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Effects of Ethylene Glycol Concentration on Cadmium Sulfide Nanowires Growth

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ABSTRACT: One dimensional (1-D) cadmium sulfide (CdS) nanowires were produced by L-cystein-assisted solvothermal methods. A series of experiments were carried out with different concentrations of ethylene glycol. X-ray diffraction (XRD) and scanning electron microscope (SEM) results show that the crystalinity of CdS nanowires structures are depending on the ethylene glycol. Moreover, with the concentration of ethylene glycol at 16 M, continuous nanowires with regular and smooth morphology were obtained. The width of each nanowires recorded were between 50-65 nm. The band gap of the samples measured by UV-vis spectroscopy increases from 2.42 eV to 2.54 eV with the increase of ethylene glycol concentration. The mechanism for L-cystein reaction with cadmium during the synthesis of the nanowires was also discussed.
Keywords: *Cadmium sulfide; nanowires; solvothermal; band gap*

1. Introduction

Cadmium sulfide (CdS) is a well-known semiconductor which has been used in many applications such as solar cells, photo-sensors, or other electronic devices [1-4]. Recently, the semiconductors QDs (quantum dots) are one of the most studied materials because of the unique optical properties due to the quantum confinement effects on their band structure [5]. Ethylene glycol and L-cystein are usually used as the surface active agent, which favour the formation of nanowire with a narrow size distribution [1-5].

Many methods have been introduced to synthesize the CdS QDs including vapor deposition, electrodeposition, and solvothermal method [6-7]. Solvothermal methods are widely used for producing CdS nanowires because it promising abundant and well-structured nanowires with simple preparing routes. In this paper, CdS nanowires were prepared based on reaction of template Cd-cystein with ethylene glycol under solvothermal condition with different concentration ethylene glycol to study the effects of ethylene glycol to nanowires growth and their properties changes during the changes.

2. Experimental

All reagents were analytical grade and used without further purification. L-cystein (Sigma) was chosen as sulfide source, beside as-template to control the size and shape of nanostructures. Appropriate amount of $CdCl_2 \cdot 2.5H_2O$ (Sigma-Aldrich) are dissolved in the distilled water with L-cystein at room temperature and resulted a clear solution. After continuous stirring about an hour, the solution was added quickly with ethanol amine and kept stirring until it formed a white solution. The white powder, which is the precursor for nanowires CdS were collected by centrifugation and washed with absolute ethanol for several times. The obtained white powder was dried at 60 ºC for 12 hours. The as-prepared white powder Cd-cystein are then been transferred into a Teflon-line stainless steel autoclave containing 4, 8, 12, and 16 M of ethylene glycol (Sigma-Aldrich). The Teflon were sealed and heated at 120 ºC for 16 hours. After the thermal process, the precipitate is changed to yellow color due to the presence of sulfur in the CdS formation. Then the colored powder once again had been collected by centrifugation and washed with absolute ethanol. The prepared nanowires been dried at 60 ºC about 12 hours for characterization.

UV-vis absorption spectra were recorded with an UV-Vis scanning spectrophotometer (Perkin Elmer). The scanning electron microscopy (SEM) with JEOL JSM model 6360-LA was used to observe the morphology of the sample while the molar ratio of CdS was measured by energy dispersive spectroscopy (EDS). Functional groups determination is done by fourier transform infra red (FTIR) Spectroscopy (Thermo Nicolet). XRD patterns are recorded by Rigaku Miniflex X-ray diffractometer.

3. Results and discussion

Figure 1 shows the XRD patterns of the as-prepared CdS nanowires using different concentration of ethylene glycol. By comparing all the patterns, the peaks clearly show that the crystallinity of the samples is increased by increasing concentration of ethylene glycol. There, the peaks of the samples at 16 M and above are seen more intense than the peaks at 4, 8, and 12 M. The major peaks (100), (002), (101), (110), (103), and (112) are

corresponding to the hexagonal phase according to CdS (JCPDS 06-0314) [8]. There are no peaks of impurities such as CdO or S was detected. The morphologies of the samples observed by SEM are shown in **Figure 2**. The images revealed although without ethylene glycol, nanowires of CdS are still growing using thermal method. But the nanowires are more abundant when the concentrations of ethylene glycol are increased. Also for the size of nanowires, with increasing of ethylene glycol, the size are much smaller with the shape are more continuous compared to the low concentration of ethylene glycol. Table 1 shows the different of size and shape of CdS nanowires obtained by different concentration of ethylene glycol.

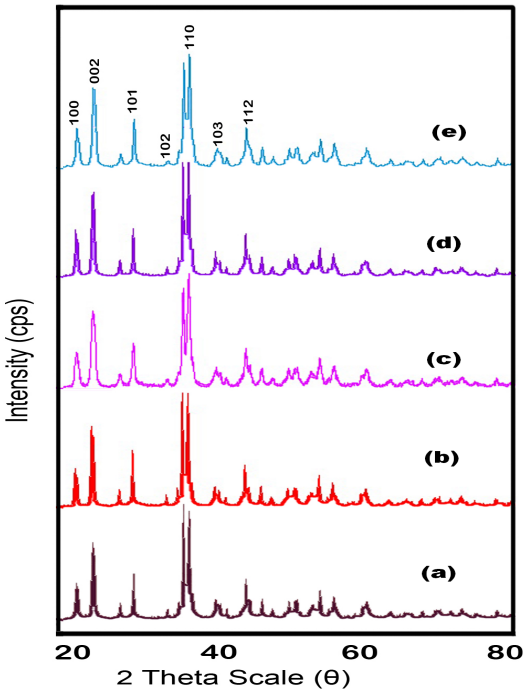


Figure 1: XRD patterns of the prepared CdS nanowires without and with different concentration of ethylene glycol (a) 0 M, (b) 4 M, (c) 8 M (d) 12 M and (e) 16 M of ethylene glycol

Table1: Average size and shape of CdS nanowires in different concentration of ethylene glycol

Concentration (Molar)	Average size (nm)	Shape of nanowires
0	210	Short, Discontinuous
4	172	Short, Discontinuous
8	136	Long, Continuous
12	88	Long, Continuous
16	54	Long, Continuous

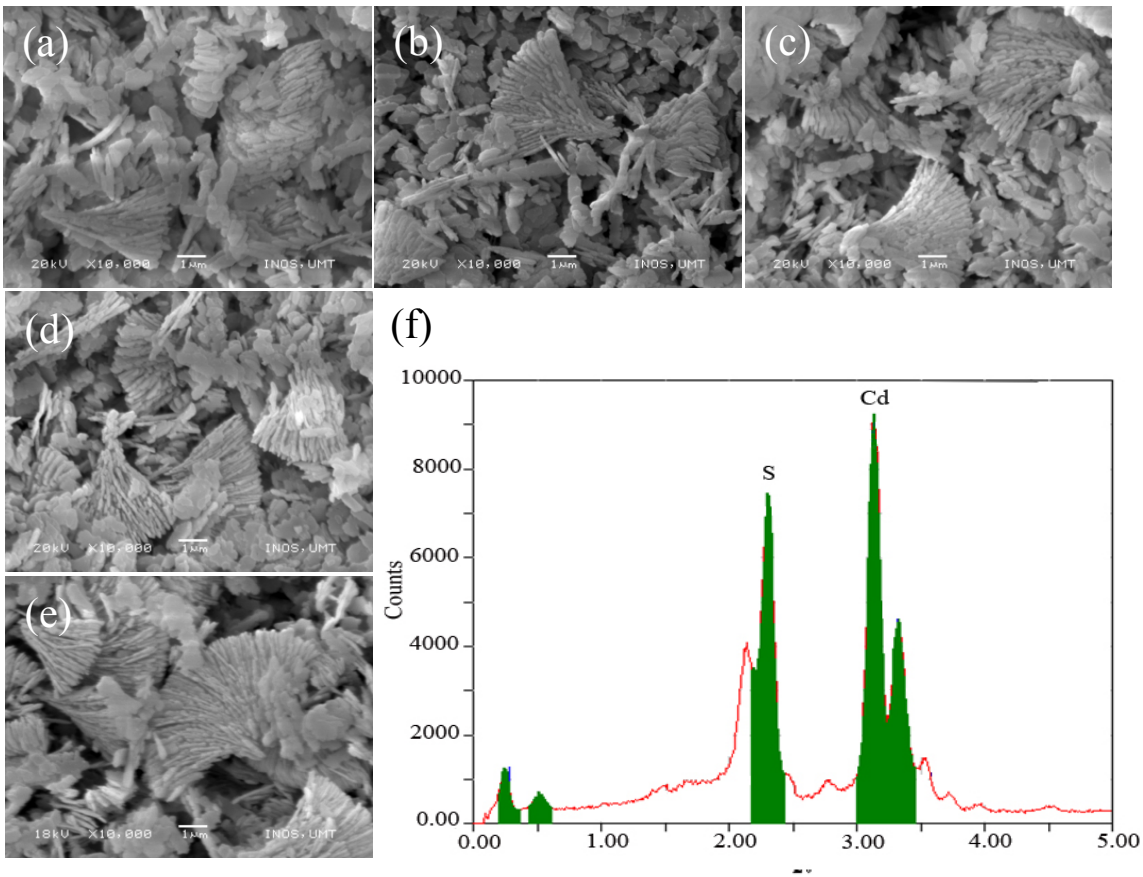


Figure 2: SEM images of the CdS nanowires obtained by solvothermal at the different concentration of ethylene glycol (a) 0 M (b) 4 M (c) 8 M (d) 12 M (e) 16M while (f) EDS spectrum of CdS nanowires

The EDS recorded that there are three major atoms found in the samples which are cadmium atoms, sulfur atoms, and carbon atoms, with ratio calculation of Cd to S are nearly to 1:1 and the carbon atoms are came from the cystein molecules used in this study.

Figure 3 shows the FTIR spectra of CdS nanowires obtained at different of ethylene glycol concentration. The peaks at 1740 cm^{-1} which is represent the peak of C=O are only been seen in spectrum (a), (b) and (c). The present of this peak because the reaction of water with L-cystein and produce C=O. It is also resulted the peaks at 3333 cm^{-1} and 3287 cm^{-1}, while the peaks of N-H at 2360 cm^{-1} are only been seen at spectra (a) to (d). The N-H group is come from L-cystein which is used as sulfide source, beside as-template to control the size and shape of nanowires. The dissapearing of N-H shows that the CdS nanowires obtained by 16 M concentration of ethylene glycol pure than others.

Figure 4 shows the UV-vis spectra of as-prepared CdS nanowires at different concentration of ethylene glycol. It was found that the absorption onsets shifted to the lower wavelength with the increases of ethylene glycol concentration, which indicated that the CdS nanowires was grown more abundant. The optical band gap energy (E_g) was calculated according to Tauc relationship which is given by the formula:

$$(\alpha h\upsilon) = A(h\upsilon - E_g)^n \quad (1)$$

Where $(h\upsilon)$ is the photon energy, A is a constant, α is an absorbance, and n = ½ for direct band gap material [10]. When $(\alpha h\upsilon)^2$ is plotted as a function of $(\alpha h\upsilon)$, the linear portion of the curve is extrapolated to $(\alpha h\upsilon)^2 = 0$ and the final equation will become $E_g = h\upsilon$.

Because of the presented of COO^- groups in the samples, each of the absorbed wavelengths should be added with 195 nm (absorption of COO^-) for the CdS nanowires actual wavelength [11]. **Figure 5** shows the absorbance are enhanced as the CdS nanowires growth abundantly, causes the E_g values increased due to the decrease of particles size to quantum dots (QDs) [12]. The obtained energy gaps of CdS nanowires are higher than pure CdS (2.40 eV) [5]. As the QDs sizes decreases, the energy gap increases, leading to a blue shift of an emission wavelength [13]. This effect can be observed by UV light test, in which the color of the samples are changed from yellow to dark brown after illuminated with the UV lights.

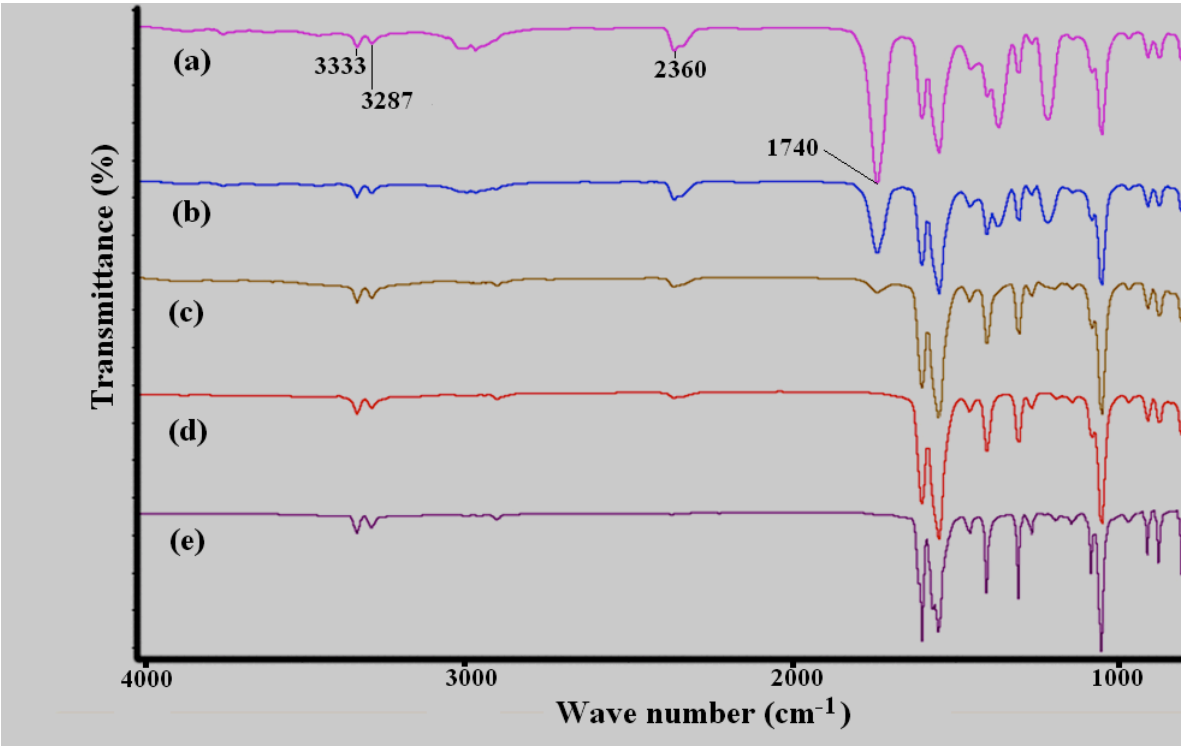


Figure 3: IR spectra of CdS nanowires (a) without ethylene glycol, (b) 4 M (c) 8 M (d) 12 M and (e) 16 M of ethylene glycol

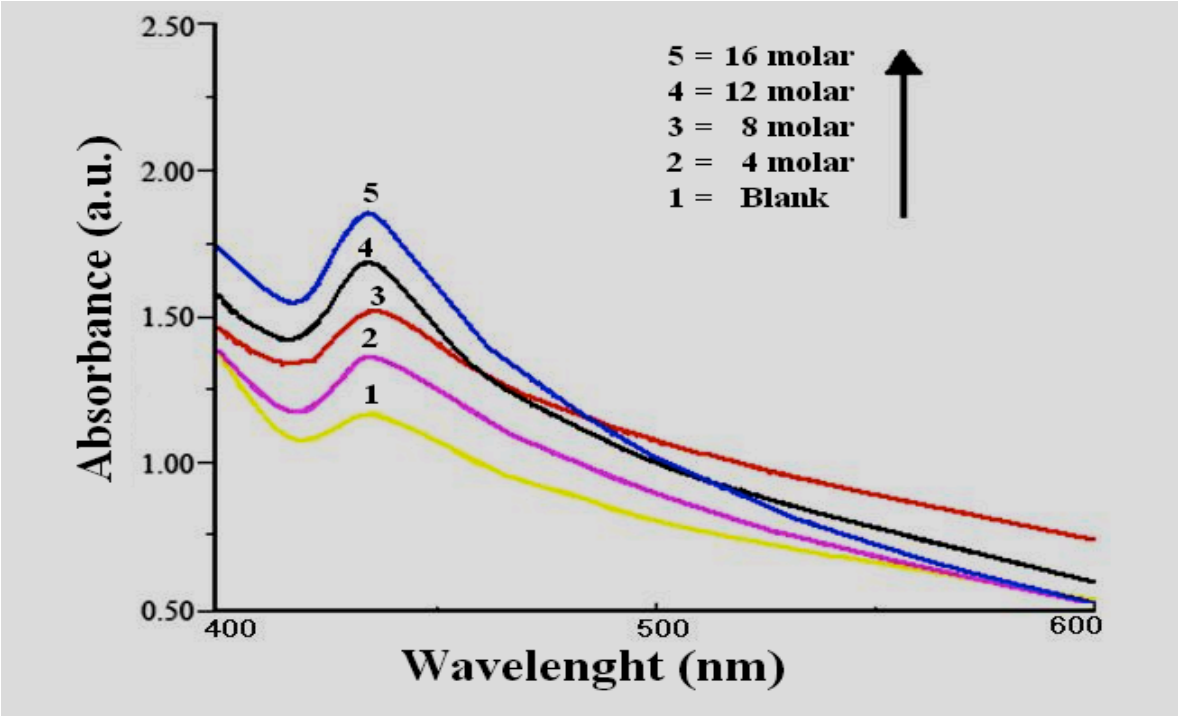


Figure 4: UV-vis spectra of the samples

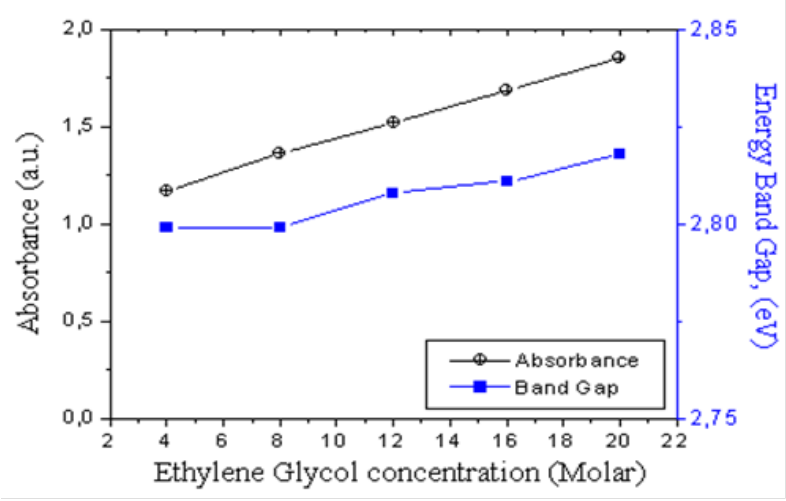


Figure 5: Absorbance and energy band gap as a function of ethylene glycol concentration

4. Conclusion

The uniformly order shape of CdS nanowires were obtained by solvothermal methods with L-cystein as the template base. The nanowires in the samples begin to grow within 12 to 20 hours of solvothermal time with optimum growth at 20 hours. The XRD pattern recorded that the crystallinity of CdS nanowires are increased with increasing the solvothermal concentration. This are verified by SEM images where it shows the morphology of the CdS nanowires are much abundant with smaller size of nanowires by the range of size is 50-60 nm. The FTIR spectrum suggested that the products are produced after the free S^{2-} anions from S-H group in L-cystein are reacted with Cd^{2+} cations to form CdS. The calculated band gap energies of the samples are increased after more nanowires growth, which agrees with the QDs size effect as the particles became smaller. The optical effects of the samples can be seen after the samples are being illuminated with UV lights, where they changed their color from yellow to dark brown color.

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