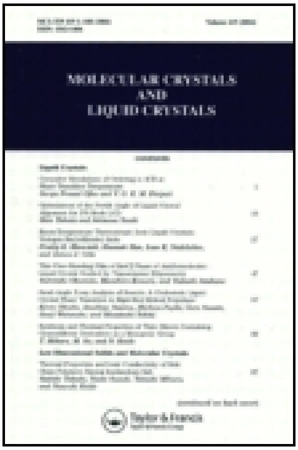

# Molecular Crystals and Liquid Crystals

# Room Temperature Synthesis of CdS Nanocrystallites

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# Room Temperature Synthesis of CdS Nanocrystallites

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*Semiconductor nanoparticles have attracted much interest during the past decade due to their unique size-dependent chemical and physical properties. These properties emerge from the high surface-to-volume ratio present in nanoparticles.*

*CdS nanoparticles have potential applications as optoelectronic devices, lasers, photocatalysts, electrochemical cells, fluorescent labelling of cell organelles.*

*A series of cadmium sulphide (CdS) nanocrystalline were synthesized by precipitation from a mixture of aqueous solutions of various cadmium salts and sodium thiosulphate at room temperature without adding any surface-termination agent. Their crystal structure and particle size were determined by X-ray diffraction. The fluorescence of CdS nanocrystalline and UV-Vis absorption spectra were also recorded.*

*The relationship between the synthesis conditions and spectroscopic properties was studied. Several factors affect the absorbance and fluorescence spectra, including the cadmium source and Cd:S molar ratio. It has found that in all cases the powders have good morphology when scanned through the SEM.*

**Keywords:** CdS nanocrystallites; semiconductors; thiosulphate

## INTRODUCTION

Over the past decade, the synthesis and functionalization of nanostructures have attracted great interest due to their significant potential application [1–3]. Due to the quantum confinement effect and the large surface to volume ratio, small nanocrystals show very special physical and chemical properties corresponding to their bulk materials, when their size is close to or smaller than that of the Bohr exciton.

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However, the aggregation of nanocrystals always decreases their original nano-effects. During the wet chemical synthesis of nanoparticles, organic stabilizers are often used to prevent them from aggregating by capping their surfaces. Moreover, the introduction of stabilizers also influences the chemical properties as well as the physical properties of semiconductor materials, from stability to solubility and to light emission. Therefore, proper surface modification by stabilizers can remove the localized surface-trap states and significantly increases the quantum yield of the excitonic emission. Commonly used stabilizers are phosphine oxide, phosphates, various thiols, biomolecules, and organic dendrons, which become the hot topic of nanotechnology [4–10].

A challenge in nanoparticles obtaining by wet chemical synthesis remains the reproducibility and the uniformity of the final material.

In this article we performed the wet synthesis of CdS nanoparticles with controlled size by using different inorganic cadmium sources ($CdCl_2$, $Cd(CH_3COO)_2$, $Cd(NO_3)_2$, $CdSO_4$) and thiosulfate as sulfur source by incorporating them in a nanoporous material (silicagel), with known pore dimension. In order to compare the synthesis conditions, two different routes and molar ratios have been selected.

## EXPERIMENTAL

All chemicals were of analytical grade and used as received. Two different routes have been followed:

A. The synthesis of CdS nanoparticle firstly and then incorporating them in nanoporous silicagel.
B. The synthesis of CdS nanoparticle in the presence of silicagel which permit their incorporation as they forming.

Route A: an aqueous solution containing 1 mmol or 2 mmol of sodium thiosulfate respectively was added to an aqueous solution containing 1 mmol of cadmium salt. The resulted clear solution is stirred at room temperature for 12 h. The bright yellow powder formed in all cases was centrifuged and the supernatant was removed. Each sample was washed with water several times, centrifuged and dried in air. X-ray powder diffraction was used to confirm CdS formation. Each sample was dispersed in water, 0.5 g silicagel was added and the mixture was stirred for 2 h. After this time the silicagel was filtered on paper, abundantly washed with water and dried in air.

Route B: To the initial aqueous solution containing 1 mmol or 2 mmol of sodium thiosulfate respectively and 1 mmol of cadmium salt

0.5 g of silicagel was added and the mixture was stirred for 14 h. After this time the silicagel was filtered on paper, abundantly washed with water and dried in air.

For the route A two molar ratios Cd:S have been used (1:1 and 1:2) and for the route B only one molar ratio has been used for a certain cadmium salt (1:1 for chloride and acetate and 1:2 for sulphate and nitrate); the molar ratio which has led to the best results was that using the route A.

UV-Vis-NIR spectra have been recorded with a Jasco V570 spectrophotometer with reflexion device ILN-472.

Fluorescence spectra have been recorded with a Jasco FT 6500 spectrophotometer.

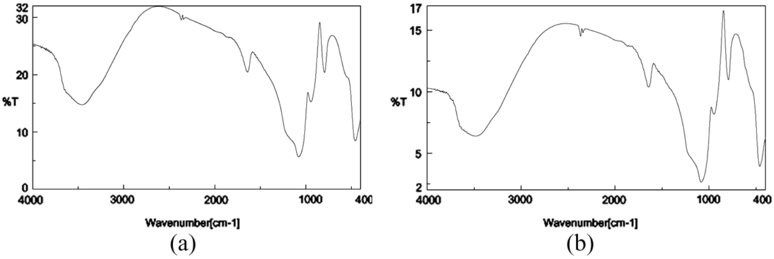
X-ray diffraction has been recorded with Bruker AXS D8 Advance diffractometer with Cu $K_\alpha$ radiation in 10–70 $2\theta$ domain and 0.02 degrees/sec.

Microphotographs obtained by scanning electron microscopy (SEM) were taken by using a JEOL JSM-6301F field emission at 3 keV. The chemical composition of the intercalated compounds was determined by energy dispersive X-ray analysis (EDX) Philips LINK-ISIS at 20 keV, coupled with the microscope.

## RESULTS AND DISCUSSION

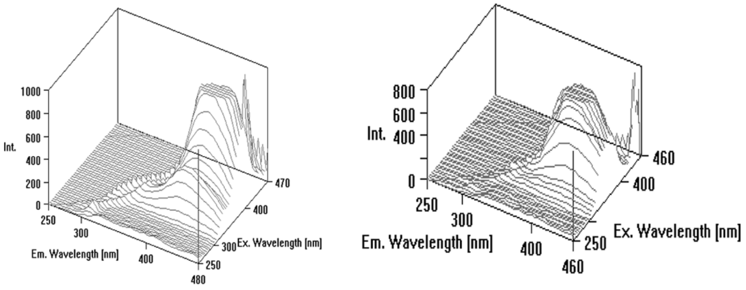
In the case of all cadmium salts, the obtained CdS particles display a wide range of dimensions up to 280 nm (measured as water dispersion, after an initial centrifugation in route A).

The ionic reaction of these processes can be: $Cd^{2+} + S_2O_3^{2-} = CdS + SO_4^{2-}$. As it can be clearly observed (Fig. 1) that the presence of CdS particles in nanoporous silicagel cannot be proved using FTIR



(a) (b)

**FIGURE 1** FTIR spectra of (a) silicagel and (b) CdS particles incorporated in silicagel.



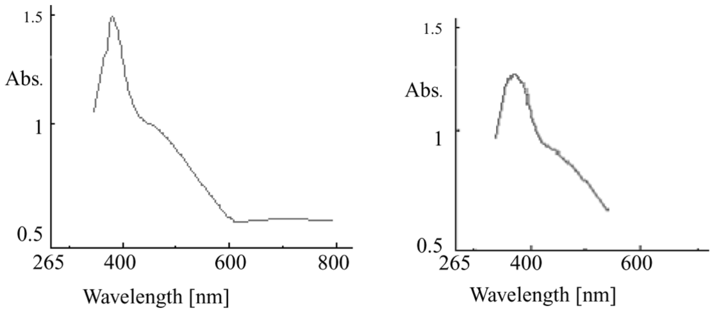
(a) (b)

**FIGURE 2** Fluorescence 3D spectra of CdS nanoparticles obtained from $Cd(NO_3)_2$ at 1:2 Cd:S molar ratio before (a) and after (b) incorporation in silicagel (by route B).

spectroscopy, probably because of the low amount of CdS embedded for detection.

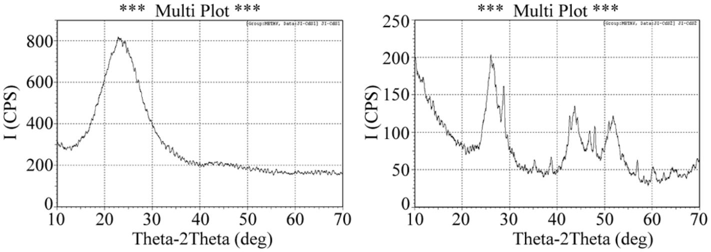
The synthesized CdS nanoparticles (Fig. 2a) exhibit fluorescence by excitation on a wide range of wavelengths between 280–600 nm, with a high intensity and a maximum fluorescence intensity emission around 460 nm. The silicagel embedded CdS nanoparticles (Fig. 2b) exhibit fluorescence emission by excitation into a narrow range of wavelength and with less maximum fluorescence intensity. Silicagel does not exhibit any fluorescence emission.

Usually, the excitation wavelength of maximum fluorescence intensity emission corresponds to the wavelength of UV-Vis absorption. In this case, the wavelength of maximum UV-Vis absorption for all CdS samples obtained by route A is blue shifted by 20 to 40 nm against



(a) (b)

**FIGURE 3** UV-Vis spectrum of CdS nanoparticles obtained from $CdCl_2$ at 1:1 Cd:S molar ratio before (a) and after (b) incorporation in silicagel (by route B).



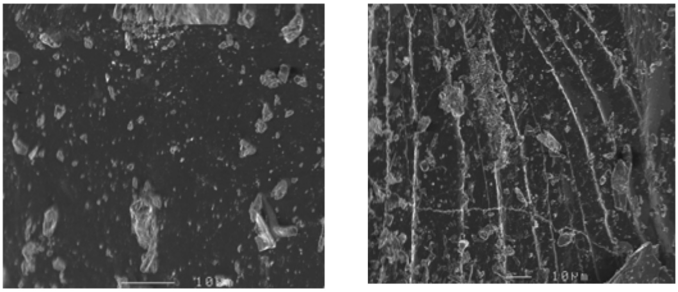
(a) (b)

**FIGURE 4** X-ray diffraction pattern for CdS particles obtained from $CdSO_4$ at 1:2 Cd:S molar ratio before (a) and after (b) incorporation in silicagel (by route B).

the wavelength of maximum of fluorescence intensity emission (Fig. 3). For CdS particles incorporated in silicagel, regardless the route followed, it can be observed a decrease of the maximum absorption intensity and a shift to lower wavelength by comparison to the corresponding samples.

In Figure 4 the CdS sample (a) shows the diffraction peaks associated with hexagonal phase. It can be observed a diffraction peak at $2\theta = 25.50$ indicating a strong preferred orientation. This peak could be associated with the (002) reflection of the hexagonal CdS. The presence of the diffraction peak at $2\theta = 22.60$ could be associated with the (100) reflection of the CdS hexagonal phase. The broadness of band confirms the nanodimension of the particles obtained.

The characteristic peaks for CdS hexagonal are also present after incorporation in silicagel, but in comparison to the signal from the silicagel sample, the characteristic CdS peaks are quite weak, suggesting



(a) (b)

**FIGURE 5** SEM image of CdS nanoparticles obtained from $Cd(CH_3COO)_2$ at 1:1 Cd:S molar ratio before (a) and after (b) incorporation in silicagel (by route B).

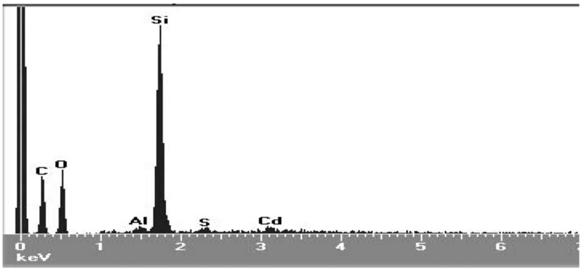


**FIGURE 6** Global EDX.

that the content of CdS embedded in silicagel is rather small in the volume region probed by X-rays (b).

The SEM investigation of the cadmium sulfide powder reveals the presence of polycrystalline aggregates of CdS hexagonal phase. Figure 5 shows such aggregates which are formed by nanometric CdS crystallites, obtained by route A (a) and the presence of CdS crystals in silicagel pores (b).

In addition, a global EDX analysis of the samples reveals the presence of our Cd–S compound inside the silicagel structure (Si–O), with a Cd/S molar ratio $\sim 1$ (Fig. 6). The presence of the Al and C is due to the plot used for the sample and it can be eliminated from our interpretation.

## CONCLUSION

An increase of fluorescence intensity it can be observed in case of CdS nanoparticles obtained by route B in comparison with those obtained by route A. This might be correlated with the presence of an increasing amount of particles in silicagel pores.

This has been expected since the dimension of silicagel pores is 2.5 nm which means that only the CdS nanoparticles with diameter equal or less than 2.5 nm could enter into the pores.

By choosing a nanoporous material with known pore size, the synthesis of CdS nanoparticles can be controlled to obtain required size of nanoparticles in an easy and safe way, in aqueous solution without using any organic agent.

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