



Controllable synthesis of nanocrystalline CdS with different morphologies by hydrothermal process in the presence of thioglycolic acid

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ABSTRACT

Nanocrystalline CdS with different morphologies and particle sizes was obtained via a simple hydrothermal reaction between $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and thioglycolic acid (TGA) at relatively low temperature. Products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), ultraviolet–visible (UV–vis) spectroscopy, photoluminescence spectroscopy (PL), Fourier transform infrared (FT-IR) spectra, and thermogravimetric-differential thermal analysis (TG-DTA). The effect of reactant concentration, molar ratio of TGA to the cadmium nitrate, temperature and reaction time on the morphology, particle sizes and phase of nanocrystalline CdS products has been investigated.

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1. Introduction

The synthesis of binary metal chalcogenides of group II semiconductors has been the focus of recent scientific research due to their important nonlinear optical properties [1], luminescent properties [2,3], quantum size effects [4–6], and other important physical and chemical properties [7]. Especially, synthesis of semiconductor nanowires (nanorods) or fibers, and investigation on their properties arises much interest [8–10]. Control over both nanocrystalline morphology and the crystal size is a new challenge to synthetic chemists and materials scientists [10,11].

Among binary compound semiconductors, cadmium sulfide (CdS) is representative of group II due to its wideband gap of 2.42 eV at room temperature and has wide potential application in many fields, such as photoluminescence devices and solar cells [12–15].

There are different methods such as microwave-solvothermal synthesis [16,17], hydrothermal route [18,19] and surfactant-ligand co-assisting solvothermal method [20] used to synthesize nano- and micro-crystalline CdS. Most of the products have different morphologies such as dendrites [21], flakes [22], spheres [23], nanorods [20,24,25], nanowires [26–28], triangular and hexagonal plates [29], flower-like shape [30] and sea-urchin-like shape [31].

Compared with nanoparticles, the fabrication and study of one-dimensional (1D) nanostructures such as nanorods and nanowires as building blocks for many novel functional materials are currently the focus of considerable interest over these years because of their special properties and wide applications in nanodevices [32,33]. Since many fundamental properties of semiconductor materials have been expressed as a function of the size and the shape, the control of nucleation and growth of 1D nanostructural materials is becoming critical, which can provide opportunities of tailoring properties of materials and offer possibilities for observing interesting physical phenomena [19].

Recently Yang's groups have developed a mild hydrothermal route to synthesize metal sulfides with the use of thioglycolic acids (TGA) as nontoxic template [34]. And it is revealed that TGA acts as the oriented growth reactant during above process. Furthermore, their previous results indicated that the crystal growth of CdS is also determined by mass transport process via control of decomposition rate of free S^{2-} from the sulfur source in the solution [35]. However, to the best of our knowledge, a general route for the synthesis of CdS nanorods under hydrothermal conditions with thioglycolic acid has still not been realized.

We have presented a hydrothermal method, which is milder, simpler, more practical, and more environmental method than other methods. The trick in hydrothermal synthesis of CdS nanorods presented here is the application of thioglycolic acid (TGA) as a sulfur source and stability agents, which was previously used as the stability agent to prevent the chalcogenide nanocrystals from aggregating [36]. TGA makes important roles in anisotropic growth of CdS crystals to rod-like shape during the hydrothermal process.

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Comparative experiments show that TGA is capable of favoring the erosion reaction and inducing the orientation growth of the resultant metal sulfide nanocrystals. We controlled the morphology and particle sizes of nanocrystalline CdS at (80–160 °C) using cadmium nitrate and thioglycolic acid (TGA) as reactants in an aqueous solution. It was found that the molar ratio of TGA to Cd^{2+} , temperature and reaction time play key roles in controlling the morphology and particle sizes nanocrystalline CdS.

2. Experimental

2.1. Materials and physical measurements

All the chemicals were of analytical grade and were used and received without further purification. XRD patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation. Elemental analyzes were obtained from Carlo ERBA Model EA 1108 analyzer. The compositional analysis was done by energy dispersive X-ray (EDX, KeveX, Delta ClassI). Scanning electron microscopy (SEM) images were obtained on Philips XL-30ESEM equipped with an energy dispersive X-ray spectroscopy. Transmission electron microscopy (TEM) images were obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 100 kV. Fourier transform infrared (FT-IR) spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets. The electronic spectra of the complexes were taken on a Shimadzu UV-vis scanning spectrometer (Model 2101 PC). Room temperature photoluminescence (PL) was studied on an F-4500 fluorescence spectrophotometer. Thermogravimetric-differential thermal analysis (TG-DTA) was carried out using a thermal gravimetric analysis instrument (Shimadzu TGA-50H) with a flow rate of 20.0 mL min^{-1} and a heating rate of $10^\circ\text{C min}^{-1}$.

2.2. Preparation of CdS nanocrystals

In a typical procedure, different molar ratios of analytical grade $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and thioglycolic acid (TGA) were added to a Teflon-lined autoclave of 150 mL capacity. The autoclave was maintained at 80–160 °C for 5–24 h and then air cooled to room temperature. The precipitate was centrifuged, washed with distilled water, and absolute ethanol added to remove residual impurities. The bright yellow products were dried in vacuum at 60 °C for 10 h.

3. Results and discussion

The XRD patterns at the different temperature showed that the crystallinities of the as-prepared products were continuously improved with increases at the reaction temperature from 80 °C to 108 °C. Furthermore, a preferential orientation and a rod-like shape were observed in the sample obtained at 108 °C. The XRD pattern (Fig. 1a) of the synthesized product with TGA (0.06 M) for 5 h at 80 °C shows that the majority of the products were poorly crystallized. When the reaction temperature increases from 80 °C to 108 °C, the crystallinity of the products will obviously improve, as shown in Fig. 1b. The diffraction peaks of (100), (002), and (101) could be well distinguished, it was noted that the diffraction peak of (002) was the strongest. This unusual diffraction peak of (002) indicates a preferential orientation along the *c*-axis and a rod-like shape [37,33]. The rod-like shape was confirmed by TEM photographs that will be discussed later. The XRD pattern of as-prepared sample at 108 °C was indexed as a pure hexagonal phase which is very close to the values in the literature (JSPDS No. 41-1049). The temperature was found to play a key role in the formation of nanocrystalline CdS. The temperature also affects on the particle sizes of CdS nanocrystals.

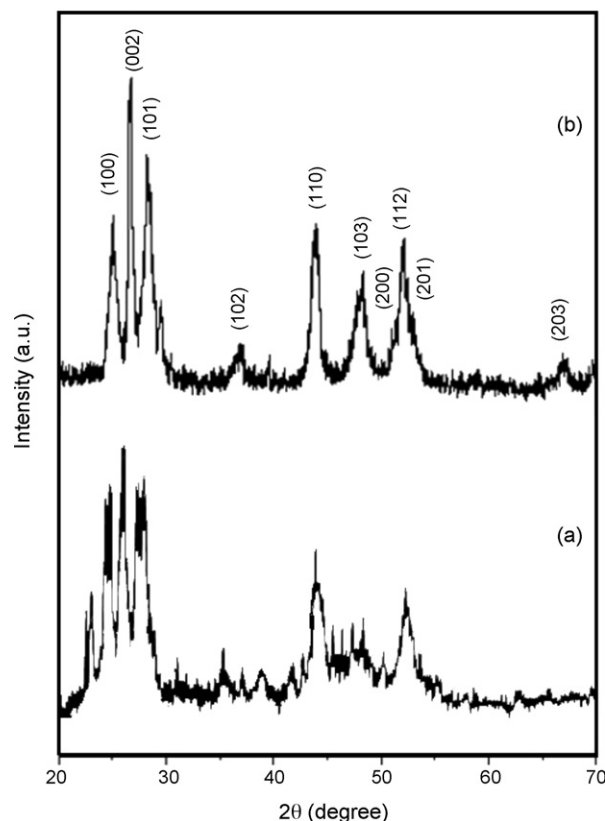


Fig. 1. XRD patterns of the CdS particles obtained with TGA (0.06 M) for 5 h at (a) 80 °C and (b) 108 °C.

The SEM image in Fig. 2a shows that CdS powders obtained with TGA (0.06 M) for 5 h at 80 °C consist of non-uniform rod-like with average width 200 nm and length 5 μm , and some spherical nanoparticles with diameters about 25 nm, whereas the product obtained at 108 °C for 5 h consist uniform nanorods of average width 25 nm and length 6 μm as shown in Fig. 2b. Upon raising the temperature to 160 °C, the product was found to consist of microspheres CdS with diameters 1–2 μm as shown in Fig. 2c. The effect of reaction time on the morphology and particle size of the products was investigated. As shown in Fig. 2d, when the reaction time was prolonged, from 5 h to 24 h at 108 °C, rod-like samples with average width 100–200 nm and length 3 μm were obtained.

The effects of the molar ratio $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ to TGA in the starting solution on the morphology and shape of CdS powders are shown in Fig. 3. In a series of experiments, the temperature was kept at 180 °C and the reaction time was 5 h. Fig. 3 shows the powder SEM images of the resultant products obtained with TGA: Cd^{2+} (1:1–6:1) at 108 °C for 5 h. With the increase molar ratio, TGA: Cd^{2+} , from 1:1 to 6:1, morphologies of the as-synthesized CdS products change. In 0.02 M TGA (Fig. 3a) rod-like samples with average width 80–200 nm and length 2 μm were obtained, while in 0.06 M uniform nanorods were observed (Fig. 3b). Upon increasing the molar ratio TGA to Cd^{2+} , the amount of the nanorods in the products decreases as illustrated in Fig. 3c and rod-like CdS with average width 150–200 nm were prepared. Chemical purity and stoichiometry of the samples were tested by EDX. The very strong peaks related to Cd and S are found in the spectrum (Fig. 4).

The typical TEM image of the CdS nanorods is indicated in Fig. 5. Very long CdS nanorods with length up to 6 μm can be seen. It should be noted that bundles of CdS nanorods were formed in the sample.

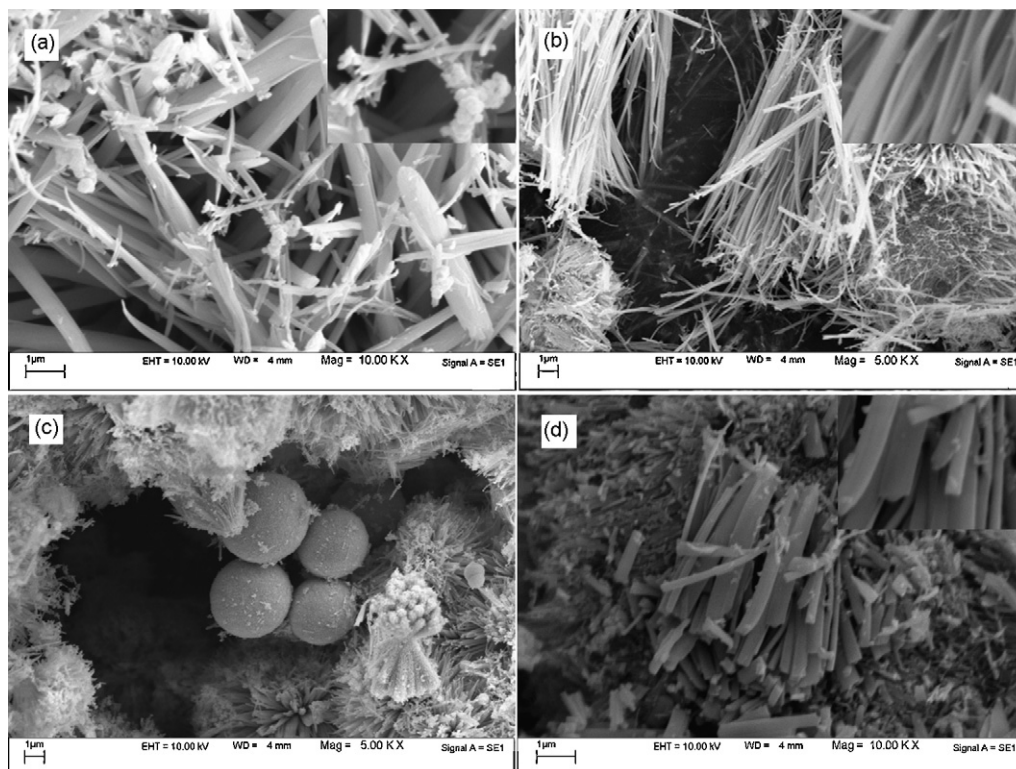


Fig. 2. SEM image of as-synthesized CdS with TGA (0.06 M) for 5 h at: (a) 80 °C, (b) 108 °C, (c) 160 °C and (d) 108 °C for 24 h.

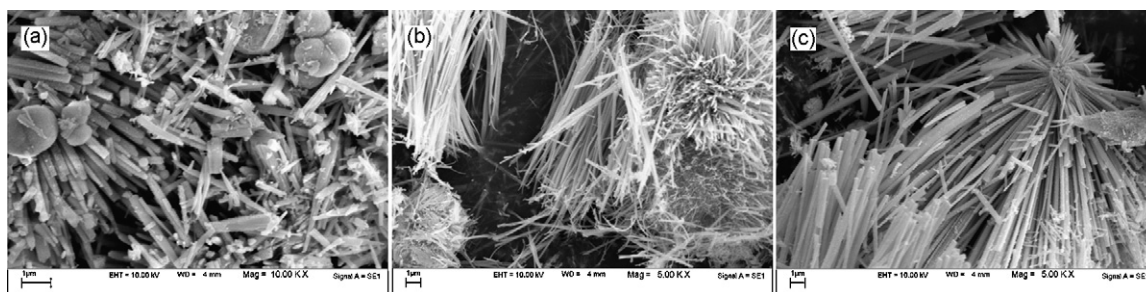


Fig. 3. SEM images of the as-synthesized product at 108 °C for 5 h at different concentration of TGA: (a) 0.02 M, (b) 0.06 M and (c) 0.16 M.

The UV–vis absorption spectra of the CdS with different morphology were recorded as shown in Fig. 6. According to Fig. 6 when temperature increased to 108 °C, and 160 °C, the products shows a strong absorption edge at about 476 nm, 485 nm, respectively (Fig. 6a and b). Compared with CdS bulk material, which

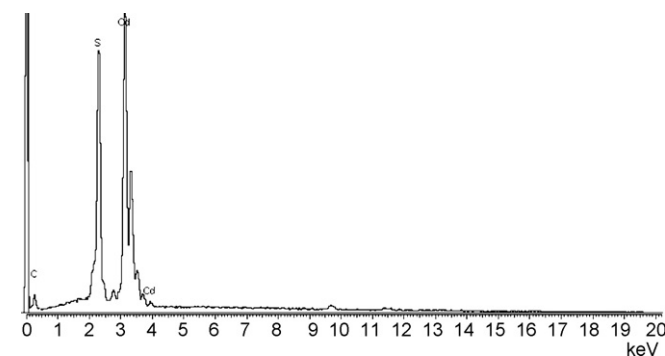


Fig. 4. EDX spectrum of a representative CdS nanorods synthesized in 0.06 M (TGA) at 108 °C, for 5 h.

shows maximum absorption around 515 nm [34,38], all of the CdS nanomaterials have shown obvious blue shift due to quantum confinement. The color of the solution turns to milky and then bright yellow as the temperature is increased. This illustrates how the nanoparticle size can be effectively controlled by setting the growth temperature. Upon raising the reaction time to 24 h at 108 °C (Fig. 6c), the band red shifts to 509 nm accompanying a significant increase in the absorbance, which could result from the increase in the mean particle size of CdS and so, the color of the product turns to deep yellow. During preparation there is generally an increase of particle size of the nanoparticles with time, which is consisting with an ostwald ripening process. By taking advantage of the optical property difference between CdS bulk and nanomaterial, it should be possible to apply the CdS nanomaterials on the UV filter, photocatalysis, and special optical device.

Photoluminescence (PL) measurement was carried out at room temperature with wavelength 350 nm (Fig. 7). The PL spectrum consists of one strong peak at 425 nm that can be ascribed to a high level transition in CdS semiconductor crystallites. It has been reported that this kind of bandedge luminescence arises from the

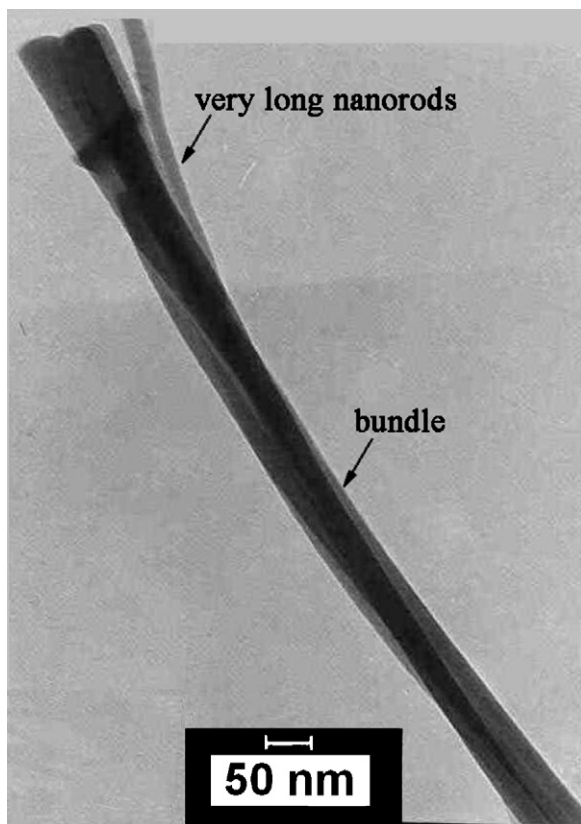


Fig. 5. TEM images of the as-synthesized CdS nanorods using the TGA (0.06 M) at 108 °C for 5 h.

recombination of excitons and/or shallowly trapped electron-hole pairs [39,40].

The composition and quality of the product was analyzed by the FT-IR spectroscopy. The IR spectrum of the samples obtained from the as synthesized CdS nanorods is shown in Fig. 8. Since CdS has no absorption peaks in the range of 4000–500 cm^{-1} therefore these peaks (positioned at 1000 cm^{-1} , 679 cm^{-1} , 622 cm^{-1} , 597 cm^{-1} and 522 cm^{-1}) must be caused by the thioglycolic acid molecule absorbed on the surface of CdS. We believe that these absorption peaks are close to those of $(\text{CdS})_m(\text{SHCH}_2\text{COOH})_k^{2+}$ [34].

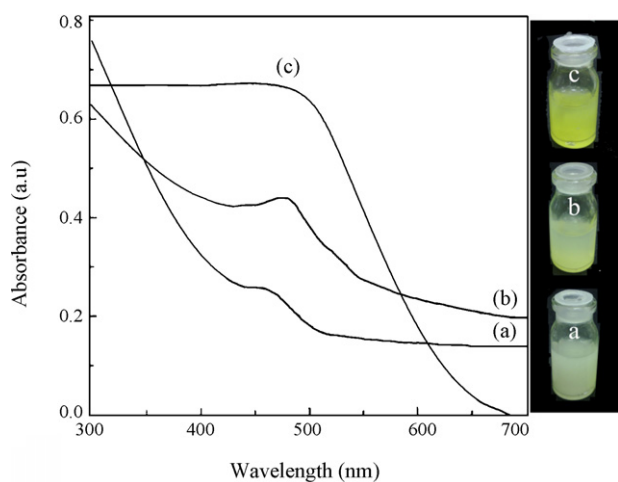


Fig. 6. UV-vis absorption spectrum of CdS prepared with TGA (0.06 M) for 5 h at: (a) 108 °C, (b) 160 °C and (c) 108 °C for 12 h.

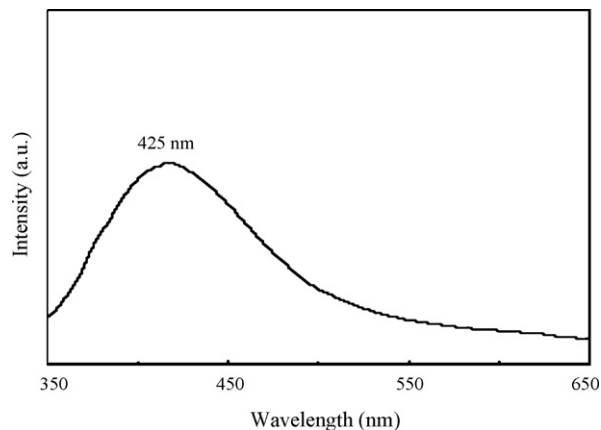


Fig. 7. Room temperature photoluminescence (PL) spectrum of CdS nanorods.

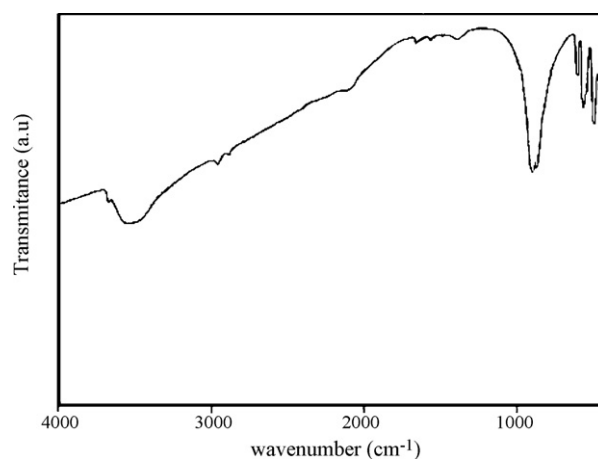


Fig. 8. FT-IR spectrum of as-synthesized products in (0.06) M TGA at 108 °C for 5 h.

Considering all of these results, the whole process can be expressed as follows [34]:

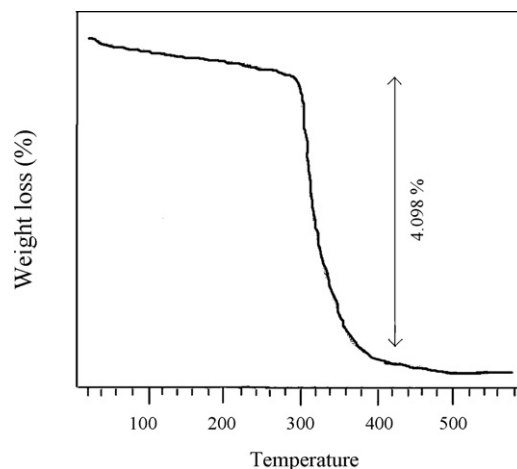
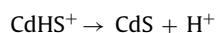
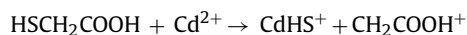
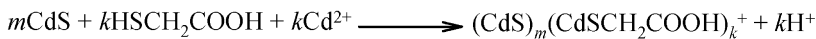


Fig. 9. TGA of CdS nanorods obtained after removal of the liquid crystal phase by washing with ethanol.



Complexed CdS

According to above mechanism, the TGA acted as a 'soft template', leading to the anisotropic growth of CdS nanocrystals.

Previous report [35] suggests that the formation of CdS nanorods bundles can be explained as follows: prior to the hydrothermal process, the dissociation of S^{2-} from TGA is significantly slow, and the formation of complexed CdS clusters, $(\text{CdS})_m(\text{SHCH}_2\text{COOH})_k^{2+}$ is fairly limited. Meanwhile, during the hydrothermal process, the formation of $(\text{CdS})_m(\text{SHCH}_2\text{COOH})_k^{2+}$, is remarkable due to the enhanced dissociation S^{2-} from TGA at high temperature and pressure. In this case, it is invisible that the complexed CdS clusters aggregate somewhere because they are formed at a high rate. Therefore, CdS nanorods bundles were formed in this sample.

In order to have further investigation on the organic template, TGA analysis of the as-synthesized material showed the thermal stability of the organic template. The TGA curve was recorded from room temperature to 600 °C. Fig. 9 indicates that there is one distinct weight loss step that could be observed. According to the TGA curve, the weight loss of CdS is about 4.098% from 380 °C to 444 °C. After the sample was heated over 500 °C, the sample weight did not change anymore. This indicates that only a small amount of the organic molecules (TGA) was bound to the CdS nanorods. Combining the results of the FT-IR spectra, it was proved that organic surfactant molecule still exists in the as-prepared product.

4. Conclusions

Nanocrystalline CdS with different morphologies and particle sizes was obtained via a simple hydrothermal reaction between $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and thioglycolic acid (TGA). The effect of different parameters such as the molar ratio TGA to Cd^{2+} , temperature, reaction time, which are known as the key parameter on the morphology and particle size of products were investigated.

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