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# A STUDY OF CADMIUM SULFIDE NANOPARTICLES WITH STARCH AS A CAPPING AGENT

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## ABSTRACT

Capping agents such as starch can be used to protect semiconductor nanoparticles from aggregation and obtain uniform structures. Cadmium sulfide (CdS) nanoparticles with starch as a capping agent were prepared with an aqueous precipitation technique at different pH levels to study the optimum condition for producing a narrow distribution of nanoparticles. The morphology of the prepared nanoparticles was measured by scanning electron microscopy (SEM). Grain sizes of the samples determined by X-ray Diffraction (XRD) with Scherer's equation were relatively dependet on the pH applied in the synthesized process. Infrared spectroscopy (FT-IR) indicated that the starch and the nanoparticles were bonded by R-N=C=S bonds, but bondinbg depended on the pH used. The band gap of the CdS nanoparticles measured by UV-Vis spectroscopy was 2.39 eV, which was lower than CdS in bulk phase because of distorted structures in obtained CdS nanoparticles.

*Keywords:* Aqueous technic; Cadmium sulfide (CdS); Capped agent; Nanoparticles; Starch

## 1. INTRODUCTION

Cadmium sulfide (CdS) is a semiconductor that exists in two mineral forms, greenockite and hawleyite. CdS is also known as a direct band gap semiconductor with a band gap value of $E_g = 2.42$ eV at room temperature, where $Eg$ represent the energy of the band gap (Ashour, 2003; Liu & Zhu, 2009). As a semiconductor, CdS has been used in vital applications, such as flourescent probe (Phuruangrat et al., 2009), sensors, solar cells (Wijayantha et al., 2004), photo-electrocatalysis (Chen et al., 2002), and laser light-emitting diodes (Shao et al., 2002). When semiconductor materials are fabricated in nano-scale, their density of electronic states will change in a systematic manner, which strongly influences the optical and electronic properties of the materials (Rossetti et al., 1983).

Compared with the bulk materials, the nano-size semiconductor particles exhibit some unique properties, such as nonlinear optical properties (Wang & Herron, 1991), quantum size effect (Steigerwald & Brus, 1988), and other important physical and chemical properties. Their potential application in both mesoscopic research and development of nano devices is also very extensive. Until now, the fabrication of semiconductor nanoparticles (NPs) has been attracting considerable attention from material scientists (Luan et al., 2006).

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However, there is a problem in obtaining CdS in nanosized and uniformed structures due to the high surface energy and low surface area of the NPs that restrict control over particles and result in aggregation of NPs (Pattabi & Amma, 2006). The synthetic route for obtaining NPs with narrow size distribution, good crystallinity, high photostability, desired surface properties, and high photoluminescence quantum efficiency is a topic for further studies in the effort to develop the highest quality of semiconductor NPs. An excellent method currently employed to obtain high-quality semiconductor NPs is caps the particles with polymer to prevent flocculation (Priyam et al., 2004).

The capping process is suitable forncontrolling particle size and uniformity of nano-sized materials. We noted that starch is a good polymer to cap nano-sized materials because of the polar groups in its structures, such as $SO_3^-$ and $OH^-$, which act as coordination sites for ion aggregation between particles (Thomas & Atwell, 1999). Starch-capped CdS NPs can be obtained through an aqueous precipitation technique. The pH level of the solution during the capping process should be suitable for starch to cap the NPs because starch is very sensitive to the pH changes. The objective of the present study is to develop an effective method for synthesizing NPs with the desired size distribution and high surface area.

## 2. METHODOLOGY

All chemicals purchased for this experiment were used in the condition in which they were acquire. Cadmium chloride ($CdCl_2$), starch, and thiourea were purchased from Sigma. Sodium hydroxide (NaOH), potassium hydroxide (KOH), and ammonium nitrate ($NH_4NO_3$) were obtained from Merck; acetone was obtained from EMD Laboratory. In an experimental procedure, $CdCl_2$ (0.02M), KOH (0.5M), $NH_4NO_3$ (0.5M) and thiourea (0.2M) were mixed and stirred at 80$^o$C. In less than 2 hours, the uncolored mixture changed to yellow-orange, indicating that CdS had formed. Meanwhile, a solution of starch (1g/100mL) was also prepared by dissolving starch in distilled water and heating it to the same temperature maintained in the CdS solution. Both solutions were then mixed slowly and stirred continuosly at 80$^o$C to maintain starch gelatinization. Five solution samples were prepared with different pH values (6, 8, 10, 12, 14) and a NaOH solution. After 30 minutes of stirring, yellow precipitates were isolated from the solutions by the gravimetric method and washed several times with distilled water. The samples were washed again with acetone and dried in an oven at 45$^o$C for 24 hours before the characterization was performed.

Scanning electron microscope (SEM) imaging was performed using the JEOL JSM model 6360-LA at an acceleration voltage of 25 kV. Energy dispersive X-ray spectroscopy (EDS) was acquired at an acceleration voltage of 20 kV. Powder X-ray diffraction (XRD) was performed with a Rigaku Miniflex X-ray Diffractometer. UV-Vis absorption spectra were recorded with an UV-Vis scanning spectrophotometer (Shimadzu 1601PC) and functional groups determination was performed using the Fourier transform infrared (FT-IR) Perkin-Elmer Spectrum 100 series.

## 3. RESULTS AND DISCUSSION

Starch-capped CdS NPs were investigated by using FT-IR to study the present functional groups in comparison to pure starch. The FT-IR spectrum in Figure 1 shows the spectrum of the functional groups present in starch and starch-capped CdS NPs. Several organic groups were present in both of the starch and the sample spectra. The OH group observed at 3340 $cm^{-1}$ in the starch spectrum (i) also existed in the starch-capped CdS NPs spectrum (ii) at 3338 $cm^{-1}$. Other similar groups observable in both spectrums were $C\text{-}H_3$ [2928 $cm^{-1}$ (i), 2920 $cm^{-1}$ (ii)], conjugated C-C [1632 $cm^{-1}$ (i), 1622 $cm^{-1}$ (ii)], C-H [1384 $cm^{-1}$ (i), 1400 $cm^{-1}$ (ii)], and C-O [1155 $cm^{-1}$ (i), 1150 $cm^{-1}$ (ii)].

These similar peaks indicate that starch was present in the sample of CdS NPs. However, three different peaks are shown by these spectra: the NH peak at 3843 $cm^{-1}$, the R-N=C=S peak at 2000 $cm^{-1}$ and the aliphatic R-H group at 2371 $cm^{-1}$. These three peaks only existed in the sample's spectrum indicating that the capped reaction between the CdS NPs with starch occurred at the N=C=S bond. We believe that the major contribution of the N=C=S bond comes from the thiourea used in the early procedure.

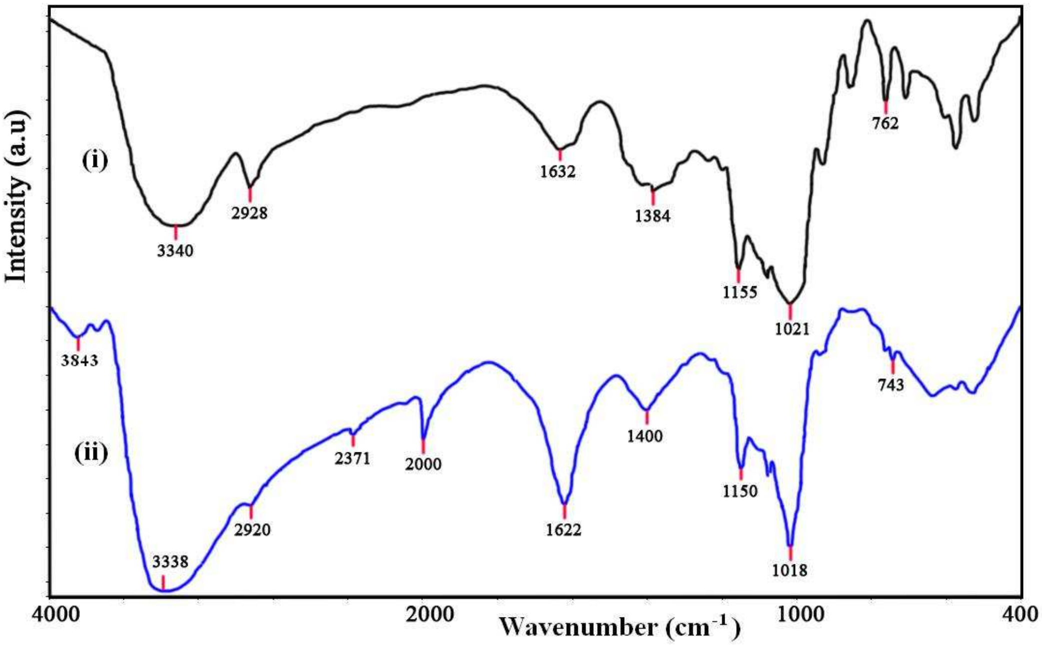

Figure 1 FT-IR spectra of the (i) starch and the (ii) starch capped CdS NPs

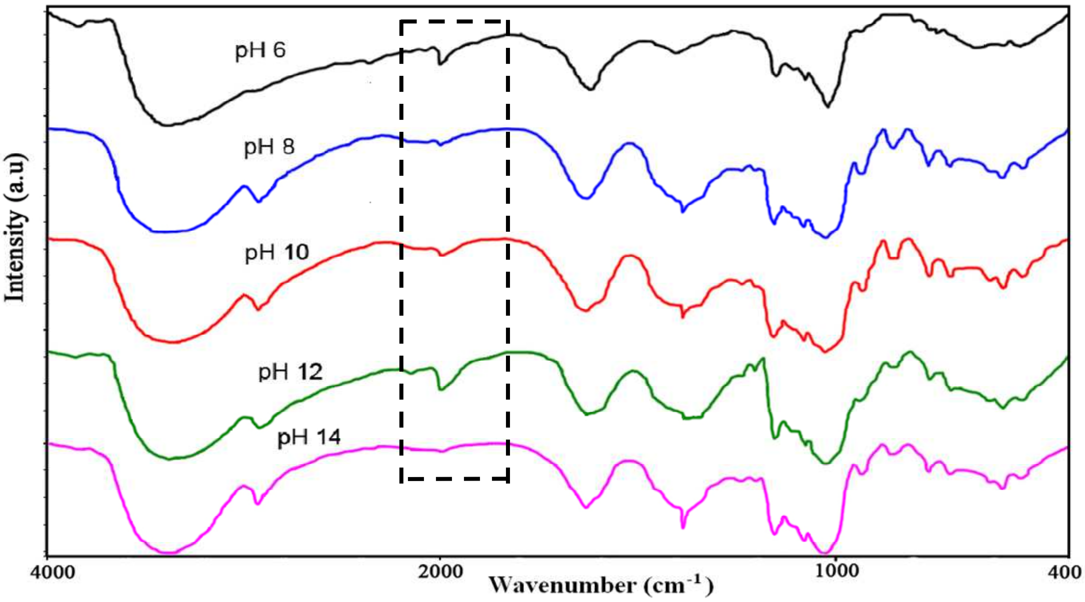

Figure 2 FT-IR spectra of starch capped CdS NPs synthesis at pH 6, 8, 10, 12 and 14. Dashed line represents the peak of R-N=C=S group at 2000 $cm^{-1}$

The CdS NPs can be capped with starch only at suitable pH levels. Figure 2 shows the FT-IR spectra of CdS NPs capped with starch in different pH solutions. The difference among spectrums can be seen at the peak of R-N=C=S group at 2000 $cm^{-1}$. Greatest peak intensity is at pH 12, which means the higher concentration of R-N=C=S groups occurred in this sample. In the spectrum of pH 14, however, there are almost no peaks of R-N=C=S groups present due to properties of the starch. Actually, starch granules are insoluble in cold water until the water is heated to the gelatinization temperature, which is usually in the range of 60-80 ºC (Rodriguez et al., 2008). We observed that gelatinization of starch will not occur when the pH value of water is higher than pH 13; rather, the starch will be sticky (French, 1973). In this study, sticky starches restricted starch molecules from bonding with CdS molecules when the pH solution was increased to pH 14.

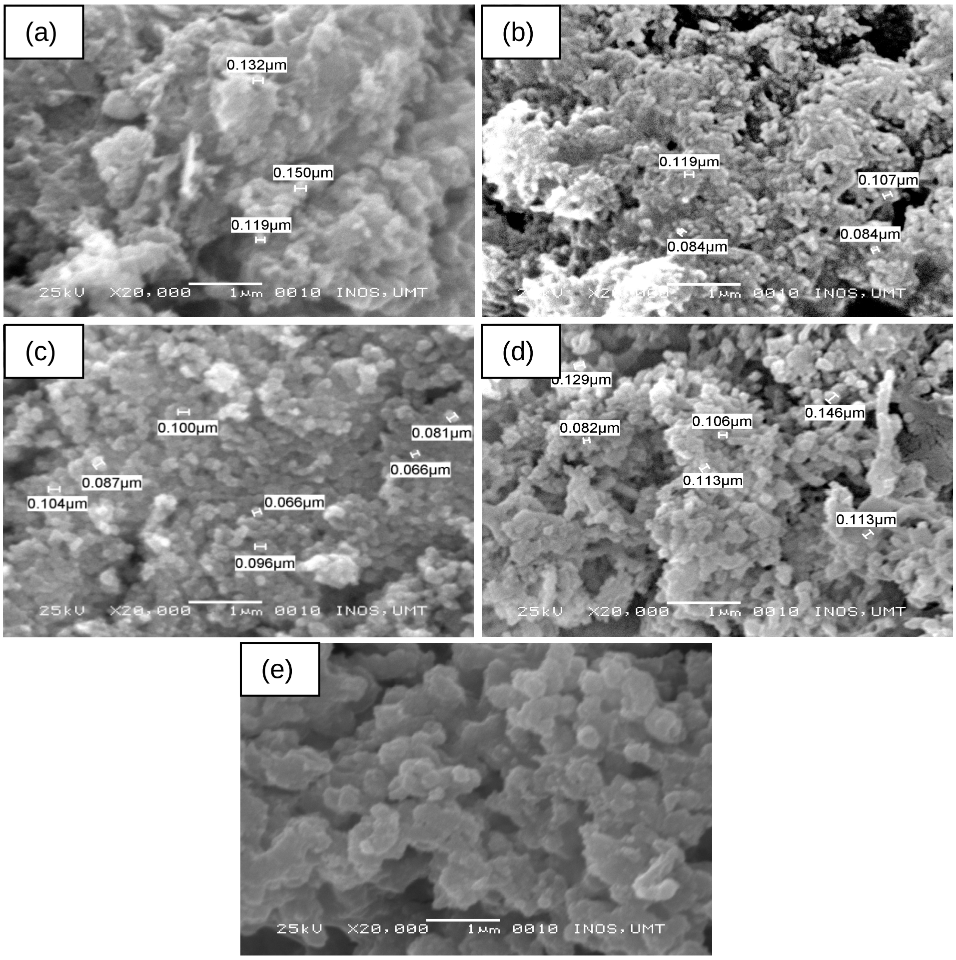

Figure 3 SEM images of starch-capped CdS NPs synthesized with different concentrations of NaOH: (a) pH 6, (b) pH 8, (c) pH 10, (d) pH 12, and (e) pH 14

At pH levels below 12, peaks are present at lower intensities because of the agglomeration process. SEM images in Figure 3 show that CdS NPs at pH 6 and pH 8 were attracted to each other because nanoparticles were not well-capped by the starch. The NPs can be distinctly seen at pH 10 and pH 12 because agglomeration did not occur during starch gelatinization. Aggregation interfered at pH 14, where the NPs grew larger because the sticky starches could not avoid particles from flocculation. The EDS results obtained showed that the atomic ratio of cadmium to sulfur was 50.04 to 49.96, which is close to 1:1 stoichiometry.

By comparing all XRD patterns of CdS NPs capped with starch in different NaOH concentrations, the peaks in Figure 4 clearly show differences in crystallinity of each sample. Peaks of pH 12 and pH10 samples were found to be sharper than peaks of other samples, which means crystallinity in their structures was higher than in other samples. Major peaks (100), (002), (101), (110), (103), and (112) in all patterns correspond to the hexagonal phase of CdS.

No peaks of impurities, such as CdO or S, were detected, indicating that all samples contained CdS in a highly pure form.

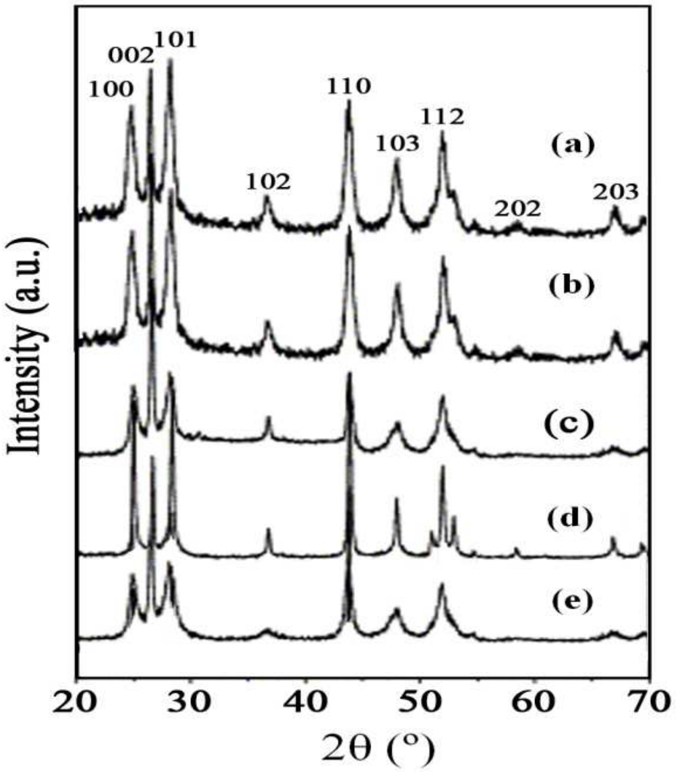

Figure 4 XRD patterns of starch capped CdS NPs synthesized in different concentrations of NaOH: (a) pH 6, (b) pH 8, (c) pH 10, (d) pH 12, and (e) pH 14

The average grain of each sample was determined by Scherer's equation, $d = 0.9\lambda/\beta cos\theta$, where $\lambda$ is the wavelength of the x-ray radiation, $\beta$ is the full-width and half-maximum (FWHM) on the most intense peak, and $\theta$ is the angle of diffraction. The calculated average grain size of the samples synthesized with pH 6, 8, 10, 12, and 14 were 122 nm, 98 nm, 100 nm, 82 nm and 263 nm, respectively. The grain size of the sample with pH 14 was much larger than that of other samples because the sticky starch restricted the movement of the $SO_3^-$ and $OH^-$ groups to capped CdS NPs.

The energy band gap of the samples was measured by the UV-Vis spectrophotometer. In Figure 5 showing UV-Vis spectra of samples at various pH levels, two different peaks are noted in samples at pH 10 and 12. The peak at 582.5 nm is due to C=N in the samples, while the peaks at 518 nm are due to CdS. Peak absorptions in samples at pH 6, 8, and 14 were lower than those for samples at pH 10 and 12 because of the agglomeration effect that obstructed UV rays from the CdS NPs. According to Zhang et al. (2009), the energy band gap ($E_g$) of CdS nanoparticles can be calculated using Equation 1:

$$E_g = \frac{1240}{\lambda} \quad (1)$$

where λ is the optical absorption threshold. From the equation, we found that the value of $E_g$ for CdS nanoparticles is 2.39 eV, which is lower than the band gap of CdS in bulk materials (2.42 eV). Findings from Kelsall et al. (2005) are consistent with this result; as the particle size of materials decreased, the allowed energy bands became narrower than in an infinite solid. The normal collective electronic properties of the bulk materials became severely distorted in this phenomenon known as quantum confinement.

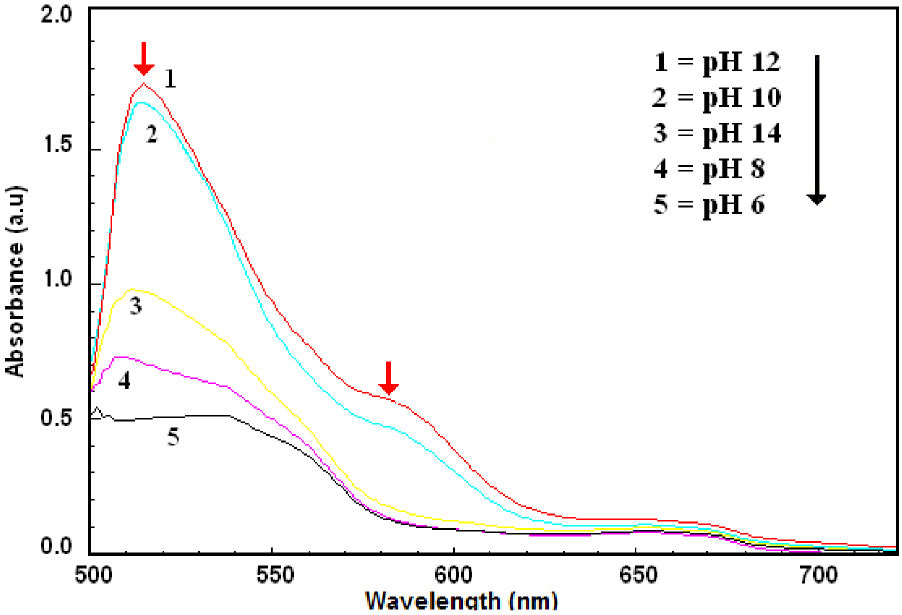

Figure 5 UV/Vis spectrum of starch-capped CdS NPs obtained under different pH conditions

## 4. CONCLUSION

Starch-capped CdS NPs were successfully synthesized with an aqueous precipitation technique. The FT-IR spectra showed that starch present in the samples and CdS NPs bonded to the starch with R-N=C=S bonds. The size of the particles measured by SEM and XRD indicates that pH value plays a role in producing smaller particles with uniform order. From this study, we found that CdS NPs characterized by narrow size distribution, good crystallinity, and low energy band gap could be obtained by capping the CdS NPs with starch at pH 10–12; agglomeration occurs if pH of the medium is below pH 12, while NPs will aggregate if the pH value is higher. Hopefully, this study provides beneficial insight into the production of CdS NPs with desired surface properties, high photostability, and lower band gap emission for semiconductor applications, especially in optoelectronic devices and solar cell devices.

## 5. ACKNOWLEDGEMENT

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