Impact of reaction temperature on the structural, surface morphology and antibacterial activity of hydrothermally synthesized CdS nanoparticles

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Abstract. Cadmium Sulfide (CdS) nanoparticles were synthesized hydrothermally at various reaction temperatures (140, 160, 180, 200) °C. Crystal structure and surface morphology were studied corresponding to the reaction temperature. The X-ray diffraction results, reveals that CdS nanoparticles were prepared have high crystallinity with polycrystalline nature and hexagonal wurtzite phase. The preferential orientation was along (002) and (110) planes. The average crystallite size was tended to increase with the increase of reaction temperature which about (21-24) nm. The structure parameters such as dislocation density and microstrain was examined. CdS nanoparticle images in Field Emission Scanning Electron Microscopy (FESEM) indicates rounded ball (cauliflower), the particle size was in the range of (23-245) nm and the smallest size was obtained for the nanoparticles at reaction temperature 200 °C. The antibacterial activity of cadmium sulfide CdS nanoparticles was estimated against two types of common bacteria (Gram-negative Escherichia coli and Gram-positive Staphylococcus aureus). It was found that there is a strong antibacterial activity and the greatest effect was for the prepared nanoparticles at reaction temperatures 160 and 180 oC, and the highest activity was found against (E. coli) bacteria as well as with the increase of nanoparticles concentration. This work combines microbiology and nanotechnology, perform probable advances in the formulation of a new kind of antibacterial.

Keywords: CdS nanoparticles; Hydrothermal method; structure properties; Antibacterial activity; Escherichia coli; Staphylococcus aureus.

1. Introduction

Cadmium sulfide (CdS) is currently an extremely interesting, semiconductor compound from the II-VI group of the periodic table with a direct band gap of 2.42 eV and conductivity n-type, it has three types of crystal structures, namely rock, zinc, and rock-salt[1]. The wurzite phase among these three phases is the most stable and simple to synthesize [2]. Therefore CdS is high potential used as sensitive photodetectors [3] heterojunction diodes, solar cells, and semiconductor devices [4]. CdS nanomaterial can be used in various life sectors due to their higher stability, outstanding electrical, Structural and chemical properties, affordability, ease of processing and handling [5]. CdS nanoparticles and thin films were widely synthesized using different chemical and physical methods due to its enormous range of applications in various fields of life, like solvothermal and hydrothermal
techniques [6, 7], thermal evaporation method [8], chemical bath deposition [9], Laser Ablation in liquid[10], spin-coating technique [11]. Cadmium sulfide and chalcogenide nanoparticles can easily prepared by using the hydrothermal method[12]due to its essential Advantages including cost-effectiveness[13]Particle size controllable, low temperature and techniques less complicated [14]. Compared to organic antibacterial agents, the antibacterial activities of inorganic compounds are of great interest due to its durability, toxicity, heat resistant, selectivity and etc. [15]. The antibacterial activities of CdS nanoparticles were evaluated against different types of bacteria by Ayodhya et al. [16], which is very promising in displaying their capability to inhibit and destroy both types of gram positive and gram-negative pathogenic bacteria. Abd-Elkader et al.[17]. The antibacterial efficacy of CdS thin films deposited with CBD was evaluated, against Gram-positive and Gram-negative bacteria in dark and sun light at 60 °C. They found that, CdS thin films have noticeable antibacterial activity in sunlight and dark and it could be used as antibacterial and antimicrobial agents in the application of medical field. Narasimman et al.[18] Studying the impact of Zr concentration on the antibacterial properties of the CdS thin film, doped films display excellent antibacterial performance against K. Bacterium pneumonia (gram –ve) making it ideal for pharmaceutical applications. Whereas Gajendiran et al. [19] worked on fabricate CdS quantum dots nanoparticles for biological applications, the antimicrobial activity against S. Aureus bacteria were found to be an impressive antibacterial agent against gram-positive bacteria by prepared nanoparticles. In the current work the effect of reaction temperature on structural surface morphology of CdS nanoparticles was investigated and the antibacterial activities the Gram-negative Escherichia coli and Gram-positive Staphylococcus areus was carried out using agar well diffusion method in order to establish their suitability for medical applications.

2. Materials and methods

Cadmium Acetate (CH₃·COO)₂Cd.2H₂O from (BDH) England, Thiourea NH₂.CS.NH₂ from (THOMAS BAKER) India, Acetone (CH₃)₂CO (TEDIA) from USA, Ethanol (C₂H₅OH) from (BDH) England, Mueller Hinton II. agar MHA from (Biolab Zrt) Hungary were used to synthesized CdS nanoparticles by the Hydrothermal method. (0.3 g) of cadmium acetate (CH₃·COO)₂Cd.2H₂O and (0.9 g) of thioureaNH₂.CS.NH₂dissolved in 40 ml of deionized water with a ratio of (1:3).The solution was well mixing by magnetic stirrer for 30 min. Then40 ml of the prepared solution was added into the Teflon-lined stainless-steel autoclave and heat up in an oven at reaction temperatures (140,160,180 and200) °C for 4 h, and allow it to cool to room temperature. The resulting solution was separated by centrifuge (Frontier 5706), for 10 min at 5000 rpm to get a deep-yellow powder. the precipitating substance (CdS) was washed twice with deionized water and absolute ethanol (C₂H₅OH)purity(99.9%), and then dried at 70 °C.

The antimicrobial activity CdS nanoparticles ws evaluate against two different types of clinical bacteria Gram-negative Escherichia coli and Gram-positive Staphylococcus areus using the agar well diffusion method. Standardized suspension of each tested bacteria (1.5x10⁸cfu/ml) by Densi Check standard (0.5N) was swabbed separately onto Mueller Hinton agar plates using sterile cotton swabs. The agar was pumped with sterilized cork borer 9 mm and 100μl from each the CdS nanoparticle were added into the four holes for four concentrations (1000, 500, 250, 100) μg/ml after making dilution at well Petri dishes were incubated for 24 hours. at 37°C, after incubating, the inhibition zones were measured in millimeter diameter. The crystalline structure of the CdS NPs examined by X-ray diffractometer (Shimadzu XRD-7000 (JAPAN), the source of X-ray radiation is Cu kα1 radiation the scanning angle varied in the range (15-70)° with wavelength 1.54056 Å, speed 1deg/min, current 80 mA, and voltage 60 kV. The morphological confirmation of various CdS nanoparticles was carried out by Field Emission Scanning Electron Microscopy (FEI FESEM Nano SEM Nova 450).
3. Results and discussion
3.1. Structural analysis.

The XRD patterns of CdS nanoparticles obtained at different reaction temperatures was identified by the presence of diffraction peaks at scattering angles (2θ) of 25°, 26.6°, 28.2°, 43.8°, 48°, 52°, 52.9°, 54.8°, and 58.2° that were indexed to the (100), (002), (101),(102), (110), (103),(112) and (201) planes, all peaks of diffraction can be indexed to the pure hexagonal CdS structure according to the standard card (JCPDS No. 77-2306). The diffraction pattern refer that CdS is polycrystalline structure, sharp and strong peaks indicate that the CdS has crystallized well [20] as shows in Fig.1.

![XRD patterns of CdS nanoparticles](https://example.com/xrd_patterns.png)

Fig.1. Diffraction pattern obtained from CdS XRD at 4 h reaction temperatures: ((a) 140, (b) 160, (c) 180, (d) 200)°C.

The high intensity sharp and narrow XRD peaks confirmed that grown CdS nanoparticle were highly crystalline. All diffraction peaks can be indexed to the pure hexagonal structure of CdS according to the standard card (JCPDS No. 77-2306) and no other peaks related to impurity phases were observed. The XRD peaks of CdS nanoparticle became narrower with shifted of peak position with increase temperature, this indicate an enhancement in crystalline quality, this agreement with study [20]. For the hexagonal structure the interplanar spacing (d), lattice constants (a) and (c) were calculated using the following equation [21].

\[
\frac{1}{d_{hkl}^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \right)
\]  

(1)
Table 1 displays the structural parameters determined, values obtained that are too close to the values seen in the investigation (a=b= 4.136 and c= 6.713) (JCPDS-77-2306) which confirms wurtzite structure [22], the average crystallite size (D) of the CdS nanoparticles was determined with the formula of Debye Scherrer [23]:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

β is the full width at the maximum half of the peak of diffraction, K is known as the 0.9 shape factor and λ is the X ray diffraction source wavelength. The average grain size for Preferred orientation (110) is within the range (18.8678- 24.1725) nm as illustrated in the Table 1. The crystallite Size for (110) preferential orientation is a gradual increase, this refers to improve crystallization with increasing reaction temperature. The constants of lattice ‘a’ and ‘c’ contracts the (c/a) values remained constant about 1.63 approximately for all the nanoparticles and nanostructure thin films, this is an agreement with the literature [18, 20].

Table 1. Structural parameters of CdS nanoparticle obtained from XRD data as a function of preparation temperature for (110) preferential orientation.

| CdS nanoparticles At: | 2θº | d_{XRD} (Å) | Crystallite Size D (nm) | a=b (Å) | C (Å) | V (a²c) (Å³) | c/a |
|-----------------------|-----|-------------|------------------------|-------|------|-------------|-----|
| 140 ºC                | 43.8| 2.06233     | 18.8678                | 4.1246| 6.665| 113.403     | 1.6289 |
| 160 ºC                | 43.9| 2.06423     | 22.5634                | 4.1284| 6.6697| 113.679     | 1.6282 |
| 180 ºC                | 43.81| 2.06331   | 18.8207                | 4.1266| 6.6678| 113.546     | 1.6306 |
| 200 ºC                | 44.01| 2.05841    | 24.1725                | 4.1168| 6.5577| 112.836     | 1.6276 |

3.2. Morphology analysis

Fig. 2a, b, c, d show FESEM images of CdS nanoparticles prepared at reaction temperatures of 140,160,180,200ºC respectively. The surface morphology consist of homogeneous and densely packed distribution of well-defined grains, which includes small and large particles and has a regular shape with fine particle size, Fig. 2 indicate a rounded ball (cauliflower) like nanospheres these results was consistent with literature [24-26].
CdS nanoparticles have an average grain size of around (94-245) nm. The particle sizes were measured by defining the known length of the FESEM scale bar as shown in Fig. 2a, which indicated the formation of microspheres (cauliflower) of CdS (160,180)°C and the majority of the particles looked in the range of about (138-209) nm, meaning, there is no noticeable change (whether in size, shape, or clusters ) compared to the first model(140°C) as shown in the Fig. 2b, c respectively. The sample microspheres (cauliflower) were of almost uniform size, the shape microspheres (200°C) were almost the same as the all of other samples microspheres (cauliflower), but it differs in the size of the grains and crystallites, where the average grain sizes of CdS nanoparticles are about (27.11- 62.11) nm, individual particles sizes as show in the Fig. 2d. This indicates that there is an effect of temperature on the crystal size this effect was evident at 200 °C, the results are in agreement with the literature [24, 25] which related to the shape and structure of the particle related to microspheres (cauliflower) and the reduction of the grains and particle size with the increase of the reaction temperature.

3.3. Antibacterial activity

The antibacterial activity of the prepared CdS nanoparticles was evaluated using the agar well diffusion method against the test cultures of gram +ve staphylococcus aureus, gram –ve Escherichia coli. The bactericidal effects of CdS nanoparticles were investigated against clinical isolates of staph.
and E. coli. Fig. 3; the presence of clear zones on the Muller Hinton agar surface proves that the CdS nanoparticles was able to inhibit the growth of E. coli and Staph. Four different nanoparticles concentrations (100, 250, 500, and 1000) (μg/ml) were taken to inhibit pathogenic bacterial growth as show in the table (2). The microbe-mediated CdS nanoparticles had the maximum zone of inhibition against disease-causing Staphylococcus and Escherichia coli about 19 mm at reaction temperature 180 °C and 30 mm at reaction temperature (160 and 180) °C respectively both at the highest concentration (100 μg/ml) of CdS nanoparticle. The minimum zone of inhibition was observed against staph. and E. Coli about 12 mm and 13 mm respectively at reaction temperature of 200 °C and concentration of CdS NPs. The area of inhibition was increases with the increased CdS NPs concentration and reaches the highest zone of inhibition at the highest CdS Nps concentration as shown in Figs 3 and 4 and all parameters and results were tabulated in Table 2.

Fig.3. Antibacterial activity of CdS nanoparticles at different concentration (1, 2, 3, 4: 1000, 500, 250, 100) (μg/ml) against staphylococcus bacteria prepared at temperature (staph. 1, 2, 3, 4: 140, 160, 180, 200) °C respectively.
Fig. 4. Antibacterial activity of CdS nanoparticles at different concentration (1, 2, 3, 4: 1000, 500, 250, 100) (µg/ml) against Escherichia coli bacteria prepared at temperature (E-coli 1, 2, 3, 4: 140, 160, 180, 200) °C respectively.

There are several mechanisms proposed for CdS NPs inhibitory action of the microbial growth. CdS NPs can cause DNA losses, impairment of its replication, and interfere with cellular proteins including ribosomal subunit proteins [27, 28]. Thus impairs the function of membrane-bound enzymes, in the aerobic strains. Also CdS get attached to the cell membrane and shrink the respiration of the bacterial cell which eventually causes the death of the cell as depicted [29, 30].

Table 2. Inhibition zone of CdS nanoparticles as antibacterial agents in millimeter (mm)

| Types of used Bacteria | CdS Nanostructure prepare at temperature (°C) | Concentration of CdS nanoparticle (µg/ml) / inhibition zone (mm) |
|------------------------|----------------------------------------------|------------------------------------------------------------------|
|                        |                                             | 1000 | 500 | 250 | 100 |
|                        | 140                                         | 17   | 16  | 15  | 13  |
|                        | 160                                         | 18   | 17  | 16  | 14  |
|                        | 180                                         | 19   | 18  | 17  | 14  |
|                        | 200                                         | 17   | 16  | 15  | 12  |
|                        | 140                                         | 23   | 15  | -   | -   |
|                        | 160                                         | 30   | 27  | 24  | 13  |
| Staph.                 | 180                                         | 30   | 25  | 23  | 16  |
|                        | 200                                         | 20   | 18  | 17  | 14  |
| E-coli                 | 180                                         | 30   | 25  | 23  | 16  |
|                        | 200                                         | 20   | 18  | 17  | 14  |

4. Conclusion

Briefly, CdS nanoparticle (cauliflower) of hexagonal phase has been successfully prepared by hydrothermal method at different reaction temperatures (140, 160, 180, 200 °C) for 4 hours. The crystal structure results indicate that the CdS crystal is of a high crystalline nature and hexagonal (wurtzite) phase. The average crystallite size was tended to increase with the increase of reaction temperature which about (21-24) nm. CdS nanoparticle micrographs images indicates rounded ball (cauliflower), the particles size were in the range of (23-245)nm and the smallest particle size was obtained at reaction temperature 200 °C. The antibacterial activity of cadmium sulfide CdS nanoparticles was estimated against two types of common bacteria (Escherichia coli and
Staphylococcus aureus). It was found that there is a strong antibacterial action and the greatest effect of them was for the prepared nanoparticles at reaction temperatures 160 and 180 °C, and the highest activity was found against (E. coli) bacteria as well as with the increase of nanoparticles concentration. The antibacterial mechanisms of CdS NPs where the particles can anchor to the bacterial cell wall and infiltrate it and lead to damage the cell membrane and cellular content leakage. Also, CdS NPs can bind to the protein present in the cell membrane and lead to adenosine triphosphate (ATP) generation. As well as the NPs penetrate inside microbial cells, and then the nanoparticles and the released ions can interact with cellular structures and biomolecules such as proteins, enzymes, lipids, and DNA. It was established that synthesized CdS NPs with a higher antibacterial activity that was synthesized in different concentrations and reaction temperatures are potentially suitable for the development of nanomedicine and its applications. Also this work combines microbiology and nanotechnology, perform probable advances in the formulation of a new kind of antibacterial.

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