

# A photochemical method for controlling the size of CdS nanoparticles

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## Abstract

The optical and electrical properties of semiconductor nanoparticles are strongly dependent on their size. A flexible control of the size of the nanoparticles is of interest for tuning their properties for different applications. Here we use a coupled method to control the size of CdS nanoparticles. The method involves the photochemical growth of CdS nanoparticles together with the use of a capping agent as an inhibiting factor. CdS nanoparticles were formed through a photoinduced reaction of CdSO<sub>4</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> in an aqueous solution. Mercaptoethanol (C<sub>2</sub>H<sub>6</sub>OS) was used as the capping agent, and we investigated the effect of illumination time, illumination intensity and the concentration of capping agent on the nanoparticle size. Transmission electron microscopy (TEM) shows crystalline nanoparticles with relatively low dispersion. Optical absorption spectroscopy was mainly used to measure the band gap and size of the nanoparticles. Increasing the illumination time or illumination intensity increases the nanoparticle size, while higher capping agent concentration leads to smaller nanoparticle size. A band gap range of 2.75–3.4 eV was possible with our experimental conditions, corresponding to a 3.2–6.0 nm size range.

## 1. Introduction

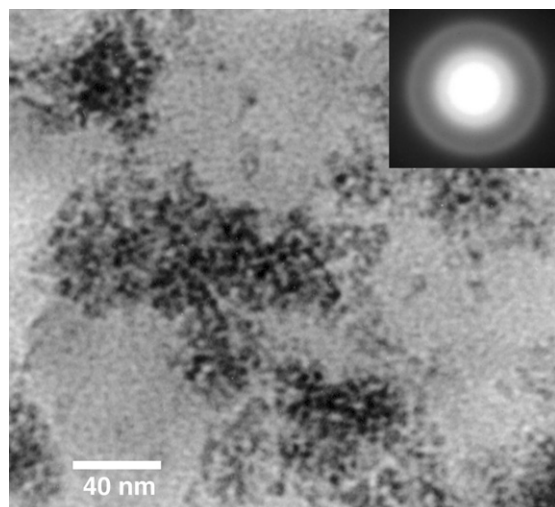
The optoelectronic properties of nanoparticles are strongly dependent on their size, due to quantum confinement effects. In semiconductors, quantum confinement modulates the band structure of nanoparticles and increases the band gap. Therefore, the optoelectronic properties of nanoparticles can be tuned by changing the nanoparticle size. The control of nanoparticle size and shape remains a challenge in nanotechnology, and a large body of research is devoted to this subject.

Nanoparticles can be synthesized in the gas phase, liquid phase, solid phase or inside the pores of a porous material. The proper method is completely dependent on the material considerations. In principle, in any of these methods there are controlling parameters by which the nanoparticle size can be controlled. Whether the synthesis process is diffusion controlled, reaction controlled or controlled by other

limiting factors, parameters such as temperature, reactant concentrations, pressure, flow speed, and so on can be utilized as the controlling parameters. In liquid phase synthesis there are several ways of forming and controlling the size of nanoparticles. Using capping agents and surfactants [1, 2], formation of the particles in the nanometre pores of a porous material [3, 4] and formation of particles in small isolated micelles [5, 6] are the most important of them.

One of the ideas for controlling the size of nanoparticles is by using light as the driving force for the reaction. In these photochemical reactions at least one of the reactants is sensitive to light, usually UV light. The reaction will proceed only when the reactants are illuminated by UV light. Therefore, the nanoparticle size will increase until the illumination ceases. There are a few recent works that employ this method to grow metal or semiconductor nanoparticles. Most of these works have concentrated on CdSe and PbSe nanoparticle growth [7–9]. Also some groups have focused on thin film deposition applying this method. Various materials have been

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**Figure 1.** TEM image of CdS nanoparticles prepared with  $0.5 \text{ mol l}^{-1}$  mercaptoethanol concentration and band gap of 3.3 eV.

tried, including CdS [10–12], ZnS [13], Se [14], CdSe [15], ZnSe [16] and  $\text{In}_2\text{S}_3$  [17].

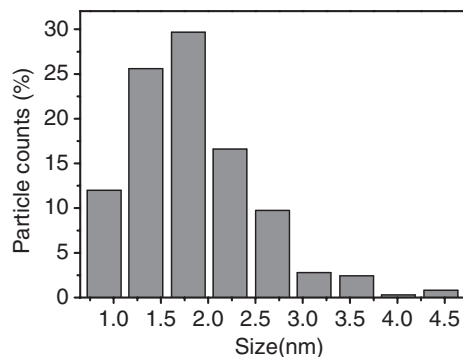
In this work we report the formation of CdS nanoparticles using a photochemical route. We employ a coupled method of size control, that is by controlling the illumination time, as well as by using a capping agent. Capping agents are materials, usually of thiol groups, that covalently bind to the surface of the grown nanoparticles and prevent their further growth. There are various reports on the growth of CdS nanoparticles using capping agents to control the size [1, 18–20]. By this coupled method a higher controllability over size and faster nanoparticle growth are achieved.

## 2. Experimental details

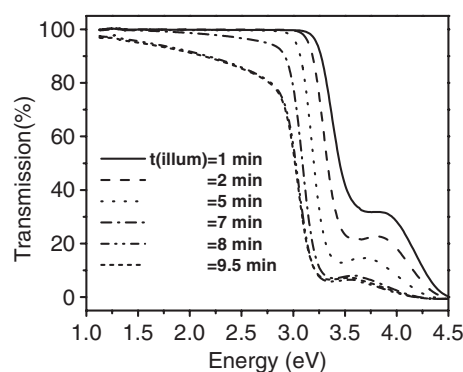
To synthesize the CdS nanoparticles, 30 ml aqueous solution of  $\text{CdSO}_4$  and  $\text{Na}_2\text{S}_2\text{O}_3$  was prepared. The concentrations of  $\text{CdSO}_4$  and  $\text{Na}_2\text{S}_2\text{O}_3$  were  $1 \text{ mmol l}^{-1}$  and  $100 \text{ mmol l}^{-1}$ , respectively. The pH was adjusted to 6 by adding small amounts of  $\text{H}_2\text{SO}_4$  to the solution. 20 ml aqueous solution of mercaptoethanol, as the capping agent, was prepared with an adjusted pH of 6 and then added to the first solution. At this pH the solution shows the best sensitivity to UV light. The concentration of mercaptoethanol ranged from  $0.005 \text{ mol l}^{-1}$  to  $0.5 \text{ mol l}^{-1}$  in different experiments. The prepared solution was exposed to UV illumination using an 80 W high-pressure mercury lamp, placed 9 cm above the solution. The solution was stirred during the illumination. The exposure time ranged from 1 to 10 min. The CdS nanoparticles were formed soon after the start of exposure. Optical characterizations were done using Jasco V530 UV–VIS spectrometer. TEM images were taken using a Philips CM200 system.

## 3. Results and discussion

CdS nanoparticles are formed through the optically stimulated reaction of  $\text{CdSO}_4$  and  $\text{Na}_2\text{S}_2\text{O}_3$ . Soon after the start of the illumination, nanoparticles form and for some of the samples the solution turns slightly coloured. It was suggested by



**Figure 2.** The histogram of particle sizes obtained from the TEM image. The sample was prepared with  $0.5 \text{ mol l}^{-1}$  mercaptoethanol concentration and 2 min illumination.

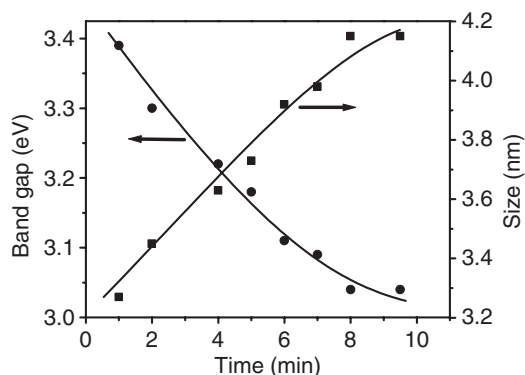


**Figure 3.** Transmission spectra of samples with different illumination time. The mercaptoethanol concentration was  $0.5 \text{ mol l}^{-1}$ .

Goto and co-workers [21] that the illumination of the solution containing  $\text{S}_2\text{O}_3^{2-}$  ions with UV light leads to the dissociation of the ion into  $\text{SO}_3^{2-}$  and S.  $\text{S}_2\text{O}_3^{2-}$  ions also undergo reactions forming  $\text{S}_4\text{O}_6^{2-}$  and  $\text{S}_3\text{O}_6^{2-}$  ions and releasing electrons needed for the final reaction of  $\text{Cd}^{2+} + \text{S} + 2e \rightarrow \text{CdS}$ . The authors do not comment on the main path of reactions occurring in the solution. However, it is evident from the absorption spectra that the photoactive agent in the solution is the  $\text{S}_2\text{O}_3^{2-}$  ion, which once activated reacts with the  $\text{Cd}^{2+}$  ions to form CdS. Therefore, the process resulting in the nucleation and growth of CdS nanoparticles is a homogeneous one.

Figure 1 shows a TEM image of the CdS nanoparticles prepared with 2 min illumination and  $0.5 \text{ mol l}^{-1}$  mercaptoethanol concentration. The image shows dispersed and fine CdS nanoparticles of about 2 nm size. The electron diffraction pattern shown in the figure demonstrates that the nanoparticles are crystalline. Figure 2 is a histogram of particle sizes derived from the image in figure 1 and similar images from the other parts. Most of the nanoparticles are below 3 nm size, with the majority at about 1.8 nm. The gradual increase of the distribution curve below the peak value and the rapid fall above the peak value is a demonstration that newly nucleated and grown nanoparticles are constantly injected into the nanoparticle pool.

Figure 3 displays the optical transmission spectra of the solutions illuminated for different times. The solutions were prepared with  $0.5 \text{ mol l}^{-1}$  mercaptoethanol. The features in the spectra are related to the CdS nanoparticles, as the starting materials in the solutions are all transparent for photon energies

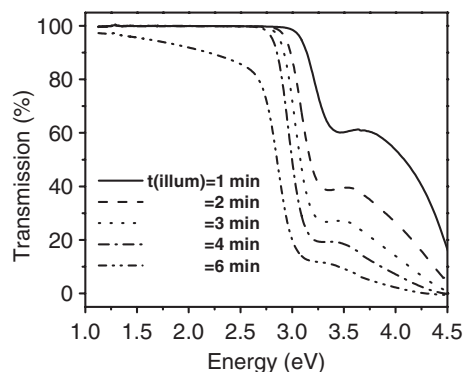


**Figure 4.** The band gaps and sizes of the samples versus illumination time. The mercaptoethanol concentration was  $0.5 \text{ mol l}^{-1}$ .

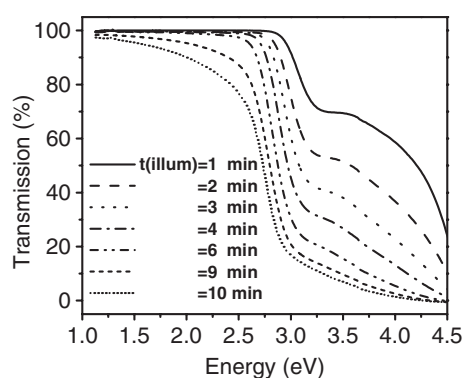
less than 4.2 eV. The absorption edge in the spectra represents the band gap of the nanoparticles. The band gap clearly shifts to lower energies as the illumination time increases. This is a consequence of the formation of larger nanoparticles at longer illumination times. We have also synthesized CdS nanoparticles by controlled chemical reaction of  $\text{Cd}(\text{NO}_3)_2$  and  $\text{Na}_2\text{S}$  in the presence of mercaptoethanol, similar to that reported by Kulkarni and co-workers [1, 19]. The sharpness of the band edge in the transmission spectra for our photochemical samples is somewhat better than for those prepared by the chemical method. This indicates that the photochemical method is capable of producing nanoparticles with low size dispersion.

Figure 4 shows the band gap of the CdS nanoparticles, as well as the nanoparticle size, for different illumination times. The nanoparticle size was calculated from the band gap values using the effective mass approximation (EMA) [22]. This model treats the electrons and holes as being caged in a spherical well of infinite depth, and takes into account the lattice effect by using the bulk electron and hole effective masses. There are known shortcomings to this model which include surface effects that become important particularly at very small cluster sizes [23]. Nevertheless, this model is widely used in the literature as a simple way of estimating the nanoparticle size from band gap values. The estimated size from this model can be regarded as the 'optical size' and is sufficient for our comparative study.

If the illumination time is extended to more than 9.5 min, a relatively fast agglomeration of nanoparticles takes place and the large agglomerates formed then precipitate. This effect is related to the higher concentration of nanoparticles that are formed for long illumination times. The transmission spectra in figure 3 indirectly evidence that both nanoparticle size and nanoparticle concentration in the solution increase with the illumination time; this is explained as follows. In the sample with 9.5 min illumination time, the transmission is decreased in the low energy side of the spectrum. The reason for this decrease is the scattering of light from the slightly agglomerated nanoparticles in the solution. As demonstrated in figure 4, for 9.5 min illumination time, the size of the CdS nanoparticles is about 4.15 nm, which is much less than the wavelength of the incident light, and cannot be the source of the increased scattering. The higher concentration



**Figure 5.** Transmission spectra of samples with different illumination time. The mercaptoethanol concentration was  $0.05 \text{ mol l}^{-1}$ .

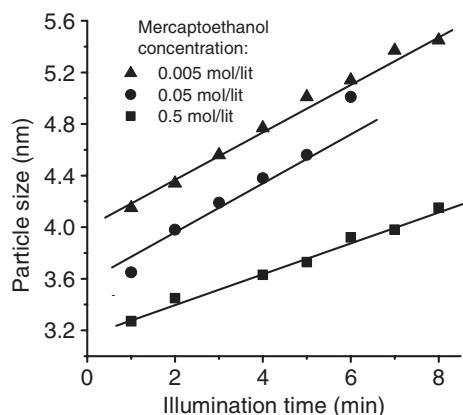


**Figure 6.** Transmission spectra of samples with different illumination time. The mercaptoethanol concentration was  $0.005 \text{ mol l}^{-1}$ .

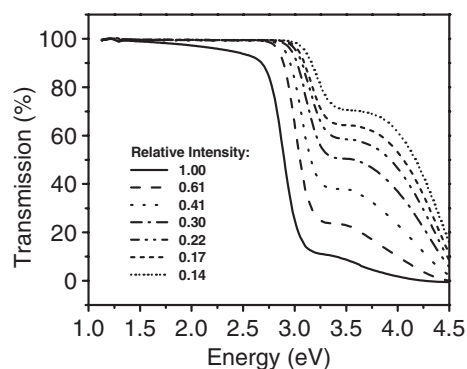
of nanoparticles for longer illumination times seems to enhance the chance of particle collisions and coagulation.

The size of the nanoparticles, as obtained from the band gap values, overestimates the actual size obtained by TEM images. According to figure 2, the peak of the distribution is at 1.8 nm size, while the measurement of the size of the same nanoparticles from the transmission spectra results in 3.2 nm. Qualitatively, the difference is justified, as in the measurement of the optical band gap of nanoparticles with a distribution of sizes, the smaller particles would make less contribution in the absorption edge than the larger particles. This is due to the larger band gap of the smaller particles, which makes them transparent at the band edge energy. For CdS nanoparticles of sizes less than 5 nm the tight binding (TB) method has been shown to provide a better fit to the experimental values [24]. For these sizes EMA has an overestimate compared to TB. The value of this overestimate is about 1.3 nm for the band gap of 3.3 eV, which justifies the difference between the TEM size and the optical size [24].

Figures 5 and 6 are the transmission spectra for the samples with  $0.05$  and  $0.005 \text{ mol l}^{-1}$  mercaptoethanol concentrations. All other experimental conditions were the same as for the samples with  $0.5 \text{ mol l}^{-1}$  mercaptoethanol, mentioned earlier. The band gap in these cases also shifts to lower energies with illumination time, representing larger particles. However, for a certain illumination time, the band gap of the formed nanoparticles is higher for higher mercaptoethanol concentration. Figure 7 shows



**Figure 7.** CdS nanoparticle size in terms of illumination time for mercaptoethanol concentrations of 0.5, 0.05 and 0.005 mol l<sup>-1</sup>. The lines are displayed to show the trends.

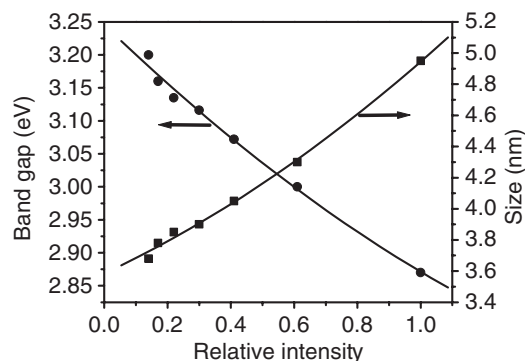


**Figure 8.** Transmission spectra for the samples prepared at different illumination intensities. The mercaptoethanol concentration was 0.05 mol l<sup>-1</sup> and the illumination time was 6 min.

the nanoparticle size versus illumination time for the three mercaptoethanol concentrations. The smallest nanoparticles of about 3.2 nm are achievable in 0.5 mol l<sup>-1</sup> mercaptoethanol solutions. Larger nanoparticles are achieved by lower mercaptoethanol concentrations. With this range of mercaptoethanol concentrations and the illuminations times used here, a nanoparticle size range of 3.2–6.0 nm can be covered.

The effect of the illumination intensity is demonstrated in figure 8. The intensity was changed by changing the distance between the UV lamp and the reactive solution. The values of intensities quoted in the figure are the relative intensities compared to the highest intensity. The illumination time was fixed at 6 min. Reducing the intensity results in a shift of the band edge towards higher energies. Figure 9 shows the band gap and nanoparticle size in terms of relative intensity. For the relative intensity of 0.14 the nanoparticle size was about 3.68 nm, while it was 4.95 nm at the relative intensity of 1. This implies that illumination intensity can also be utilized as a control parameter to change the nanoparticle size.

The photoreaction proceeds by controlled injection of sulfur species in the reaction solution. S<sub>2</sub>O<sub>3</sub><sup>2-</sup> ions are the photoactive agents in the reaction. These ions absorb photons of energy greater than 4.2 eV, as measured by the absorption measurements of the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. The 254 nm line of the mercury lamp is therefore the only spectral line that contributes to the procession of the reaction. At this wavelength Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>



**Figure 9.** Band gaps and sizes for the CdS particles prepared at different illumination intensities. The mercaptoethanol concentration was 0.05 mol l<sup>-1</sup> and the illumination time was 6 min.

in the reaction solution is strongly absorbing. Quantitative measurement of the absorption indicates that the penetration depth of the light at this wavelength is about 400 μm. Hence, the photoactive space is restricted to the very top layer of the solution. This means that the active species resulting from the photodissociation of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> ions are created in the top photoactive layer. This is also evidenced by the fact that, if the solution is not stirred, the CdS nanoparticles are formed only on the top. It seems, however, that the active species rapidly diffuse throughout the solution by vigorous stirring, and the whole solution will be influenced by the photoinduced active species. For this claim to be true, the lifetime of the active species before they react to form CdS must be much more than the characteristic time for the diffusion of the species inside the solution. A detailed understanding of the photoinduced process of CdS nanoparticle formation requires a separate study.

According to the qualitative picture of the process described above, the speed of the reactions is directly related to the illumination intensity. To create any single molecule of CdS at least one photon is required to provide the activation energy. The flux of the photons is therefore a parameter for controlling the reaction speed. Lower photon flux results in low rate of the release of reactive sulfur species, and this allows the capping agent to inhibit the nanoparticle growth at smaller size, as depicted in figure 9. The capping agent, i.e. mercaptoethanol, brings about an inhibiting effect on the growth of the nanoparticles through covalently binding to the particles. This is clearly seen in figure 7, where higher mercaptoethanol concentration leads to smaller nanoparticles.

#### 4. Conclusion

CdS nanoparticles were grown by the photochemical method. The reaction is activated by UV photon flux, and proceeds until the illumination is present. We use a capping agent to effect an inhibiting mechanism on the nanoparticle growth. With constant illumination intensity and time, the higher capping agent concentration leads to smaller nanoparticles. Illumination intensity is also effective on the growth speed, as higher intensity results in more intense activation of the solution. In this way, high controllability of the size would be possible by controlling the illumination time, illumination intensity and capping agent concentration.

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