for CdS and ZnS nanoparticles is shown in the Fig. 3. A broad absorption band in the range between 3354-3305 cm-1 is due to the -OH assigned to H2O, solvent used. The absorption bands located at 2151 and 1663 cm-1 are attributed to S-H and S-S species formed by hydrolysis of thioacetamide. The band observed at 1663 cm-1 corresponds to interactions C-H from SDS. The Cd-S bond is observed at 600 cm-1 and 585 cm-1 for ZnS in Fig. 3a and 3b respectively [11-17].



(a) *(b)*

Fig. 3. Infrared spectra for a) CdS and b) ZnS nanoparticles obtained at different SDS concentration.

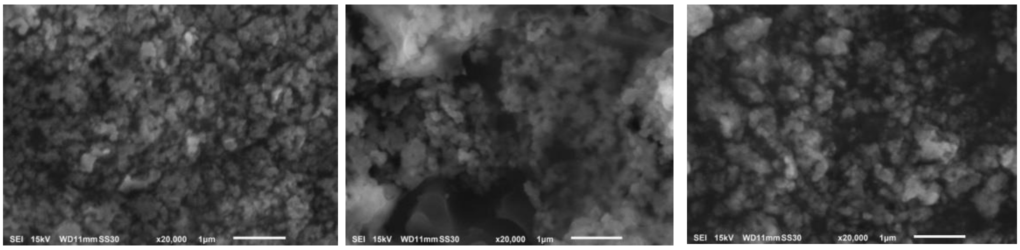
The morphology of the prepared samples can be studied by SEM. Fig. 4 shows the SEM images for CdS Nps. For the samples prepared at low and medium SDS concentration the Nps morphology is round shaped or spherical, this is more defined at low SDS concentration. The sample prepared at high SDS concentration showed rod-shaped morphology, changes in the CdS nanoparticles morphology by effect of different chemical and physical parameters in the synthesis have been observed by others [11-12, 15].



(a) *(b)* *(c)*

Fig. 4. SEM micrographs for CdS nanoparticles obtained at different SDS concentration a) 0.0025M b) 0.005M c) 0.01M.

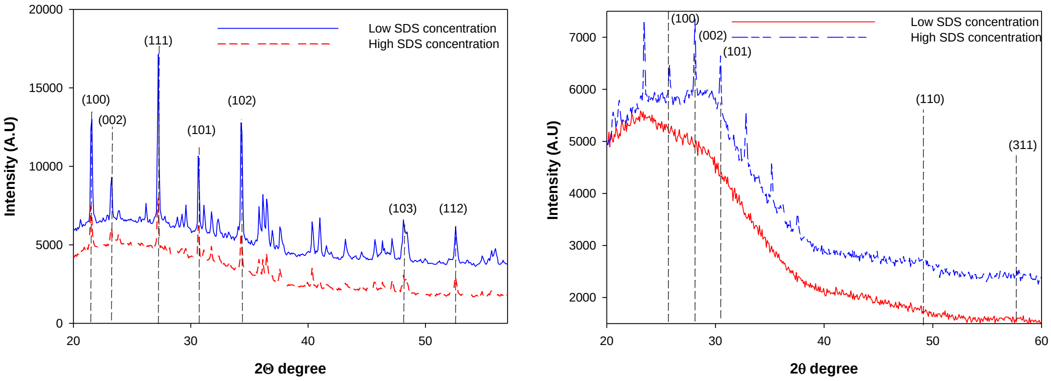
The SEM image of ZnS nanoparticles is shown in Fig. 5. The SEM microstructural analysis shows ZnS particles with spherical shape. At medium and high SDS concentration is possible to shown particles agglomeration and formation of crystals.



(a) *(b)* *(c)*

Fig. 5. SEM micrographs for ZnS nanoparticles obtained at different SDS concentration a) 0.001M b) 0.002M c) 0.004M.

The maximum particle size does not exceed 100nm for CdS and ZnS nanoparticles. Fig. 6a shows the XRD pattern of CdS NPs. Several peaks of hexagonal phase with (wurtzite-type structure), have been obtained due to diffraction from (1 0 0), (0 0 2), (1 1 1), (1 0 1), (1 02), (1 0 3), (1 1 2) planes of CdS [6, 11-13, 15]. The diffraction peak that appears at 26.5° becomes obvious as the effect of SDS at low concentration improved.



(a) *(b)*

Fig. 6. XRD patterns for a) CdS and b) ZnS nanoparticles obtained at different SDS concentration.

The diffraction patterns (Fig. 6b) for ZnS at high SDS concentration match well to hexagonal ZnS (JCPDS No. 80-0007, vertical bars) [17-19]. We cannot exclude the existence of cubic ZnS phase from XRD pattern alone because of the large similarity in the structures between cubic and hexagonal ZnS. ZnS nanoparticles prepared at low SDS concentration shows amorphous structure.

There are been reported several methods for the synthesis of CdS and ZnS nanoparticles. Xuejiao Zhu et al. [16] reported the biosynthesis of CdS nanoparticles with spherical nanoparticles spontaneously grown on the surface of biocalcite. Zamin Q. Mamiyev et al. [7] ZnS NPs have been synthesized successfully by the chemical reaction at 80°C nanoparticles. Feroz A. Mir et al. [6] produced CdS nanoparticles with hexagonal phase by chemical precipitation method with ammonia solution. Virpal et al. [17] successfully synthesized pure ZnS nanoparticles and doped with lead by chemical precipitation methods. Solankhi et al. [18] reported on the synthesis of nanocrystalline CdS by a simple chemical precipitation method using hydrazine hydrate as a complexing agent. Z. Ye et al. [19] used a simple chemical precipitation method with a capping agent to synthesize the cubic phase of ZnS nanoparticles.

In this work the results obtained for CdS and ZnS Nps synthetized by solution method at room temperature demonstrate that this method can easily compared with the others preparative routes with competitive properties.

4. Conclusions

In the present work, the development of a new method for the synthesis of CdS and ZnS nanoparticles via a solution process in the presence of an anionic surfactant is successfully demonstrated. The pH was stabilized after one month for CdS and ZnS nanoparticles, 2.2 for CdS and 5.7 for ZnS nanoparticles.

The presented route for both systems can easily fabricate nanoparticles with small dimensions at room temperature. The dependence of shape and distribution nanoparticles with SDS concentration was showed. Hexagonal structure was obtained for both system of chalcogenide nanoparticles. The calculated band gap for CdS and ZnS nanoparticles correspond to reported by others and is according values for semiconductor materials, 3 to 2.75 ev and 3.4 to 3.8 ev for CdS and ZnS Nps respectively [2-6, 12-17]. The electrical conductivity at room temperature was measurement resulting the higher value 7165 and 1230 µS for CdS and ZnS Nps respectively depending of SDS concentration. These characteristics in the CdS and ZnS nanoparticles make them suitable candidates for electronic technology.

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