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Dependence of spectroscopic and electrical properties on the size of cadmium sulfide nanoparticles

R. Seoudi [a,b,*], A.A. Shabaka [a], M. Kamal [c], E.M. Abdelrazek [c], W. Eisa [a]

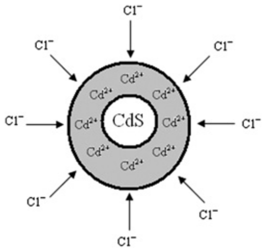
[a] *Spectroscopy Department, Physics Division, National Research Center, Dokki, Cairo, Egypt*
[b] *Faculty of Science, Department of Physics, Umm Al-Qura University, Makkah, Saudi Arabia*
[c] *Faculty of Science, Physics Department, Mansoura University, Mansoura, Egypt*

HIGHLIGHTS

- ▸ In this study cubic phase of cadmium sulfide nanoparticle with different sizes was prepared by chemical precipitation method.
- ▸ Effects of cadmium to sulfur molar ratio on the particle sizes was clarified.
- ▸ Energy gap and optical properties were affected by the particle sizes.
- ▸ Electrical conductivity was improved with decreasing the particle sizes.

GRAPHICAL ABSTRACT

We used different molar ratios of $CdCl_2$ and Na_2S to prepare CdS nanoparticles by chemical precipitation method and to control the particle sizes. The effects of the particle size on the optical and electrical properties were confirmed.



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ABSTRACT

Cadmium sulfide (CdS) nanoparticles with different sizes were synthesized using chemical precipitation method. The change of particle size, morphologies and crystal structures with the molar ratio of cadmium to sulfide salt was obtained from transmission electron microscopy (TEM) and X-ray diffraction pattern results. It should be noted that, the CdS nanoparticles were formed with different size, normal distribution and cubic phase. The effect of particle sizes on the optical properties was confirmed from UV–visible and fluorescence spectroscopic data. The optical band gap decreases from 2.9 to 2.51 eV with increasing the particle size from 5 to 9.25 nm due to the change of the molar ratio of $CdCl_2$ to Na_2S from (16:1) to (1:16). The electrical results obtained show that, DC conductivity increase with decreasing the particle sizes. The conduction mechanisms were discussed at low and high applied voltage. All samples have semiconducting behavior and can be used in the field of light emitting diodes.

1. Introduction

The unique properties of nanomaterial and its structures have received much attention in recent years due to their potential applications in many fields such as optoelectronics devices, catalysis, single-electron transistors, light emitters, photoelectrochemical and nonlinear optical devices [1–5]. A better understanding of matter at the nanoscale has led to a number of advances in materials science having novel optical and electronic properties. The formations of high strength materials have wide scale applications. Semiconductor nanoparticles of II–VI compounds are an example of a low-dimensional structure with their unique electronic and optical properties that have been extensively investigated for a wide variety of applications. Dramatic modification of their electronic and optical properties takes place due to the three-dimensional quantum confinement of electrons and holes when the size of the particle approaches the Bohr radius of exciton [6]. Cadmium sulfide (CdS) is a direct band gap material and it can be used in photoelectronic devices. Recently CdS nanoparticles have been widely investigated [7]. The luminescent CdS nanocrystals have wide potential applications in optical switches, sensors, electroluminescent devices, lasers and biomedical tags [8]. Various

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[*] Corresponding author. Tel.: +20 23308157; fax: +20 23370931.
E-mail address: rsmawed@yahoo.com (R. Seoudi).

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synthetic methods including reverse-micelle [9], colloidal [10] and arrested precipitation [11] have been developed to prepare monodispersed CdS nanocrystals. The aim of this work is to synthesise CdS with different nanoparticle sizes by a novel and simple aqueous precipitation method. The particle sizes were controlled by the change of the molar ratio of cadmium chloride ($CdCl_2$) and sodium sulfide (Na_2S). The samples were characterized using TEM and X-ray diffraction to confirm its sizes, crystallinity and purity. The effect of the different sizes on spectroscopic, optical and electrical properties will be obtained.

2. Experimental

2.1. Synthesis of CdS Nanoparticles with different sizes

Cadmium chloride dried LR. ($CdCl_2$) and sodium sulfide (Na_2S) were purchased from S.D. Fine-Chem. Ltd. All chemicals were analytical grade and used without further purification. According to our previous work the CdS nanoparticles were prepared [12–13]. To get cadmium aqueous solution of concentration 0.1 M, 0.917 g of $CdCl_2$ was dissolved into 50 ml of degassed and distilled water. 50 mL of Na_2S with different molarities (1.6, 0.8, 0.4, 0.1, 0.025, 0.0125 and 0.00625) were added to the prepared $CdCl_2$ solutions under argon gas flow with vigorous stirring to achieve $CdCl_2$ to Na_2S molar ratios of (1:16), (1:8), (1:4), (1:1), (4:1), (8:1) and (16:1) respectively. The solution was stirred and turned to yellow color immediately due to the formation of CdS. The stirring was continued further for some specific time (48 h) in order to facilitate complete nanoparticle precipitation. The precipitate was separated by centrifugation and washed repeatedly with water and ethanol to get rid of unreacted species and byproduct. The sample was dried at 40 °C for 6 h and then the free standing powder was collected and preserved in an airtight container.

2.2. Measurements

The shape and the nanoparticle size distribution of CdS were studied using Transmission Electron Microscope (JEOL JEM 2010, Japan) operated at 200 kV accelerating voltage. The powder samples were suspended in distilled water using ultrasonic water bath. The suspension was centrifuged to collimate the large size particles. Then a drop of the suspension was put into the carbon grid and left to dry. The crystal structure was studied and confirmed from X-Ray Diffractometer Philips (PW 13900, Netherlands), using Cu Kα ($\lambda = 1.54$ A). The UV–visible spectra were measured in the range of 1000–200 nm using Jasco 570 UV–visible–NIR spectrophotometer. The samples were prepared as suspensions in distilled water. The fluorescence spectra were measured using spectrofluorometer (Jasco FP-777, Japan) and with light source xenon arc lamp at 150 W. Electrical properties were carried out of the samples in the form of disk. The surfaces were well polished, coated with silver paint (BDH) and checked for good contact. Current–voltage (I–V) characteristics were measured at room temperature using an electrometer high resistance meter, Keithely 6517 A. The electrical conductivity σ $(\Omega\,\mathrm{cm})^{-1}$ was determined using $\sigma = \mathrm{Id/VA}$, where I is the current passing through the sample of thickness d and V is the applied voltage and A is the silvered contact area of the sample.

3. Results and discussion

3.1. Transmission electron microscope (TEM) of CdS nanoparticles.

Fig. 1(a–g) shows the transmission electron microscope images of CdS nanoparticles prepared at different molar ratios of $CdCl_2$ to Na_2S. From this figure it can be confirmed that, the CdS was formed in spherical shape and a number of well-dispersed are observed with a fairly even size distribution. The calculated grain size in Table 1, was increased from 5 to 9.25 nm with decreasing the molar ratio of $CdCl_2$ to Na_2S from (16:1) to (1:16). The dependence of particle size on the starting salt concentration is discussed by three different situations [14]. First, if the number nuclei increase faster than that of total ions then smaller particles would be obtained. Second, if the increase of nucleus number was proportional to total ions, the particle size might remain unchanged. Third, when the number of nuclei remained constant, the particle size becomes larger [14]. Based on the above observation, our samples appeared to belong to the third situation. According to these discussions the CdS nanoparticle can be prepared by controlling their size using Cd ions as a probe.

3.2. X-ray diffraction analysis of CdS nanoparticles

Fig. 2(a–g) shows the X-ray diffraction (XRD) patterns of CdS nanoparticles. Three peaks were observed at $2\theta^\circ = 26$, 43 and 51° and its indexes are (1 1 1), (2 2 0), and (3 1 1) planes of CdS. This is indicated to cubic structure according to (JCPDS no. 80-0019). The cubic structure was attributed to the rapid nucleation and growth from a supersaturated solution and it may be formed from closer similarity of spherical nucleus which was expected during the initial stage of nucleation and then turn to hexagonal structure. The change in the diffraction patterns is due to the change of $CdCl_2$ to Na_2S molar ratios and it is discussed in four steps. The step one, when the samples are crystalline due to XRD features at three prominent lattice planes rather than amorphous. This is in agreement with the work done by Murray [15]. Second, the XRD peaks of cubic CdS are broad due to the small grain size and low degree of crystallinity [16]. Third, no characteristic peaks were observed for the other impurities, such as $CdCl_2$ or Na_2S which may reflect the purity extent of prepared CdS nanoparticles. However, many shoulders are noticed corresponding to (1 0 0) ($2\theta = 25^\circ$) and (1 0 1) ($2\theta = 28^\circ$) peaks of wurtzite phase riding over the (1 1 1) peak of the cubic phase which suggests the presence of small fraction of wurtzite phase in the as-synthesized sample. Fourth, the XRD patterns become weaker and broader with increasing the molar ratio of $CdCl_2$ to Na_2S. This is indicating to the reduction in particle size of CdS nanoparticles. The particle size D is calculated based on the regular broadening of XRD peaks as a function of decreasing crystallite size. This broadening is a fundamental property of XRD described by well-established Scherer theory Eq. (1) [17]:

$$D = k\lambda/\beta\cos\theta \tag{1}$$

where β is full width at half maximum of the peak corresponding to plane (1 1 1), k is the so-called shape factor which usually takes a value of about 0.9, and θ is the angle obtained from 2θ value corresponding to maximum intensity peak in XRD pattern. The peak position and resolution were determined using Gaussian peak fitting method. The calculated values of (d) spacing, lattice constant (a) and particle size (D) were calculated on the basis of changes in the main peak at 26° and is listed in Table 1. It is seen that, the position and the shape of the reflection peak (1 1 1) is shifted from 26.96° to 27.21° for the molar ratio of $CdCl_2$ to Na_2S change from (1:16) to (16:1), d-spacing from 3.32 to 3.27 Å, lattice constant from 5.75 to 5.66 Å and particle size from 3.8 to 6.8 nm. The change of d-spacing is expected due to the high surface-to-volume ratio [18]. It can conclude that, the $CdCl_2$ to Na_2S ratio can be used as a determining factor for controlling the particle size. The particle size measured from TEM micrograph i larger than the value calculated from XRD data and this change is