

## SYNTHESIS OF CADMIUM SULFIDE NANOSTRUCTURES BY NOVEL PRECURSOR

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### ABSTRACT

A thioglycolic acid (TGA)-assisted hydrothermal process has been developed to synthesize cadmium sulfide nanostructures via the reaction between a new precursor cadmium (II) phthalate and TGA. X-ray diffraction (XRD), transmission electron microscopy (TEM), photoluminescence spectroscopy (PL) and Fourier transform infrared (FT-IR) were employed to characterize the obtained product. The effect of the reactant concentration, mole ratio of TGA to the  $\text{Cd}^{2+}$ , temperature and reaction time on the morphology, size of particles and phase of nanocrystalline CdS products were investigated.

**Key words:** Chemical synthesis, CdS, Nanostructured materials, Inorganic materials.

### INTRODUCTION

Cadmium sulfide (CdS), with a wide band gap of 2.42 eV (in bulk), is among one of the most important nano-structured semiconductors that have been widely studied due to their potential applicability in the possible application in optoelectronic devices, photocatalysis and potential applications in solar cells [1]. In 2004, Yang *et al.* developed a mild hydrothermal route to synthesize metal sulfides using thioglycolic acids (TGA) as nontoxic template [2], which shows that TGA acts as the oriented growth reactant during above process. Recently, our group reported synthesis of metal sulfide nanoparticles via hydrothermal process in the presence of TGA [3–5]. In our research novel inorganic complex precursor, [bis(salicylaldehydato)zinc(II)], was applied for synthesis of ZnS nanoclusters in the presence of TGA via hydrothermal method for the first time. We found out that precursors also play an important role in controlling size of particles and morphology. Meanwhile a major interest is in the development of organometallic or inorganic precursors. Our strategy has been to use a thioglycolic acid as capping agent for hydrothermal synthesis of CdS nanoparticles. It still remains a great challenge in the way of developing facile

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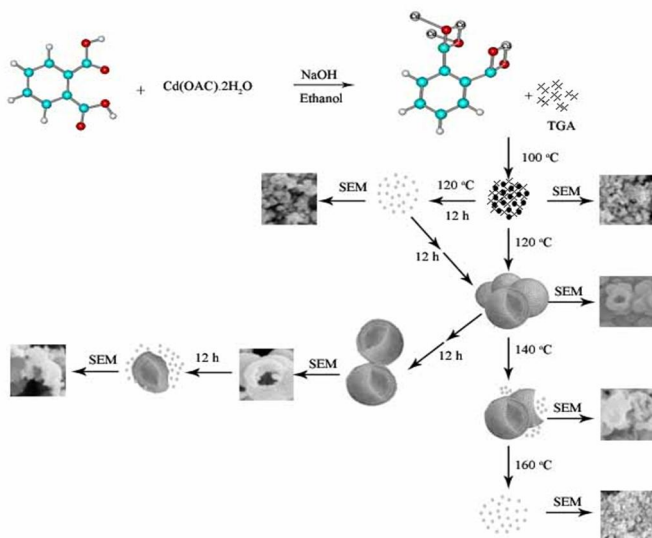
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and environmentally benign methods for creating CdS nanoparticles through a simple method. In this paper, we report a novel thioglycolic acid (TGA)-assisted hydrothermal method to fabricate well-crystallized CdS nanoparticles.

We have presented a hydrothermal method, which is milder, simpler, more practical, and more environmental than any other methods. The trick in hydrothermal synthesis of CdS nanostructures presented here is the use of thioglycolic acid (TGA) as sulfur source and stability agent, which was previously used as the stability agent to prevent the chalcogenide nanocrystals from aggregating [6]. In this method cadmium (II) phthalate was used as a new precursor. We discussed three critical factors for hydrothermal formation of the CdS nanoparticles, namely,  $\text{Cd}^{2+}$ /TGA mole ratio, hydrothermal temperature, and reaction time. It is reasonable to believe that the TGA-assisted hydrothermal process offers great opportunities for preparation of tin chalcogenide nanostructures. To the best of our knowledge, this is the first report on the synthesis of CdS nanoparticles via hydrothermal method from cadmium phthalate in the presence of TGA as sulfur source.

### METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

In a typical synthesis 10 ml of thioglycolic acid (TGA) were added into 0.6 g  $[\text{Cd}(\text{Pht})(\text{H}_2\text{O})]_n$  under stirring and heating. The precursor complexes  $[\text{Cd}(\text{Pht})(\text{H}_2\text{O})]_n$  was prepared according to the literature [7]. After 40 min the solution was stirred vigorously.



**Fig. 1** – The proposed evolution process for preparation of CdS nanostructures.

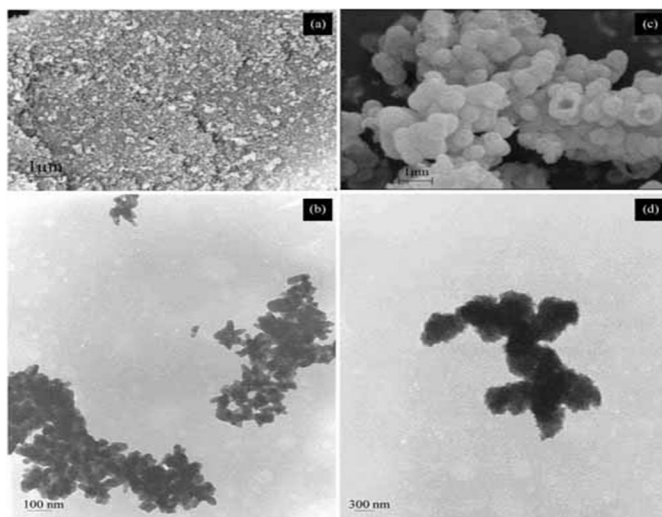
The final solution was put into a Teflon-lined stainless steel autoclave under stirring. Then, the autoclave was maintained under a static condition at 100–160 °C for 12–36 h and then gradually cooled down to room temperature. The mixture turned yellow due to the formation of CdS precipitates. The product was centrifuged, washed with alcohol and distilled water for several times, and dried in the air at 60 °C for 8 h (*Fig. 1*).

## RESULTS AND DISCUSSION

The XRD pattern of the synthesized product for 24 h at 100 °C shows that the majority of the products were poorly crystallized and diffraction pattern matched with no JCPDS card No. When the reaction temperature increases from 100 °C to 120 °C, the crystallinity of the products will improve. The X-ray powder diffraction pattern of the CdS nanoparticles showing the reflections from (100), (002) and (101) planes, which indicates the formation of a pure hexagonal phase with space group of P6<sub>3</sub>mc, which is close to the values in the literature (JSPDS No.41–1049 with cell constant  $a = 4.1409$  Å,  $b = 114.1409$  Å,  $c = 6.7198$  Å).

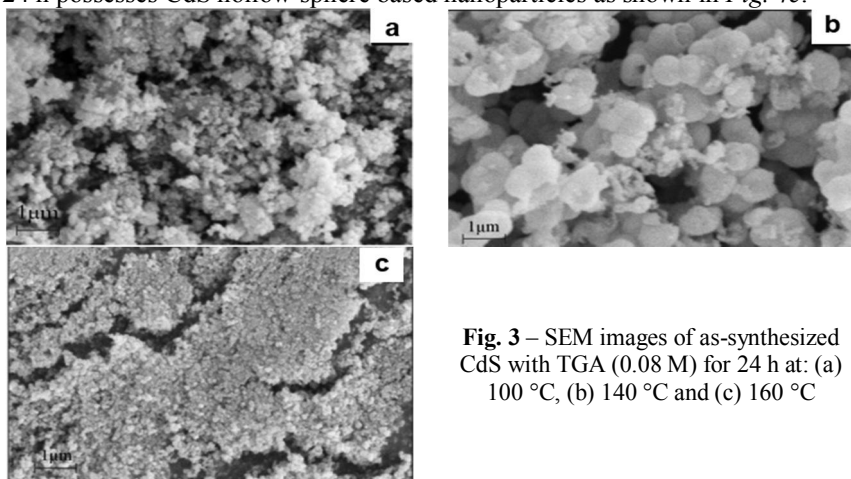
Synthesis was carried out in different experimental conditions to get the optimum condition for the formation of CdS nanostructures. In solvothermal/hydrothermal process the decomposition of the precursors at a particular solvent depends on the temperature and pressure inside the reaction vessel. Here, pressure was related to the filling fraction of the solvent and was kept constant for all the experiments. Initially synthesis was performed in water with different concentrations of thioglycolic acid (TGA) using the same cadmium source. Then synthesis temperature was adjusted to achieve the favorable condition for the synthesis of CdS hollow spheres and subsequently the experiments were carried out with different reaction time of the TGA solutions.

The effects of the Cd<sup>2+</sup> to TGA mole ratio in the starting solution on the morphology and shape of CdS powders are shown in *Fig. 2*. In a series of experiments, the temperature was kept at 120 °C and the reaction time was 24 h. *Fig. 2* shows the powder SEM and TEM images of the resultant products obtained with TGA: Cd<sup>2+</sup> (1:1 to 3:1) at 120 °C for 24 h. With the raising mole ratio, TGA: Cd<sup>2+</sup>, from 1:1 to 3:1, morphologies of the as-synthesized CdS products change. When synthesis was performed with the mole ratio of TGA/Cd<sup>2+</sup> was 1:1, quasi nanospheres were formed (*Fig. 2a*). The typical TEM image of the CdS nanoparticles prepared with TGA: Cd<sup>2+</sup>, from 1:1 at 120 °C for 24 h is indicated in *Fig. 2b*. CdS nanoparticles with 40–50 nm diameters are shown in *Fig. 2b*. Upon increasing the TGA: Cd<sup>2+</sup> mole ratio to 2, hollow sphere was produced (*Fig. 2c*). This data indicates that how reactant concentration could change the morphology of the product. Increasing the molar ratio to 3:1 hollow spheres, including some of nanoparticles were observed (not shown here).



**Fig. 2** – SEM and TEM images of the as-synthesized product at 120 °C for 24 h at different concentration of TGA: (a, b) 0.04 M and (c, d) 0.08 M.

To further probe the effect of growth conditions has been hanged the synthesis temperature with constant TGA/ $\text{Cd}^{2+}$  mole ratio, i.e. 2:1. The SEM image in Fig. 3a shows that CdS powders obtained with TGA (0.08 M) for 24 h at 100 °C consist of irregular nanoparticles, whereas the product obtained at 120 °C for 24 h possesses CdS hollow-sphere based nanoparticles as shown in Fig. 4c.



**Fig. 3** – SEM images of as-synthesized CdS with TGA (0.08 M) for 24 h at: (a) 100 °C, (b) 140 °C and (c) 160 °C

As shown in *Fig. 3b* one can see that by increasing the reaction temperature to 140 °C, CdS hollow sphere was observed. It is noticeable that these hollow spheres were stable at 140 °C. Upon raising the temperature to 160 °C, all of the CdS hollow-sphere based nanoparticles collapsed and irregular nanoparticles were obtained (*Fig. 3c*). This occurs at higher reaction temperatures, TGA decomposed faster and thus the nanocrystallites grew at a relatively higher rate to larger sizes.

The photoluminescence spectrum of the CdS samples obtained at 120 °C at different TGA concentration: (a) 0.04 M and (b) 0.08 M, show an emission maximum at 594 nm and 580 nm ( $\lambda_{\text{exc}} = 392$  nm). It presents some blue-shift compared to bulk CdS at 650nm, which are consistent with the result of above UV-vis absorption spectrum. Previous reports suggest that the emission arises from the recombination of an electron trapped in a sulfur vacancy with a hole in the valence band of CdS [8]. As the crystallite size decreases, intensity of emission peak increases and the peak shifts to higher frequencies that indicates the quantum confinement effect.

### CONCLUSIONS

CdS nanostructures have been successfully synthesized through a thioglycolic acid-assisted hydrothermal processing using a new precursor  $[\text{Cd}(\text{pht})(\text{H}_2\text{O})]_n$  as the source of  $\text{Cd}^{2+}$  and thioglycolic acid (TGA) as sulfiding reagent. The possible growth mechanism of formation of the CdS nanostructures was discussed and the effects of TGA concentration, reaction time and reaction temperature on morphology and phase were proposed. We believe that this synthesis process can be extended to become a general method for the preparation of other novel structure function materials.

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