A novel method for the synthesis of CdS nanoparticles without surfactant

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A B S T R A C T

Cadmium sulfide nanoparticles with a hexagonal phase (~10 nm) were prepared at a relatively low temperature (70 °C). This synthesis was carried out shortly (30 min) through a new micro-emulsion (O/W) induced by ultrasound without surfactant. Ultrasound can provide an excess energy for new interface formation and obtain emulsions even in the absence of surfactants. This technique avoids some problems that normally exist in conventional micro-emulsion synthesis such as the presence of different additives and calcinations. In addition, it was possible to tune the particle size, the band gap, and the phases of CdS nanoparticles by changing the variables such as ultrasonic irradiation time, intensity, precursor, and ratio of the components. It was also found that the synthesized nanoparticles have a band-edge emission at about 460 nm with a blue-shift to a higher energy which is due to the typical quantum confinement effects. The product was characterized by different techniques such as UV–visible absorption spectroscopy, X-ray powder diffraction, and high resolution transmission electron microscopy (HRTEM).

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1. Introduction

Semiconductor nanocrystals are of great interests for both fundamental research and industrial development. This is due to their unique size-dependent optical and electronic properties and their exciting utilization in the fields of light-emitting diode [1], electrochemical cells [2], laser [3], hydrogen producing catalyst [4], biological label [5]. They are usually prepared in the liquid reaction system at high temperatures for several hours. These methods are either expensive, explosive, moisture sensitive or extreme toxic, energy consuming. Therefore, developing novel facile preparation methods under mild conditions is still of challenge for both industry and academic works [6,7]. Recently, much attention was paid to develop liquid–liquid approach for synthesizing nanocrystal metals, metal oxides and metal sulfides [8,9]. In most cases, the particles are formed by arresting precipitation of reaction precursors of reverse w/o micro-emulsions under certain conditions [10,11]. It is worth mentioning that micro-emulsions and ultrasound irradiation are two synthetic methods for nanosized sulfides that have been studied intensively and arousing more and more attention [12,13].

There are relatively rare reports on the formation of nanoparticles using the combination of ultrasound and micro-emulsion [14]. The sonochemical formation of CdS nanoparticles have been reported with hexagonal phase in the range of 80–120 nm in CS2–water–ethylenediamine micro-emulsion [15]. Wang et al. have prepared CdS nanoparticles with cube shape by a sonochemical method in an O/W micro-emulsion [16]. De et al. have synthesized semiconductor nanoparticles (CdS and ZnS) in w/o media and reported that the photo-absorption threshold of semiconductors increases as the H2O content of reverse micelles increases [17]. Cavitation is responsible for the mixed phase reactions, emulsification and extraction in a liquid–liquid heterogeneous system and it increases the surface area and the mass transfer between two phases. This behavior leads to the enhancement of diffusion coefficient on the interface mixing better than conventional agitation [18,19]. Ultrasonic irradiation is a fast-growing research due to some advantageous such as rapid reaction rates, controllable reaction conditions and the ability to form nanoparticles with high purity [20]. It is also confirmed that ultrasound can produce smaller size with higher surface area than those reported by other methods [21].

In this investigation, a new method has developed to produce CdS nanoparticles with sizes smaller than 10 nm by using ultrasonic waves and micro-emulsion. In this work CS2 was employed as the sulfur source for CdS and also as the oil phase in the micro-emulsion.

2. Experimental

2.1. Materials

Ethylenediamine (Merck), CS2, CdCl2, 2H2O from Fluka have been used without further purification. De-ionized water was used for the sample preparation.
2.2. Synthesis of nanoparticles

First, ethylenediamine (0.6 mL) was dissolved in water (40 mL) in a Rosset Cell at about 298 K. Then, C52 (0.2 mL) was introduced into the solution as an oil phase. The mixture was irradiated with ultrasound (20 kHz Sonifier W-450, amplitude % 75, normal horn, acoustic power, 41 W) at about 35 °C. The turbid solution became clear after ~2 min sonication. Then an aqueous solution of cadmium chloride (CdCl2·2H2O, 021 g dissolved in 10 mL solution) was introduced into the cell and it was sonicated for another 10 min at the same temperature. In another step by stopping the circulating bath during sonication, the temperature was increased from 35 to 70 °C and the nucleation processes were began after 5 min. The precipitate was separated by centrifugation, washed with distilled water and then 2–3 times with absolute ethanol, and finally dried in air at room temperature.

2.3. Characterization of CdS nanoparticles

The structure and morphology of the final products has been studied by transmission electron microscopy (HRTEM, Hitachi 300 kV H-9500 TEM with accelerate voltage 300–100 kV and resolution 0.1 nm for crystal lattice and 0.18 nm for point to point). The X-ray diffraction (XRD) patterns were recorded in a wide angle range (2θi = 10°–70°) by Bruker-axs, D8 Advance in scanning step of 0.02°/s with monochromatized Cu K radiation (λ = 1.5406 Å). The optical properties of the nanoparticles were studied by UV–visible spectroscopy (Agilen 8453).

3. Results and discussion

3.1. Type of precursor

The X-ray diffraction patterns of CdS obtained from different precursors such as Cd(CH3COO)2·2H2O, Cd(SO4)2·6H2O, Cd(NO3)2·6H2O, and CdCl2·2H2O are shown in Fig. 1. The XRD patterns show that the CdS prepared from Cd(SO4)2·6H2O and Cd(CH3COO)2·2H2O are in cubic and hexagonal phase, respectively but, the CdS from CdCl2·2H2O and Cd(NO3)2·6H2O are as a mixture of cubic and hexagonal phases. The Sato’s works have also confirmed that the crystal structure of CdS is governed by the kind of cadmium salt solution used in the preparation of the sample [22]. The effect of cadmium salt as a precursor on the structure of CdS was studied by different groups [22,23]. These experiments have done in classical method or sonicated with ultrasonic bath. Our results are in agreement with some works [22–24] and in contrast to some others [15]. It should be mentioned that the kind of sonication in our work is different than others. This means that the structure of CdS is not only influenced by the kind of cadmium salt but also it is affected by ultrasound and kind of sonication. Additionally, the solvation of the reagents and interfacial forces are different in various kinds of cadmium salt solutions. Both the solvation and interfacial forces can be also affected by ultrasound. Therefore the lattice type of particles might be different under various conditions.

Table 1 summarizes the effect of precursor type on the characteristics of nanoparticles produced by this new combined method.

3.2. Precursor concentration

In order to consider the effect of initial precursor concentrations, the synthesis was carried out at two different initial concentrations of CdCl2. Fig. 2 shows the XRD patterns of the samples prepared under sonication. The precursor concentrations affect the crystallinity and the particle size of the product. The crystallization process is also faster when one of the reactant is in excess. Our results are in agreement with the results of the others [25].

3.3. Intensity of ultrasound

The UV–visible absorption spectra of CdS samples prepared under different intensities of ultrasound are shown in Fig. 3a. It is seen that an absorption edge located at about 460 nm occurs in case of CdS nanoparticles prepared at intensity of 75%. The maximum absorption for CdS as a bulk material is around 515 nm. The blue-shift of the absorption onset indicates that this sample and other CdS clusters are quantum-confined. In addition, the optical absorption edges observed for the samples prepared with intensity more than 80% are almost equal but show a little red-shift compared with the spectrum of samples at 75% and 80%, implying that CdS nanoparticles of sample at intensity of 75% is smallest with respect to other intensities.

The photoluminescence (PL) spectrum (Fig. 3b) obtained by Shimadzu RF 540 through dispersing 0.1 mL sample in 10 mL ethanol. It emits blue light in the range of 440–450 nm under photoluminescence excitation at 350 nm. It may be attributed to the small dimensions of nanoparticles and the quantum confinement effects. This result is in agreement with UV–visible spectra, where the band gap absorption was at 460 nm (Fig. 3a). The band-edge emission peak was difficult to observe which is due to the low exciton binding energy of CdS, especially when the crystal size is very small and atomic concentration on the surface is very high. However, the band–band transition of CdS nanocrystals may be observed on the PL spectra [9].
The band gap values of the CdS nanoparticles are obtained by optical absorption measurements and plotting $(a h m)^2$ versus photon energy $(h m)$ (Fig. 3c) using the following equation [26]:

$$(a h m)^2 = A(h - E_g)$$

where $a$ is the absorption coefficient, $A$ and $E_g$ are constant and band gap of the nanoparticle, respectively.

In semiconductors the confinement effects are strong for particles with radius $(r)$ smaller than the exciton Bohr radius $(a_B)$, $(r < a_B)$. It is intermediate for those with $r \sim a_B$ and weak for particles that are small but their radius are still a few times larger than $a_B$ $(r \approx a_B)$. Fig. 4 exhibits a strong confinement for CdS particles with diameter less than $\sim 6$ nm $(r \sim 3$ nm), and this is consistent with the strong confinement effect for particles with $r \approx a_B$. The size dependence of the band gap for CdS was calculated by tight binding method [27].

![Table 1](image)

Table 1: Effect of kind of precursor on the characteristics of CdS nanoparticles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Precursor</th>
<th>Cd/S mole ratio</th>
<th>Structure</th>
<th>Optical size (nm)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>CdSO₄</td>
<td>1:3</td>
<td>Cubic</td>
<td>4.06</td>
<td>2.77</td>
</tr>
<tr>
<td>b</td>
<td>Cd(CH₃COO)₂</td>
<td>1:3</td>
<td>Hexagonal</td>
<td>3.93</td>
<td>2.79</td>
</tr>
<tr>
<td>c</td>
<td>CdCl₂</td>
<td>1:3</td>
<td>Hex.+cub.</td>
<td>4.87</td>
<td>2.67</td>
</tr>
<tr>
<td>d</td>
<td>Cd(NO₃)₂</td>
<td>1:3</td>
<td>Hex.+cub.</td>
<td>4.77</td>
<td>2.68</td>
</tr>
</tbody>
</table>

![Fig. 2](image)

Fig. 2. Powder X-ray diffraction spectra of CdS synthesized by two different mole ratios of Cd:S (sonication 30 min, intensity 75%, temp. 70 °C, reactant CdCl₂).

![Fig. 3](image)

Fig. 3. (a) UV–visible spectra of CdS nanoparticles synthesized by sonochemical method at different intensities, (b) photoluminescence spectrum of CdS nanoparticle, and (c) a typical plot of $(a h m)^2$ versus $(h m)$ (sonication time, 30 min; Cd:S = 1:3; temperature, 70 °C; reactant, CdCl₂; intensity 75%).
On the basis of the results in Fig. 5, the particle size and the band gap of the nanoparticles are dependent on the intensity of ultrasound. As it is shown, by increasing the intensity of ultrasound the band gap of nanoparticles increased and then decreased. Therefore, there is an optimum intensity (75%) for higher band gap. This behavior could be explained by the rate of production of hydrogen sulfide through the cavitation process. The ultrasound intensity also strongly influences the nucleation process and the following formation steps of the CdS nanoparticles. As the irradiation power is increased, the pressure amplitude of the applied sound increases. This will increase the extent of cavitation in terms of the number and the intensity of cavitation collapse. The number of cavity increases with increasing the acoustic intensity until it reaches to the certain intensity which is related to the properties of the medium. Further increasing the intensity produces less effect which is due to the coalescence of the bubbles. The enlarged bubbles produced during sonication float to the surface of the liquid and can not affect more on the process. Therefore, the band gap reduced in higher acoustic intensities.

3.4. Effect of temperature

It is well-known that the temperature plays an important role in crystal structure, shape, and size of the particles [28]. According to Fig. 6, the CdS particles are nearly amorphous at 40 °C but by increasing the temperature to 70 °C, the crystallinity of the sample improves as indicated by stronger XRD peaks. In point of structure, the CdS particles are a mixture of cubic and hexagonal forms at 70 °C. It is interesting that the crystallization occurred at temperatures as low as 70 °C. This is due to the sonication of micro-emulsions which causes a rapid and localized heating of the droplets with a strong and transient thermal gradient between the outer water and the inner oil phases. It is well-known that nanoparticle’s growth in micro-emulsions is strongly affected by heating which leads to a higher matter exchange among different micelle units [29]. The important point is that the required temperature in classical method is as high as 400–500 °C for cubic to hexagonal transformation of CdS particles under air atmosphere [30]. It is about 460 °C under helium which is very high with respect to the sonication method [31].

3.5. The ratio of ethylenediamine to CS₂

The XRD patterns in Fig. 7 confirm that the increase of the ratio (ethylenediamine to CS₂) can affect the crystallinity, the phase structure, and the size of the nanoparticles. The sample obtained at higher ratio has a better crystalline structure, larger size, and different phase than the sample prepared at lower ratio. Adding more ethylenediamine to the solution can change the physical chemistry properties of the solution such as viscos-
ity. By increasing viscosity of the solution, the cavitation threshold increases and leads to the stronger shockwaves at higher temperatures. These conditions can promote the reaction of ethylenediamine in water phase with CS$_2$ (oil phase) to release more H$_2$S at the oil–water interface. Therefore the formation, growth and crystallization of CdS nuclei are accelerated under these conditions. In addition, CdS prepared at lower ratio has a cubic structure and at higher ratio has a hexagonal structure. Synthesis of CdS with ratio between two mentioned limits leads to a mixture of two structures. The present study shows that both ethylenediamine and ultrasound have an important role on the properties of the synthesized CdS.

Table 2
Design of experiments to investigate the proposed mechanism.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Composition</th>
<th>Kind of method</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CS$_2$ + H$_2$O</td>
<td>Classic</td>
<td>Heterogeneous</td>
</tr>
<tr>
<td>2</td>
<td>CS$_2$ + H$_2$O + en</td>
<td>Classic</td>
<td>Heterogeneous</td>
</tr>
<tr>
<td>3</td>
<td>CS$_2$ + H$_2$O + en + heat</td>
<td>Classic</td>
<td>Heterogeneous</td>
</tr>
<tr>
<td>4</td>
<td>CS$_2$ + H$_2$O + Cd$^{2+}$</td>
<td>Ultrasonic irradiation (30 min)</td>
<td>Low yield observed$^a$</td>
</tr>
<tr>
<td>5</td>
<td>CS$_2$ + H$_2$O + Cd$^{2+}$ + en</td>
<td>Ultrasonic irradiation (30 min)</td>
<td>High yield</td>
</tr>
</tbody>
</table>

$^a$ The sonochemical oxidation of CS$_2$ in the presence of air is proposed to proceed via the initial reaction of -OH in the interface of the bubble with CS$_2$ to produce the intermediate H$_2$S$^{[33]}$:

\[
\text{CS}_2 - \text{OH} \xrightarrow{\text{OH}} \text{CS}_2\text{OH}^+ \xrightarrow{\text{OCS}} \text{HS}^{-} \xrightarrow{\text{H}_2\text{O}} \text{H}_2\text{S} + \text{CO}_2
\]

Fig. 8. (a) TEM, (b) HRTEM image, and (c) SAED.
3.6. TEM micrograph

Fig. 8a shows the TEM micrograph of CdS nanoparticles. The size of the prepared CdS particles is less than 10 nm and this is in agreement with the estimated sizes deduced from analysis of XRD patterns. Fig. 8b is related to the HRTEM image of a single crystal with a growing direction of (0 0 2). The lattice spacing is about 0.34 nm which corresponds to the (0 0 2) plane of the hexagonal phase of CdS.

Structure and crystallinity of the particles can also be proved by the SAED pattern (Fig. 8c). It displays that the CdS nanoparticle is single crystalline of hexagonal phase, and this is consistent with XRD patterns. The diffraction peaks for hexagonal phase are due to (1 0 0), (0 0 2), (1 0 1) (1 0 3), (1 1 2) planes (JCPDS code 41-1049), and for the cubic phase are related to (1 1 1), (2 2 0), (3 1 1) planes (JCPDS code 10-0454). The bright diffraction spots are indicative of its high crystallinity. Moreover, exhibiting several diffraction spots instead of uniform bright rings means the orientation of the sample rather than random position of species on the TEM grid.

3.7. Reaction mechanism

Liquid–liquid heterogeneous mixture of CS₂ and water can lead to a clear solution by ultrasound. The critical conditions during sonication can disrupt the oil phase to very fine droplets and then disperse it in water phase. The final clear solution behaves the same as micro-emulsion but, without surfactant. Addition of cadmium ion to this solution leads to CdS nanoparticles with low yield (Table 2). Another experiment was designed in the presence of ethylenediamine, the yield was very high. The higher yield in the presence of ethylenediamine may be attributed to the following reactions [32].

\[ \text{H}_2\text{N}—\text{CH}_2—\text{CH}_2—\text{NH}—\text{CS}_2 \rightarrow \text{H}_2\text{N}—\text{CH}_2—\text{CH}_2—\text{NH}—\text{CS}—\text{SH} \]
\[ n(\text{H}_2\text{N}—\text{CH}_2—\text{CH}_2—\text{NH}—\text{CS}_2) \rightarrow (—\text{HN}—\text{CH}_2—\text{CH}_2—\text{NH}—\text{CS}—)n + \text{H}_2\text{S} \]

The turbulent flows generated by ultrasound facilitate the first reaction by attacking ethylenediamine to carbon–sulfur double bond of CS₂. Under sonication, the product of first reaction can polymerize and then disperse it in water phase. The critical conditions produced during sonication can disrupt the oil phase to very fine droplets and then disperse it in water phase. The final clear solution behaves the same as micro-emulsion but, without surfactant. Addition of cadmium ion to this solution leads to CdS nanoparticles with low yield (Table 2). Another experiment was designed in the presence of ethylenediamine, the yield was very high. The higher yield in the presence of ethylenediamine may be attributed to the following reactions [32].

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\[ n(\text{H}_2\text{N}—\text{CH}_2—\text{CH}_2—\text{NH}—\text{CS}_2) \rightarrow (—\text{HN}—\text{CH}_2—\text{CH}_2—\text{NH}—\text{CS}—)n + \text{H}_2\text{S} \]

The turbulent flows generated by ultrasound facilitate the first reaction by attacking ethylenediamine to carbon–sulfur double bond of CS₂. Under sonication, the product of first reaction can polymerize according to the second reaction and produces H₂S. The gas product (H₂S) reacts very fast with cadmium ion present in the solution and leads to the final product (CdS).

Moreover, the polymer molecule produced in the second reaction may bridge the oil droplets and water at the CS₂–water interface to prevent the agglomeration of the droplets. Thus ultrasound not only provides energy for the reactions, but also it greatly accelerates the nucleation of CdS and depresses the straightforward growth of the newborn CdS nuclei due to the intense friction and collisions of the created molecules. On the other hand, there is a possibility for small droplets of oil to accumulate at the interface of the bubble produced during the sonication. This behavior arises from the higher tendency of the oil droplets for the bubble interface than water phase. The implosion of the bubble generates many local hot spots in the solution and promotes the reactions. The formation, growth and crystallization of CdS nuclei are accelerated under these conditions (Fig. 9).

The high temperature produced during cavitation can facilitate the crystallization of the product. It means that the hot spots produced during sonication play the role of calcination in the conventional method.

The results confirm that both ethylenediamine and ultrasound play important roles in the formation of the final nanostructure.

4. Conclusions

In the present work, we have developed a new method for the synthesis of CdS nanoparticles through micro-emulsion (O/W) induced by ultrasound. Nanoparticles with a hexagonal phase were prepared at a relatively low temperature (70 °C), short time, and fast transition phase. The important point of this work is to achieve the nanosized CdS in the presence of ultrasound without additives and calcinations.

We have investigated the effect of ultrasound intensity, type of precursor, concentration ratio of ethylenediamine to CS₂, and temperature on the nanoparticle size, structure, and band gap. In the case of intensity effect, there was an optimum intensity for the higher band gap of nanoparticles. The phase structure of nanoparticles was affected by changing the concentration ratio. It is also possible to prepare a pure phase with small size and large band gap by controlling the intensity, concentration ratio en/CS₂ and kind of precursor. The synthesized CdS nanoparticles have a blue-shift to higher energy which is due to a typical quantum confinement effects.

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