

The Role of *pH* on Infrared Spectral, Structural and Morphological Properties of Room-temperature Precipitated CdS Nanoparticles

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In this work, room-temperature treated CdS nanoparticles were prepared in KOH solution via precipitation at different *pH* values by varying the ammonium nitrate (NH_4NO_3) concentration. The crystallite phase and size, surface morphology and infrared frequencies of functional groups were characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy, respectively. The SEM images show that the CdS nanoparticles are spherical in shape. Meanwhile, the FTIR result reveals that a broad band occurred in the range of $400\text{-}700\text{ cm}^{-1}$ could be attributed to the molecular bonding structure of CdS. The XRD patterns exhibit four well-resolved crystalline peaks that represents the diffraction planes of a cubic CdS phase. Nevertheless, a minor decrement in the intensity for both infrared and crystalline bands denotes a slight reduction in structure crystallinity and further indicates that a higher purity of finer CdS nanoparticles is obtained as the *pH* value decreases. Also, the diffraction peak becomes slightly wider that implies a decrease in the mean crystallite size as validated by Debye-Scherrer method. Owing to their unique nanostructural and morphological features, the CdS nanoparticles obtained in this study have potential applications in photonic devices, optoelectronics, photocatalysis and solar cells.

Keywords: CdS nanoparticles, Functional group, Crystalline cubic structure, Surface morphology.

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1. INTRODUCTION

In recent years, research scientists discovered that semiconductor quantum dots (QDs) in nanometer-size could exhibit some unique physical and chemical properties as compared to the bulk materials due to the quantum confinement effect on their band structure. Nowadays, the II-IV group semiconductor has emerged as one of the most studied materials because of its advanced optical and electronic properties. Cadmium sulphide (CdS) is one of the well-known and most studied II-IV group semiconductor materials due to its wide and direct band gap (2.42 eV) and also unique non-linear optical properties. Besides, it has been exploited in many vital applications, such as optical sensors, fluorescence probe, solar battery, photo-electrocatalysis and other optoelectronic devices [1-7].

Many methods have been introduced to synthesize the CdS nanoparticles including vapor deposition, biosynthesis, sonochemical, electrodeposition, solvothermal and precipitation methods [8-13]. Among them, precipitation has been recognized as one of the most effective methods to produce the CdS nanoparticles with a well-defined structure through a simple preparation route. In this work, the CdS nanoparticles were synthesized by aqueous precipitation in the KOH based alkaline medium that involves a reaction between the metastable precursors of thiourea and cadmium chloride at different *pH* values. The *pH* values were adjusted by varying the concentration of ammonium nitrate, which acts as a surface-active agent that favors the formation of nanoparticles with a narrow size distribution. The elemental analysis and structural properties were characterized by FTIR and XRD, and the morphological properties were characterized by SEM.

2. MATERIALS AND METHOD

In the current study, all the chemical reagents were of analytical purity and used as received without further treatment. Cadmium chloride (CdCl_2), potassium hydroxide (KOH), ammonium nitrate (NH_4NO_3) and thiourea were procured from Merck with 99.9 % purity. Distilled water was used as a solvent for the aqueous solution preparation under air atmosphere conditions.

CdCl_2 and thiourea were used as the precursors in generating the Cd^+ and S^- ion sources in the KOH alkaline medium, respectively. The ammonia nitrate was used as a complexing agent and *pH* buffer in the chemical reaction for the purpose to control the formation and properties of CdS nanoparticles by adjusting the *pH* value of the solution at a desired level. Firstly, an aqueous solution was prepared by dissolving the CdCl_2 (0.02 M) and thiourea (0.2 M) into the KOH (0.5 M) solution. Then, a desired amount of NH_4NO_3 was gradually added into the aqueous mixture solution. The solution was constantly stirred under magnetic stirring at $80\text{ }^\circ\text{C}$ in the water bath for 2 hours. The color of the mixture turned slowly from milky into light yellow. After that, the yellow precipitates were collected by filtration from the aqueous solution. The precipitates were then repeatedly washed with distilled water and acetone several times to remove the unreacted reagents and further dried at room temperature overnight prior to characterizations. The CdS nanoparticle samples were prepared at different *pH* values by varying the NH_4NO_3 concentration.

The crystalline structure of the as-synthesized CdS nanoparticles was characterized using the XRD (Rigaku Miniflex-TM II) with $\text{CuK}\alpha$ radiation ($\lambda = 1.541\text{ \AA}$) generated at operating voltage of 40 kV and 40 mA current.

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The samples were scanned at room temperature in the diffraction angle range $2\theta = 20-80^\circ$ with a scan speed of 0.02° per second. The mean crystallite sizes of the samples were then calculated by Debye-Scherrer method. Morphology of the samples was examined using SEM of model JSM JEOL-6360 at an acceleration voltage of 15 kV with $\times 20,000$ magnification. The functional groups of the samples were identified by FTIR spectrometer (Thermo Nicolet Alvarar 380 FTIR), at which the FTIR spectrum was scanned in the mid-infrared spectral region between 4000 and 400 cm^{-1} with 2 cm^{-1} resolution.

3. RESULTS AND DISCUSSION

FTIR analysis was executed to identify the characteristic functional groups of the CdS samples. Fig. 1 displays the FTIR spectra of the CdS synthesized at room temperature with different pH values in the range of 10-13. From the spectra, the wide band emerged in the range from 400 to 700 cm^{-1} is related to the molecular structural bonding of CdS nanoparticles [14]. This band becomes slightly smaller and narrower as the pH increases, which implies that the arrangement of CdS nanocrystallites becomes less ordered and would result in a minor decay in transmission efficiency. The broad band positioned in the range of $3600-3000\text{ cm}^{-1}$ is ascribed to O-H stretching vibrations of the water molecules [15]. As the pH value decreases, the intensity and size of this band also decrease, which is mainly due to the repellence of water molecules from the particle surface, since more OH^- ions would contribute to the hydrolysis of thiourea for CdS formation at increased NH_4NO_3 concentration. Furthermore, the peaks situated at 2341 cm^{-1} , 2000 cm^{-1} , 1624 cm^{-1} , 1380 cm^{-1} and 1120 cm^{-1} are associated with S-H stretching vibration, R-N=C=S groups, CO_2 molecules attached to the CdS surface, CH_3 bending deformation and S-O bonding, respectively [12, 15-18]. As the pH value decreases at higher NH_4NO_3 concentration, the intensity of these peaks decreases or becomes negligible, which could be simply due to the surface area reduction of the nanoparticles, once evidenced from the smaller crystallite size formation as validated by XRD analysis.

The pH value plays a crucial role in controlling the morphology and size of the synthesized nanoparticles. The growth behavior can be greatly influenced by the OH^- concentration [19]. Subsequently, the surface morphology of the CdS nanoparticles was examined by (SEM). The SEM images of the as-synthesized CdS nanoparticles grown under different pH values are displayed in Fig. 2. Clearly, the SEM images reveal that most of the nanoparticles are spherical in shape with an average particle size distributed in the range of 70-130 nm. This implies that the nanosized CdS particles were successfully synthesized in the present alkaline medium. Additionally, it can be observed from the figure that there is an obvious variation in morphology at different pH values.

The CdS exhibits smaller particle size at higher pH values. As the pH value decreases or the solution becomes less alkaline, the nanoparticles tend to grow abundantly with larger particle size as initiated by higher ammonium nitrate content. The average diameter of nanoparticles for the CdS synthesized at pH of 12.90,

11.28 and 10.00 is estimated to be $\sim 73\text{ nm}$, $\sim 82\text{ nm}$, and $\sim 88\text{ nm}$, respectively. Moreover, it can also be observed the formation of agglomerates of small grains and some dispersed individual nanoparticles at higher pH value. Meanwhile, as the pH decreases, the nanoparticles synthesized were in the mixtures of larger oval and spherical shape and exhibited a more uniform and homogeneous particles size distribution. According to Alrababah et al. [20], the nanoparticles could be built up from the aggregation of many small nanocrystallites. The corresponding crystallite size can be determined from the XRD analysis, which will be discussed as follows.

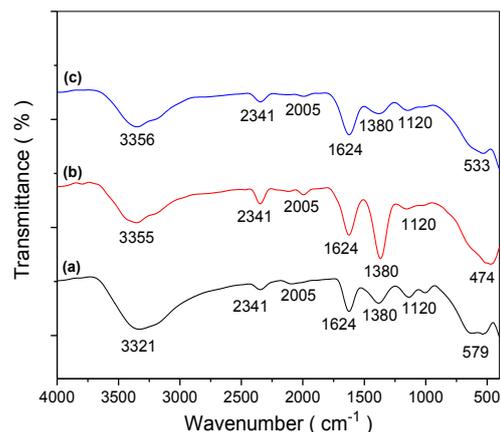


Fig. 1 – FTIR spectra of the CdS synthesized at room temperature with pH values of 12.90 (a), 11.28 (b), and 10.00 (c)

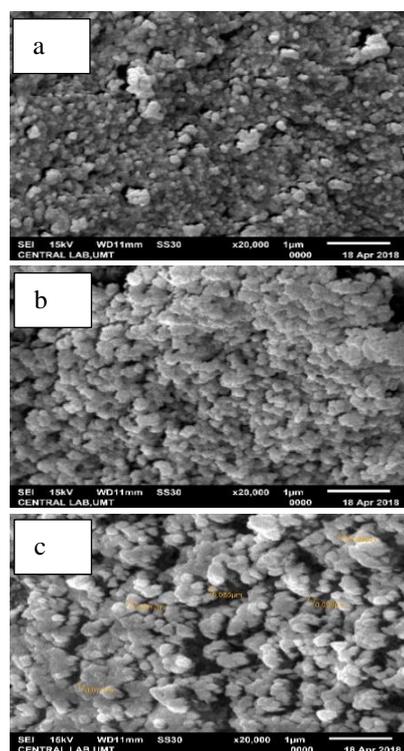


Fig. 2 – SEM images of CdS nanoparticles synthesized at pH values of 12.90 (a), 11.28 (b), and 10.00 (c)

It is well known that XRD is an effective method to characterize the crystallite structure and size of the CdS samples. Fig. 3 depicts the XRD pattern of the precipitated CdS nanoparticles synthesized at different pH

values by adjusting the ammonium nitrate concentration. Commonly, CdS can crystallize in cubic zinc blende and hexagonal wurtzite structures with so-called mineral names of hawleyite and greenockite, respectively [21]. From the recorded XRD pattern, four major well-resolved broad peaks were identified at 2θ values of 26.3° , 43.7° , 51.9° , and 70.8° , which correspond respectively to diffraction planes of (111), (220), (311), and (331) of a cubic crystal system of CdS, referring to JCPDS card, file no. 75-1546. Moreover, no peaks related to other phases were detected, implying that a pure cubic CdS was formed in this study. The mean lattice constant obtained is $a = 0.5820$ nm for the present CdS cubic structure, which is in accordance with the literature reported value for zinc blende structures [13, 22]. In addition, the broad band discernible in the XRD pattern indicates that very fine dimension of CdS nanocrystallites is attained in this study. Also, all the CdS nanoparticles show a prominent and sharp diffraction peak, which denotes a high degree of crystallization.

However, when the *pH* value decreases, the diffraction peak becomes slightly broadened accompanied with a minor reduction in peak intensity. This phenomenon indicates that the crystallite size becomes much finer and the sample crystallinity is reduced for the CdS nanoparticles synthesized at higher ammonium nitrate concentration. The average crystallite size of the CdS nanoparticles was evaluated from the XRD diffractogram using the well-established Debye-Scherrer equation $D = 0.9\lambda/\beta\cos\theta$, where D represents the crystallite size, λ is the X-ray wavelength, β denotes the full width at half maximum (FWHM) of the crystalline peak in radians and θ is the Bragg diffraction angle explicated from the angle between the incident and reflected beams of lattice planes [6, 8]. The average crystallite sizes for the samples prepared at *pH* values of 12.90, 11.28 and 10.00 are determined to be 3.52 nm, 3.38 nm, and 2.97 nm, respectively. This result indicates that a desired crystallite size can be produced at room temperature by adjusting the *pH* to within a proper range. Furthermore, the crystallite size becomes smaller as the *pH* value decreases, which could be attributed to the increase of ammonium nitrate content that initiates the gradual construction of the isolated cell lattice in agglomerated form. The present finding implies that the room temperature treated CdS remains cubic structure at the studied *pH* value range. However, as reported earlier by Alrababah et al. [20], the CdS would be transformed into hexagonal phase at increased ammonium nitrate concentration with specific annealing heat treatment temperature up to 160°C .

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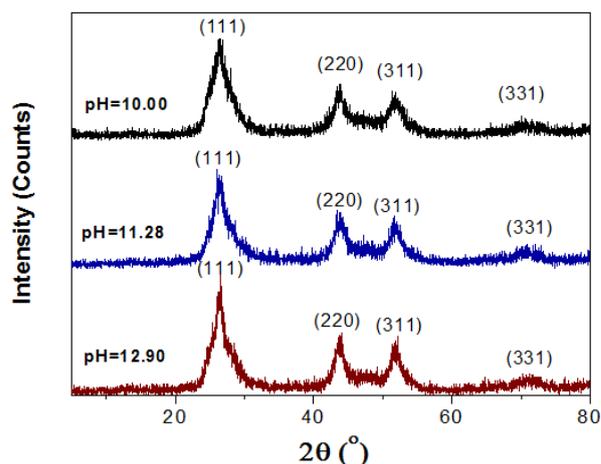


Fig. 3 – XRD pattern of CdS nanoparticles synthesized at different *pH* values

4. CONCLUSIONS

In conclusion, we have successfully investigated the effect of *pH* value on the structure, bonding and morphology of high-quality CdS nanoparticles synthesized via precipitation in the KOH solution by varying the ammonium nitrate concentration. The *pH* value could play a key role in modifying the morphology and size of the synthesized nanoparticles. XRD patterns indicate that the as-prepared CdS nanoparticles show a good crystallinity with cubic phase. The intensity of the diffraction peak decreases and the peak becomes slightly broader when the *pH* value is decreased. Also, the calculated average crystallite sizes were in the range of 2.90-3.50 nm and increased with *pH* value. SEM images reveal that the CdS nanoparticles were spherical in shape. The particle size grows larger and becomes more visible and homogeneous with the increase in NH_4NO_3 concentration. Meanwhile, the FTIR spectrum confirms the existence of a broad band in the range of $400\text{-}700\text{ cm}^{-1}$ that belongs to CdS molecular bonding. In addition, the FTIR result indicates that the organic or hydrogen bonds attached to the surface of CdS molecules become weaker, leading to the formation of CdS with high purity.

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Вплив pH на інфрачервоні спектральні, структурні та морфологічні властивості наночастинок CdS, осаджених за кімнатної температури

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У роботі наночастинок CdS, оброблені за кімнатної температури, готували в розчині KOH шляхом осадження при різних значеннях pH , змінюючи концентрацію аміачної селітри (NH_4NO_3). Кристалічна фаза та розмір, морфологія поверхні та інфрачервоні частоти функціональних груп характеризувалися відповідно рентгенівською дифрактометриєю (XRD), скануючою електронною мікроскопією (SEM) та інфрачервоною спектроскопією з перетворенням Фур'є (FTIR). Зображення SEM показують, що наночастинок CdS мають сферичну форму. Тим часом, результат FTIR демонструє, що широка смуга, яка виникла в діапазоні $400-700\text{ cm}^{-1}$, може бути віднесена до структури молекулярних зв'язків CdS. Картини XRD ілюструють чотири добре помітні кристалічні піки, що представляють собою дифракційні площини кубічної фази CdS. Тим не менш, незначне зменшення інтенсивності як для інфрачервоних, так і для кристалічних смуг позначає незначне зниження кристалічності структури і далі вказує на те, що більш висока чистота менших наночастинок CdS проявляється із зменшенням значення pH . Крім того, дифракційний пік стає дещо розширеним, що означає зменшення середнього розміру кристаліту, яке підтверджується методом Дебая-Шеррера. Завдяки своїм унікальним наноструктурним та морфологічним особливостям наночастинок CdS, отримані в рамках цього дослідження, мають потенційне застосування у фотонних пристроях, оптоелектроніці, фотокаталізі та сонячних елементах.

Ключові слова: Наночастинок CdS, Функціональна група, Кристалічна кубічна структура, Морфологія поверхні.