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# TWO-STEP SYNTHESIS OF CdS (hcp) NANORODS USING SONOCHEMICAL AND HYDROTHERMAL PROCESSES

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CdS (hcp) crystals were synthesized using $CdCl_2.2H_2O$ in $C_4H_{11}N$ containing 20 % $(NH_4)_2S$ by the 5 h sonochemical process followed by the hydrothermal reaction at different temperatures and times. CdS (hcp) crystals composing of Cd and S were detected using XRD, SAED and EDX. A Raman spectrometer revealed the presence of fundamental and overtone modes at 299 and 596 $cm^{-1}$, respectively. The crystals are nanorods growing in systematic array analyzed using TEM and HRTEM. Their photoluminescence is in the blue spectral region at 409-422 nm (2.94-3.03 eV).

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*Keywords:* CdS, Nanorods, Sonochemical and hydrothermal processes

## 1. Introduction

Nanostructured CdS, such as nanoribbons [1], nanowires [2], nanoparticles [3] and nanorods [4], has much attractive attention due to its unusual properties. It has a wide variety of applications for using as solar cells, photoelectronic devices and photocatalysts. There are several methods used for preparing the sulfide. Among them are microwave irradiation [1-3], solvothermal process [4], ultraviolet irradiation [5], hydrothermal process [6] and others.

For the synthesis of nanostructure CdS by two-step sanochemical and hydrothermal processes, The nanorods CdS are obtained by sonochemical process but it is low crystallization. After that, The nanorods CdS followed by the hydrothermal reaction to improved the crystallization.

## 2. Experimental

For the present research, 0.005 mol $CdCl_2.2H_2O$ was dissolved in 30 ml $C_4H_{11}N$ in which 1.73 ml of 20 % $(NH_4)_2S$ was subsequently added. The sonochemical reaction proceeded in ambient atmosphere for 5 h. The precipitate was washed with water and ethanol, and dried at 70 $^oC$ for 12 h. The 0.1 g precipitate was put in an autoclave containing 16 ml water. Hydrothermal reaction proceeded at different temperature and time. The final products were then analyzed.

The final products were analyzed using an X-ray powder diffractometer (XRD) on Cu-Kα line of SIEMENS D500. A Raman spectrometer of HORIBA JOBIN YVON T64000 was carried

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*Corresponding Author : phuruangrat@hotmail.com out using 50 mW Ar laser with 514.5 nm wavelength. A transmission electron microscope (TEM) of JEOL JEM-2010 were operated at 200 kV with energy dispersive X-ray analyzer (EDX, Oxford instruments, INCA). Photoluminescence (PL) emission was recorded at room temperature by PERKIN-ELMER LS50B luminescence spectrometer.

## 3. Results and discussion

XRD spectra (Fig 1) were compared with those of the JCPDS standard (reference code : 06-0314) [7]. The products were specified as CdS (hcp) with P63mc space group. For 5 h sonochemical process only, the spectrum is rather broad showing that the product composes of very fine particles. The XRD peak diffracting from the (002) plane is unusually narrow and strong as compared to other peaks. Its intensity is the highest which shows the preferred growth along the c-axis [1,2]. For 5 h sonochemical process followed by 100 oC hydrothermal process at different temperatures and times, not only more peaks were detected but they were also higher and narrower. Growth along the c-axis is the highest as well. For 5 h sonochemical process with 200 $^{o}$C and 10 h hydrothermal reaction, calculated lattice parameters [8] are a = b = 0.4127 nm and c = 0.6745 nm. For JCPDS standard [7], a, b and c are 0.4136, 0.4136 and 0.6713 nm, respectively. The c (calculated) is longer than the c (standard) showing that the c (calculated) is in accord with the growth along the c-axis. The degree of crystallinity was increased with the increasing in the temperature and time, but the products remain as the same phase. No other characteristic peaks of impurity were detected, showing that the products are pure phase.

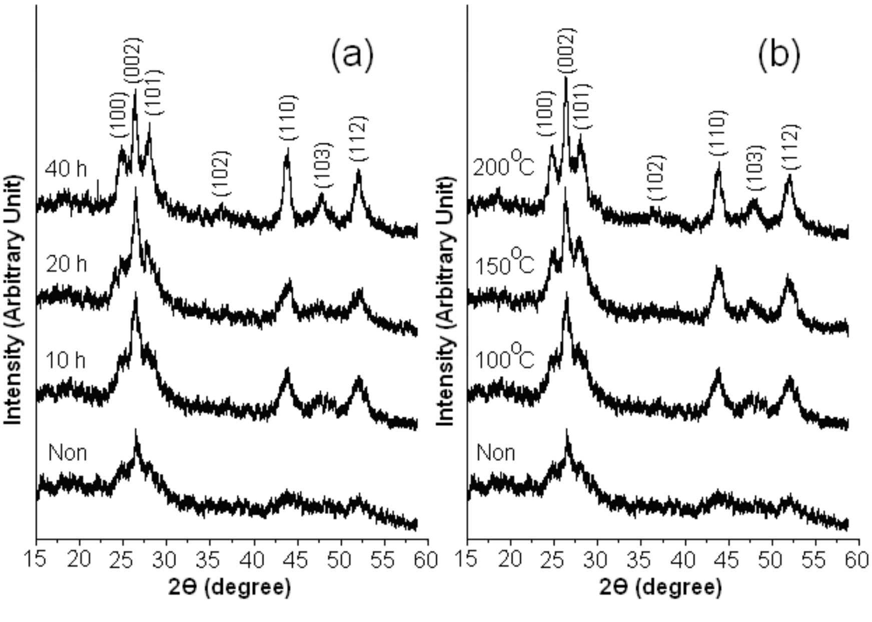

*Fig 1. XRD spectra of the products prepared using sonochemical process for 5 h followed by hydrothermal reaction at (a) 100 $^{o}$C for different prolonged times and (b) different temperatures for 10 h.*

All Raman spectra (Fig 2) are almost identical. The minor differences are caused by defects in the products. For 5 h sonochemical process without and with hydrothermal reaction at different temperatures and times, the peaks were still at the same wavenumbers. These show that the products remain to exist as the same phase. Two peaks correspond to the first and second longitudinal optical (LO) phonon modes [9,10]. They are respectively at 299 and 596 cm$^{-1}$, due to phonon vibration. Comparing to CdS (single crystal), the LO modes shifted to the lower values due to the particle-size effect [9]. It is the dimension effect on the phonon vibration of the products with nano-sized crystal.

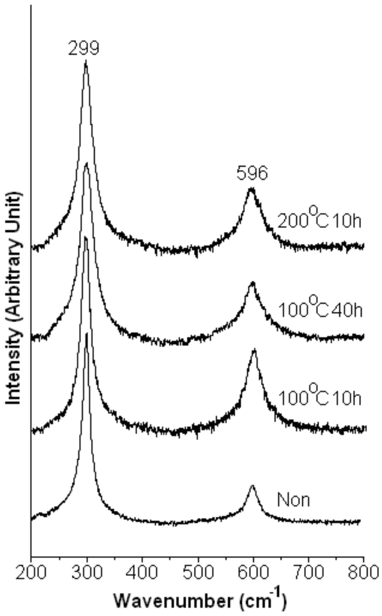

*Fig 2. Raman spectra of the products prepared using sonochemical process for 5 h followed by hydrothermal reaction at different temperatures and times.*

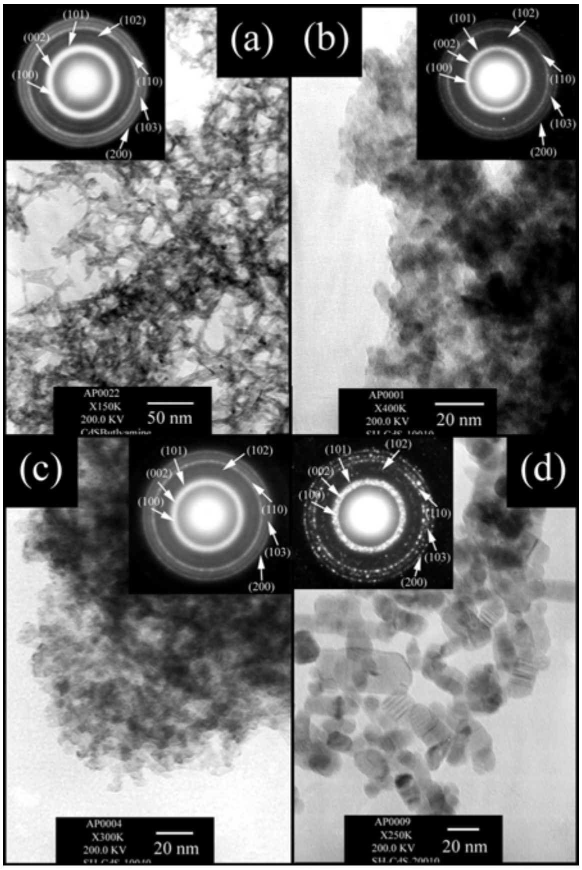

*Fig 3. TEM images and SAED patterns of the products prepared using sonochemical process for 5 h (a) without hydrothermal reaction, and (b-d) with hydrothermal reaction at 100 °C for 10 h, 100 °C for 40 h and 200 °C for 10 h, respectively.*

TEM images (Fig 3a) show that the product prepared using 5 h sonochemical process composes of a number of nanorods. Those prepared using the sonochemical process followed by the 100 oC hydrothermal reaction for 10 and 40 h (Figs 3b and 3c) compose of nanorods in clusters. The clusters are so tiny that the images show the morphologies as the dark and light domains. For the 5 h sonochemical process with 200 $^{o}$C and 10 h hydrothermal reaction (Fig 3d), a number of nanorods were also detected. Their facets are clearly visible showing that the nanorods have crystalline characters. Their crystallinity is also improved. Hydrothermal process has the influence on the product sizes by the crystallization under high temperatures in the autoclave, but the phase remains unchanged. SAED patterns (Figs 3a-3d) show light concentric rings corresponding to diffraction planes of the crystalline products. The rings are diffuse and hollow showing that the products composed of very fine particles. Diameters of the rings were measured from the diffraction patterns on the films. The interplanar spaces of the diffraction planes were calculated [11] and compared with those of the JCPDS software [7]. The patterns correspond to CdS (hcp). HRTEM images (Fig 4) show the (101) planes which are aligned in systematic array. There are several domains in the images. Each of them, belonging to a cluster of nanorods, composes of a number of planes aligning in the same direction. By using XRD spectra in Fig 1a and Bragg's law for diffraction, calculated interplanar spaces of (101) plane (0.3274 and 0.3294 nm for 5 h sonochemical process with 100 $^{o}$C hydrothermal reaction for 10 and 40 h) are very close to the corresponding values (0.3220 and 0.3239 nm) measured from Fig 4, respectively. The measured values are less than the calculated ones due to the quantum size effect.

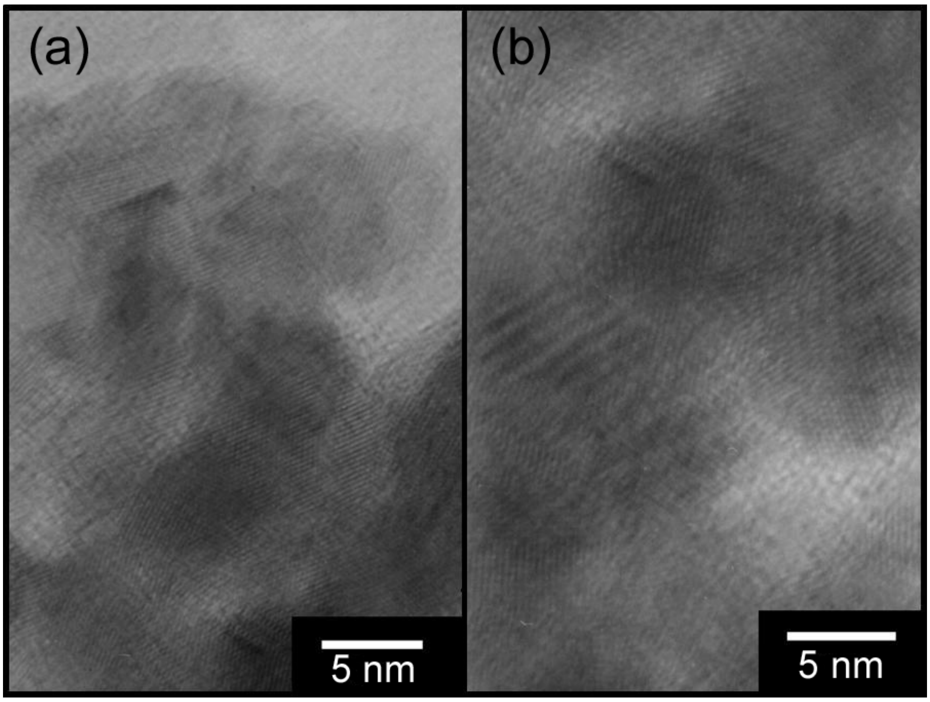

*Fig 4. HRTEM images of the products prepared using sonochemical process for 5 h with 100 $^{o}$C hydrothermal reaction for (a) 10 h and (b) 40 h.*

EDX analysis (Fig 5) [12] revealed the presence of Cd at 3.13 keV ($L_{\alpha}$), 3.32 keV ($L\beta_1$) and 3.53 keV ($L\beta_2$), and S at 2.31 keV ($K\alpha_{1,2}$). Other peaks were detected at 8.04 keV ($K\alpha_{1,2}$), 8.91 keV ($K_{\beta}$) and 0.93 keV ($L_{\alpha}$) for Cu from a Cu grid, and 0.28 keV ($K\alpha_{1,2}$) for C of carbon tape. The detection of Cd and S using EDX, and CdS using XRD and SAED are in good accord.

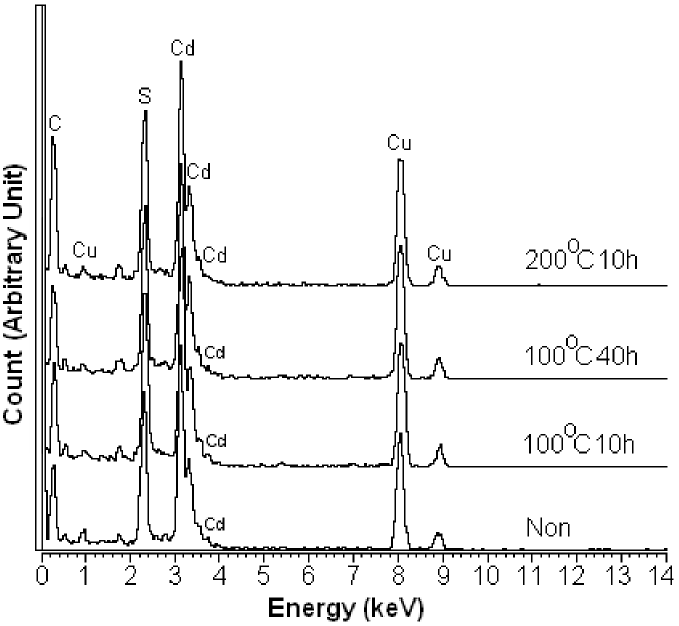

*Fig 5. EDX spectra of the products prepared using sonochemical process for 5 h without and with hydrothermal reaction at different temperatures and times.*

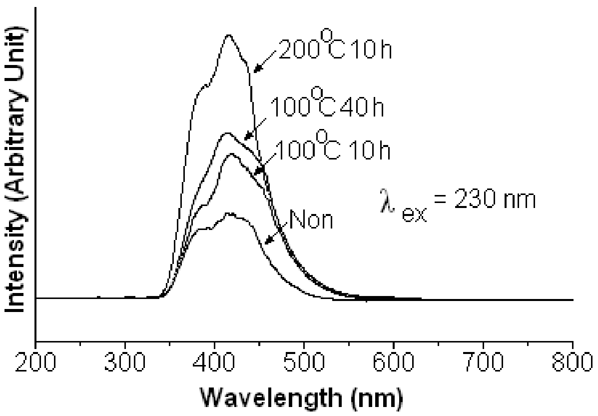

*Fig 6. PL spectra of the products prepared using sonochemical process for 5 h without and with hydrothermal reaction at different temperatures and times.*

Photoluminescence (PL) (Fig 6) was analyzed using 230 nm exciting wavelength ($\lambda_{ex}$). The spectra show the narrow central (intrinsic) peaks with their surrounding shoulders due to some defects and impurities. The shoulders are interpreted as extrinsic transition [13]. PL energies of the products are in the blue spectral region at 409-422 nm (2.94-3.03 eV). Shapes, sizes, degree of crystallinity and others can play the role in their emission peaks, but PL intensity is controlled by the number of charged transfers. Comparing to the estimated band gap of bulk CdS (2.42 eV, 512 nm) [14], the PL energies are blue shifted. However, band gap can be modified by high temperature treatment [15].

## 4. Conclusions

The nanorods CdS were synthesized using $CdCl_2.2H_2O$ in $C_4H_{11}N$ containing 20 % $(NH_4)_2S$ by the 5 h sonochemical process. After that, The nanorods CdS were controlled by the hydrothermal reaction at different temperatures and times in order to improve the crystallization. Their photoluminescence increases after hydrothermal reaction and show peaks in the blue spectral region at 409-422 nm (2.94-3.03 eV).

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