

## OPTICAL, STRUCTURAL AND MORPHOLOGICAL PROPERTIES OF CdS NANOPARTICLES CAPPED BY AMMONIUM NITRATE IN ALKALI MEDIUM BY PRECIPITATION METHOD

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Cadmium sulphide (CdS) nanoparticles have been prepared by aqueous precipitation technique in the KOH alkali medium at a pH value of 13.82. Ammonium nitrate was used as a capping agent to prevent the semiconductor nanoparticles from the aggregation and to obtain a well-uniformed nanostructure. The formation of the spherical nanoparticles was observed by scanning electron microscope (SEM). Fourier transform infrared spectroscopy (FTIR) result indicates the formation of CdS and the particles are bonded to N-H stretching mode. The XRD result reveals that the CdS exists in a crystalline cubic phase. The band gap of the sample measured by UV-Vis spectrophotometer is higher than the CdS in bulk phase, which indicates a presence of tunable thermal and electrical conductivity for the CdS nanoparticles.

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### 1. Introduction

The II-IV group semiconductors are the most studied materials because of their advanced optical properties. Cadmium sulphide (CdS) is one of the semiconductors in II-IV group that exist in two mineral forms, greenockite and hawleyite. CdS is a direct band gap semiconductor with band gap value of 2.42 eV [1, 2]. As a semiconductor, it has already shown vital applications in fluorescence probe, sensors, solar cell, photo-electrocatalysis and laser light-emitting diodes [3-5]. The nano-semiconductor material has their density of electronic states that change in a systematic manner, which strongly influences the optical and electronic properties of the materials [6, 7]. As compared with the bulk materials, the nano-size semiconductor particles exhibit some unique properties such as nonlinear optical properties [8,9], quantum size effect [10-13] and other important physical and chemical properties [14-16]. Moreover, their potential applications in the development of nano-devices are also very extensive. So, the fabrication of semiconductor nanoparticles has been attracting great attention from the material scientists [17].

Many researchers has successfully prepared the CdS nanostructures using different synthesis methods [1-17]. However, it is difficult to obtain the CdS in nano-sized and well-uniformed structure because of their inhomogeneous reactions during the formation process. Precipitation method is one of the most appropriate methods in order to obtain a uniform order of nano-sized material by using the alkali medium and capping agent in the reaction [18, 19], which acts as a buffer, keeping the pH value of the solution at a desired level and act as the co-ordination sites for ion aggregation [18, 19]. In this study, the CdS nanoparticles were prepared by aqueous precipitations technique that involves a chemical reaction between metastable precursors of thiourea and cadmium chloride. Potassium hydroxide (KOH) acts as the alkaline medium in order to yield cadmium and sulphur ions in the solution. Since the solubility product of CdS is low, ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) is used as a capping agent and also as a surfactant in the reaction [18], which also acts as a buffer by keeping the pH value of the solution at a desired level.

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## 2. Materials, synthesis and characterizations

All chemicals used were analytical grade without further purification. Cadmium chloride ( $\text{CdCl}_2$ ) was purchased from Sigma Aldrich, while potassium hydroxide (KOH), ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), thiourea ( $\text{CS}(\text{NH}_2)_2$ ) were purchased from Merck.

The aqueous solution of  $\text{CdCl}_2$  (0.02M), KOH (0.5M),  $\text{NH}_4\text{NO}_3$  (0.5M) were prepared by constant stirring at room temperature for 30 minutes. These solution were then mixed and stirred continuously for another 30 minutes to obtain a homogeneous solution. The thiourea  $\text{CS}(\text{NH}_2)_2$  solution with concentration of 0.1 M was then slowly added into the aqueous mixture. The mixture solution was then heated at 80 °C with continuous stirring at 300 rpm for 2 hours until it turns into light yellow. The yellow precipitates were collected by filtration from the aqueous solution. The precipitates were then washed with distilled water and acetone and dried at room temperature for 24 hours before further characterizations.

The prepared samples have been characterized by X-ray diffraction (XRD) Rigaku Miniflex-TM II diffractometer, scanning electron microscopy (SEM) with JEOL JSM model 6360-LA operated at 20 kV. UV-Vis absorption spectra were recorded by UV-Vis scanning spectrophotometer (Shimadzu 1601PC). The functional group of starch was characterized by Perkin-Elmer Fourier transform infrared (FTIR) spectrometer and the weight loss due to thermal heating was determined by Metler Toledo TGA/SDTA 851.

## 3. Results and discussion

The functional groups of CdS nanoparticles have been investigated by FTIR. Figure 1 shows the FTIR spectra of the CdS nanoparticle. There are several vibrating groups present in the sample. The O-H stretching group of water molecules was observed at  $3320\text{ cm}^{-1}$  in the CdS nanoparticles. The peak emerged at  $2350\text{ cm}^{-1}$  corresponds to the vibration of S-H mode, while the weak band occurred at  $2084\text{ cm}^{-1}$  corresponds to the R-N=C=S functional groups. The major contribution of the C=N bonds comes from the thiourea that used during the synthesizing process. The peaks at  $1630\text{ cm}^{-1}$  and  $1380\text{ cm}^{-1}$  are respectively assigned to the C = O bonds originated from  $\text{CO}_2$  bonds. The presence of a peak at  $1000\text{ cm}^{-1}$  shows the existence of NH bending groups, proving the effect of capping agent on the CdS particles. The broad band occurred around  $620\text{ cm}^{-1}$  represents the formation of Cd-S lattice stretching mode of the present CdS nanoparticles.

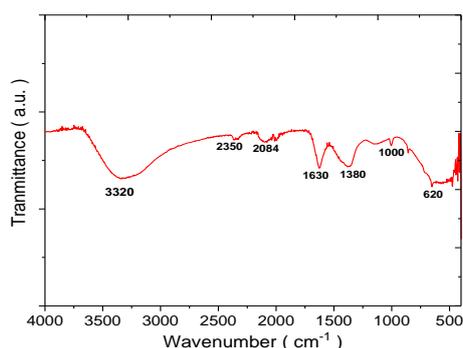


Fig. 1. FTIR spectra of CdS nanoparticles.

Fig. 2 shows XRD spectra of the present CdS nanoparticles. The (111), (220) and (311) planes located at  $26.34^\circ$ ,  $43.69^\circ$  and  $51.89^\circ$  are well indexed to a cubic structure with a lattice constant of  $a = 0.5820\text{ nm}$  according to JPDS card file 75-1546. This result indicates that the sample obtained is in a pure cubic CdS phase and no other impurities were detected in the samples. The XRD analysis could also reveal the samples were nano-sized and crystalline in nature, where the fine particle nature of the samples were reflected in the X-ray line broadening. The size of the

synthesized cadmium sulfide nanoparticles was then calculated using Scherrer equation as given by:

$$D = 0.9 \lambda / \beta \cos\theta \quad (1)$$

where  $\lambda$  represents the wavelength of X-rays,  $\beta$  represents half width at full maximum and  $\theta$  is the diffraction angle [10]. The average crystallite size of the particles was determined to be 4.45 nm, confirming that the particles were in nano sized.

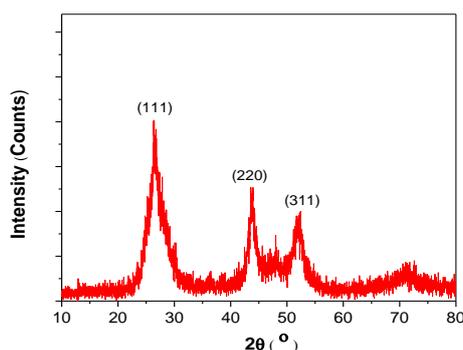


Fig. 2. XRD pattern of the as-prepared CdS nanoparticles.

Fig. 3 shows the SEM images of the CdS nanoparticles. From the figure, it can be clearly seen that the nanoparticles surface is smooth with a large outgrowth of CdS particles in a regular manner. The SEM images also show that the nanoparticles have a uniform spherical shape with particles size lying between 71 and 130 nm. On the other hand, these nanoparticles might be built up by the aggregation of many small nanocrystallites as determined by Scherer method.

The UV-Vis absorption spectra of the CdS samples is shown in Fig. 4. A well-resolved spectral lines could be observed from the figure. Also, there is a small sharp absorption peaks observed in the spectra at wavelength position of 330 nm. This indicates that the sample has a prominent UV absorption that may induce the photochemical or photocatalytic reaction with other photosensitive compounds. By using the Tauc's model, the energy gap was determined from the abscissas of the plots of the optical coefficient ( $\alpha$ ) versus photon energy ( $h\nu$ ) as shown in Figure 5. The band gap of the sample was calculated to be 2.85 eV, which is higher than the band gap of CdS in bulk phase (2.42 eV). This result can be well interpreted by the formation of CdS nanoparticle with quantum size effect [19].

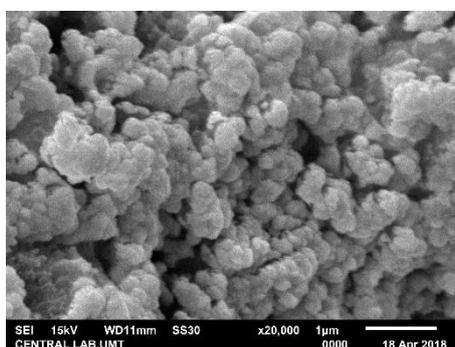


Fig. 3. SEM images of the CdS nanoparticles.

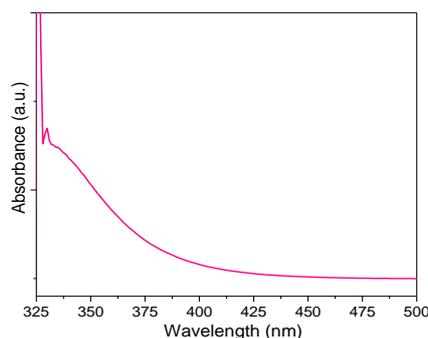


Fig. 4. UV-vis spectra of CdS nanoparticles.

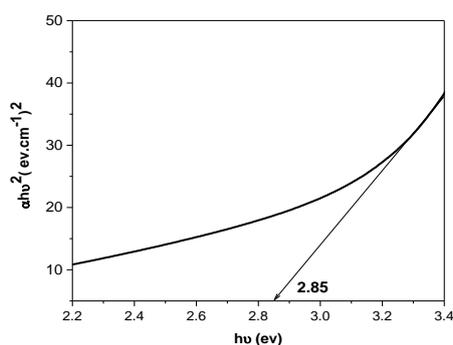


Fig. 5. The plot of  $(ah\nu)^2$  versus  $(h\nu)$  for the CdS nanoparticles.

## 5. Conclusions

CdS nanoparticles have been successfully synthesized via aqueous precipitation technique. The FTIR spectra shows that the CdS nanoparticles are bonded to the N-H stretching mode due to the effect of capping agent on the particles. SEM images show the formation of spherical nanoparticles in homogeneous size.

The XRD results indicate the formation of cubic phase structure with good crystallinity of structure arrangement. From this study, higher band gap of 2.85 eV is obtained for the nanoparticle when compared to the bulk CdS. This study may provide a better and easy production of CdS with uniform and ordered nanometer-sized structures and higher band gap transition for semiconductors application especially in optoelectronic and solar cells devices.

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