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Full Length Research

EFFECTS OF CONCENTRATION ON PREPARATION AND CHARACTERIZATION OF CADMIUM SULPHIDE NANOPARTICLES

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ABSTRACT

Cadmium sulphide nanoparticles were synthesized at room temperature via wet chemical precipitation method using cadmium chloride and sodium sulphide with methanol as capping agent and the effect of concentration on the absorption peaks was studied. The microstructure and morphology of the synthesized CdS nanoparticles were characterized by x-ray diffraction analysis. XRD pattern reveals that the synthesized CdS nanoparticles exhibit both sphaleritte and wurtzite phases. The size of the particles calculated by Debye Scherrer formula according to XRD spectral was found to be about 4.44 to 40.24 nm. X-Ray peak broadening analysis was used to calculate the crystalline size and lattice strain by the Williamson –Hall (W-H) plot. The optical properties of the sample were studied by UV-visible spectroscopy. The existence of blue shift in UV-Visible spectroscopy revealed the quantum confinement effect of CdS nanoparticle. Wet chemical method using methanol as capping agent could be a more suitable method of preparation CdS nanoparticles, which may provide a suitable alternative for use in semiconductor devices.

Keywords; CdS nanoparticles, X-ray diffraction, optical properties, quantum confinement, UV-Visible spectral.

INTRODUCTION

Recent investigations in nanotechnology reveal that nanometer-sized inorganic semiconductor compounds have attracted considerable attention due to their novel size-dependent characteristics, different physico-chemical and optoelectronic properties, compared with the corresponding bulk counterparts (Park *et al*., 2000; Peng *et al*., 2000; Sodipo *et al*., 2014).

Nanoparticles like ZnS, ZnO and CdS exhibit the size dependant properties such as blue shift of absorption onset, change of electrochemical potential of band edge magnetic properties, optical properties (optical emission and adsorption) and enhancement of photo-catalytic activities (Rama – Rao *et al.,* 2007).

In particular chalcogenides such as CdS, with a direct band gap of 2.43 eV at room temperature, is one of the most important semiconductors and is given considerable attention by the researchers and scientists for potential applications in the future opto-electronic, nano-devices and biological labeling due to the tunable electronic band gap depending on the size

and shape of nanocrystals. A great interest has been shown in cadmium sulphide (CdS) because of the availability of discrete energy levels, tunable band gap, size dependent optical properties and well developed synthetic protocols, good chemical stability and easy preparation techniques (Antolini *et al.*, 2005). Hence, the major thrust is concentrated towards the technological applications of CdS nanoparticles ranging from microelectronics to non-linear optics, optoelectronics, catalysis, optical windows for solar cell and photo-electrochemistry (Karl *et al*., 2002).

Currently there has been an increasing demand to explore the optoelectronic applications of CdS semiconductor in the frontier areas such as photo electrocatalysis, biotechnology and communication among which the optoelectronic properties of CdS nanomaterials are strongly influenced by their morphologies and structures. Hence, it is very important to establish the simple and mild methods to achieve the controlled synthesis of isolated inorganic semiconductor nanostructures belonging to this category.

Cadmium sulphide is a well-known semiconductor that can be prepared either by chemical or physical methods. Several methods have been developed to synthesize CdS in nanophase with different morphologies and structures such as nano crystals, quasi-nano spheres, nano rods, nano whiskers, nano wires, nano belts and nano tubes etc (Lincot and Gary, 2006). In the present work, a simple aqueous chemical method for the preparation of cadmium sulphide nanoparticles with comparable size was reported and fine nanoparticles of very low size distribution were obtained successfully. The synthesized CdS nanoparticles were characterized by X-ray diffraction (XRD) and UV-Visible spectroscopic analysis (Lincot and Gary, 2006). The size of the as-prepared sample was calculated by Debye-Scherrer formula from the XRD spectra which was found to be of the order of 4 – 40 nm.

MATERIAL AND METHODS

Materials

The materials used include Varian Carry 5E Model spectrophotometer, LS 55 Perkin Elmer spectrophotometer, Oaktron pH meter, $CdCl_2$ $Na_2S.9H_2O$, distilled water, Schimadzu Labx X-ray powder diffractometer among other reagents.

Synthesis of CdS nanoparticles

CdS nanoparticles were synthesized by wet chemical method at room temperature using analar grade sodium sulphide, $Na_2S.9H_2O$ as the source for S^{2-} ions and cadmium chloride as the source for Cd^{2+} ions with methanol as the capping agent.

Briefly, 2.5 mL of methanol was measured into a 1000 mL standard flask, 20 mL of 0.1 M NaOH was added to the flask drop by drop with constant stirring, and the solution was stirred magnetically for 1hr. 34.6 mL of 0.20 M solution of $Na_2S.9H_2O$ was added to the mixture drop by drop while constantly stirring, and 34.6 mL of 0.20 M solution of $CdCl_2$were added into the solution. The colour and temperature changes were noted. Acetone was added to accelerate precipitation and settling, the mixtures were centrifuged for 30 mins. Precipitates were separated via decantation and were dried at 60^{o}C in an oven for few hours to obtain CdS nanoparticle. The procedures above were repeated using different concentration ranging from 0.175 M to 0.01 M for $CdCl_2$ and $Na_2S.9H_2O$ as tabulated in Table 1.

The chemical equation of the reaction is as follows:

$$CdCl_2 + Na_2S.9H_2O \rightarrow CdS + 2NaCl + 9H_2O \quad \ldots(1)$$

Table 1: Concentrations and volumes of reagents used for CdS Preparation

S/NO	Volume Prepared (mL)	Conc. of Solution (M)	Vol. required (mL)	Amount of $Na_2S.9H_2O$ (g)	Amount of $CdCl_2$ (g)
1	50	0.20	34.6	2.4	1.83
2	50	0.175	39.5	2.1	1.60
3	50	0.15	46.1	1.8	1.34
4	100	0.125	55.4	3.01	2.29
5	100	0.10	69.2	2.4	1.83
6	100	0.075	92.3	1.8	1.34
7	250	0.05	138.4	3.01	2.29
8	500	0.025	276.8	3.01	2.29
9	1000	0.01	692	2.4	1.83

Physical Measurement

The X-ray diffraction (XRD) patterns for cadmium sulphide samples were recorded on a Schimadzu Labx X-ray powder diffractometer with CuKα radiation (λ - 1.5406Å) with 2θ ranging from 20^{o}C to 90^{o}C at the scanning speed of 10^o per minute. The optoelectronic properties have been studied by ultraviolet-visible absorption spectra in the range 200-1000 nm using VARIAN CARRY 5E Model spectrophotometer and LS 55 Perkin Elmer spectrophotometer was used for

recording the photoluminescence spectra of CdS nanoparticles.

RESULTS AND DISCUSSION

UV- Visible Spectroscopic Analysis

The optical absorption of CdS nanoparticles recorded between 200 to 1000 nm are as shown in Figures 1 to 9, and the absorption onset edges from UV-Visible Spectroscopy analysis are as shown in Table 2. It is observed from the spectrum that the absorption onset edges were found to be at lower wavelength corresponding to the absorptions between 207 nm to 221 nm indicating blue shift for all the crystals prepared at different concentration (Lincot and Gary, 2006). This confirms quantum confinement effect and the existence of blue shift also revealed the decreasing size of the nanoparticles with respect to the decrease in the precursor concentration (Maleki, 2007). When a solid material is tested with UV-visible spectrum and the result shows decrease in the absorbance with respect to increase in wavelength, it is an evidence that the solid sample posses blue shift which is referred to as semiconductor and such materials has a small but non-zero band gap. The information above revealed that blue shift is an evidence of decrease in crystal size which leads to quantum confinement effect (formation of new electronic energy level due to electron excitation) and increase in band gap between the valence band and conduction band, hence result to decrease in wavelength from bulk to nanosize sample. Considering the concentration under investigation in this work, the result of UV-visible analysis shows decrease in size with respect to decrease in concentration of the precursors.

Table 2: Absorption onset edges from UV-Visible spectroscopy analysis on methanol capped CdS nanoparticles prepared at different precursor concentrations

SNO	Precursor Concentration (M)	Absorption Edge (nm)
1	0.20	218
2	0.175	220
3	0.15	220
4	0.125	216
5	0.10	221
6	0.075	213
7	0.05	210
8	0.025	207
9	0.01	208

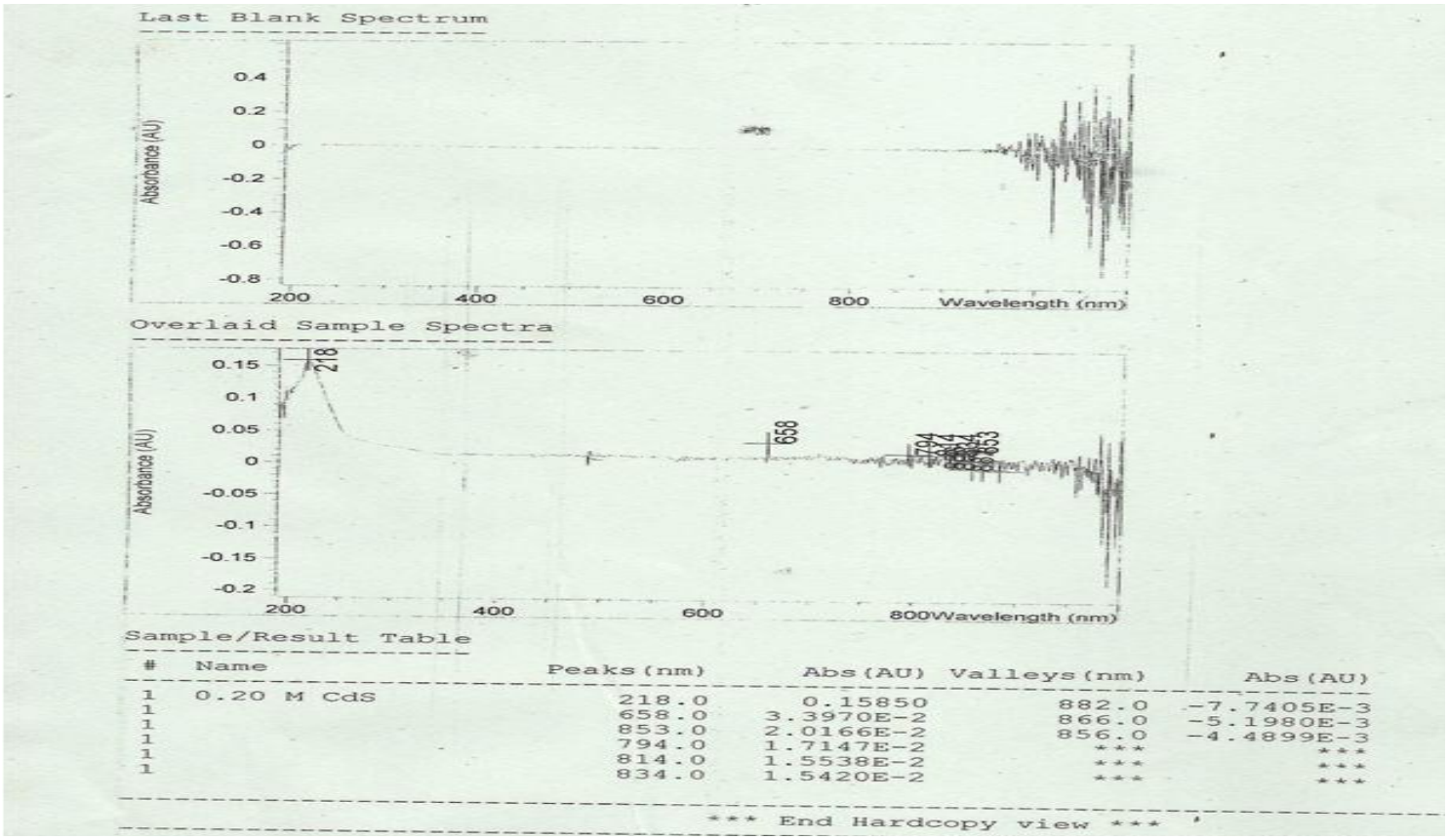


Figure 1: UV result showing the absorption peaks for CdS at concentration 0.20 M

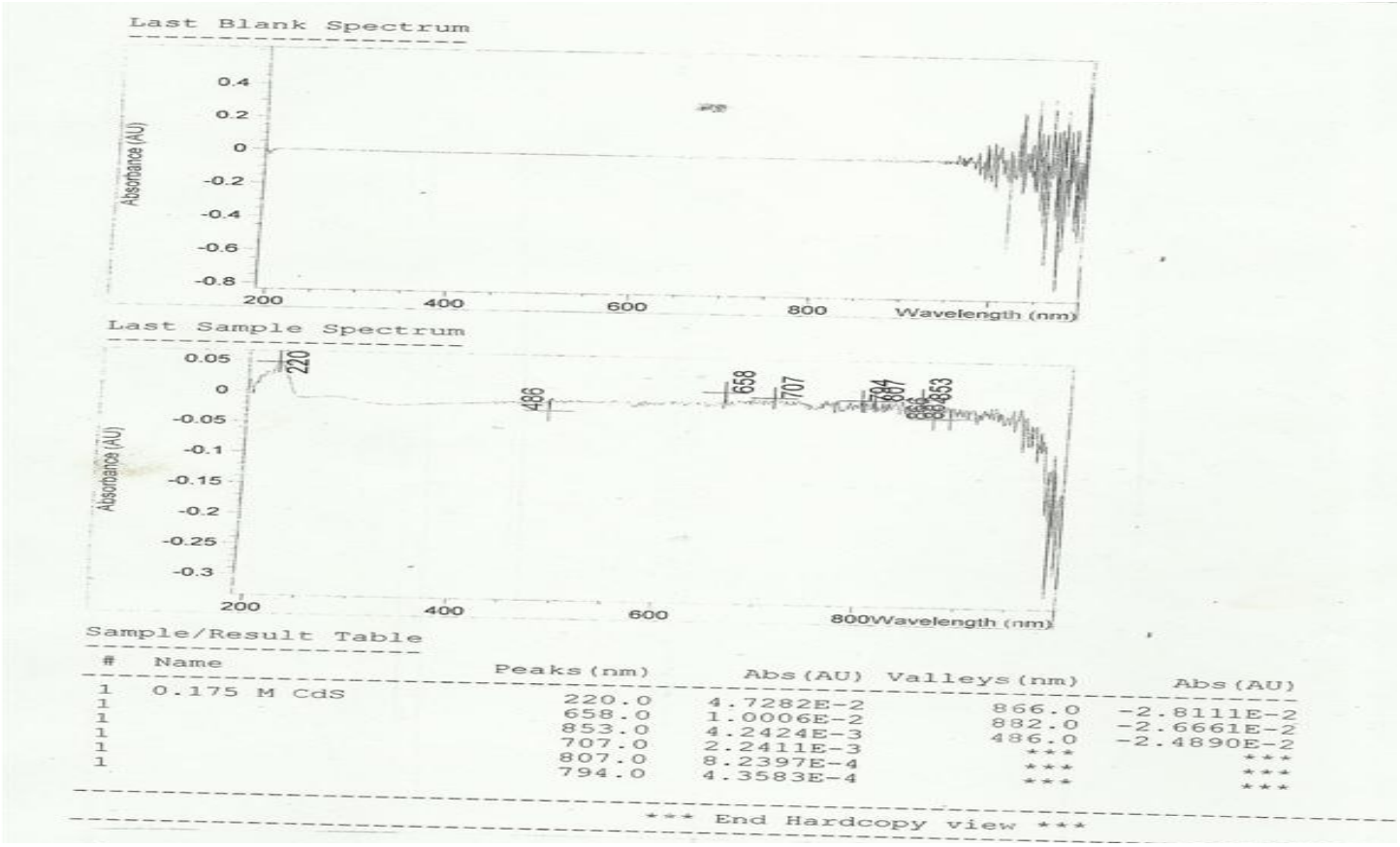


Figure 2: UV result showing the absorption peaks for CdS at Concentration 0.175 M

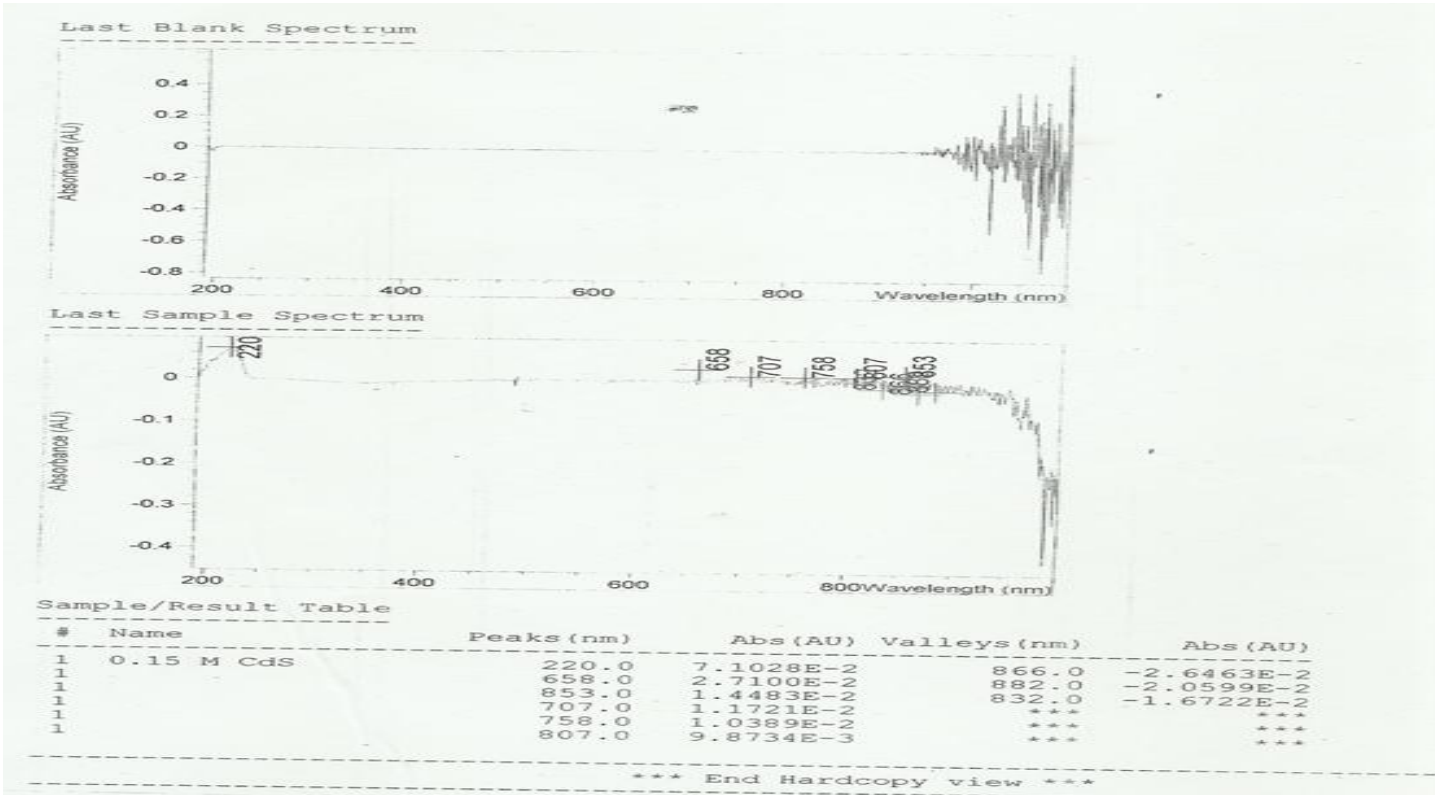


Figure 3: UV result showing the absorption peaks for CdS at concentration 0.15 M

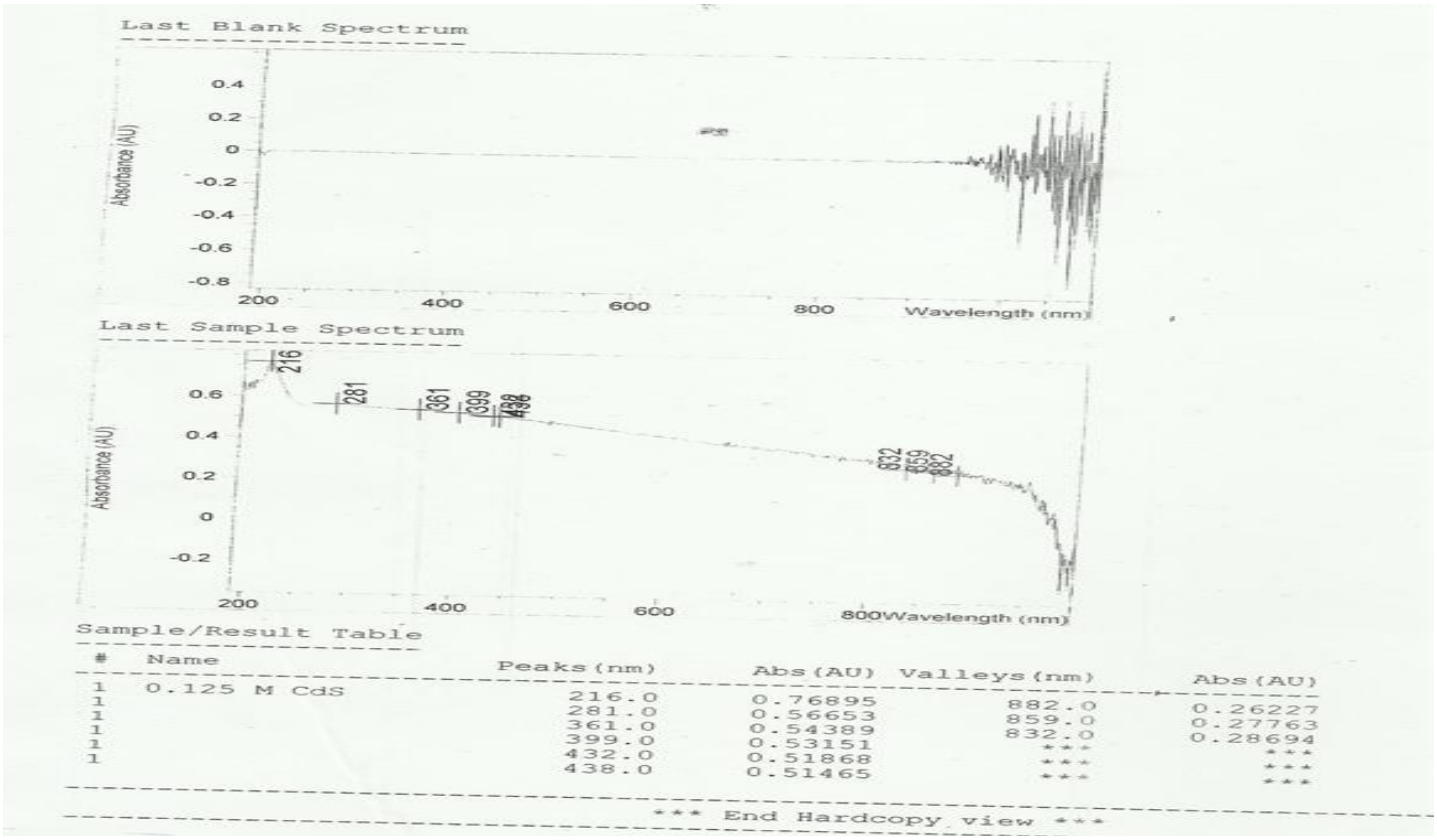


Figure 4: UV result showing the absorption peaks for CdS at concentration 0.125 M

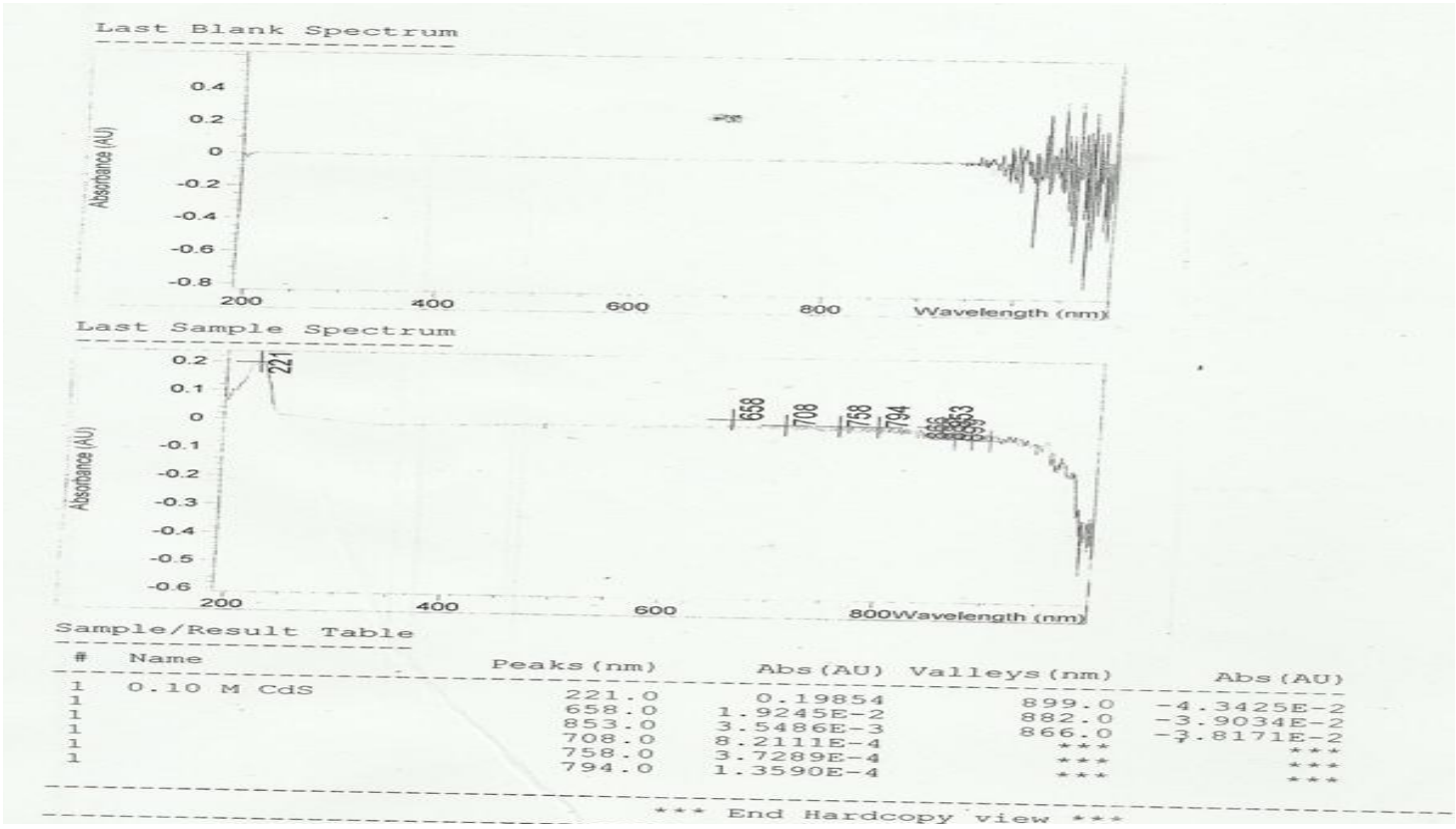
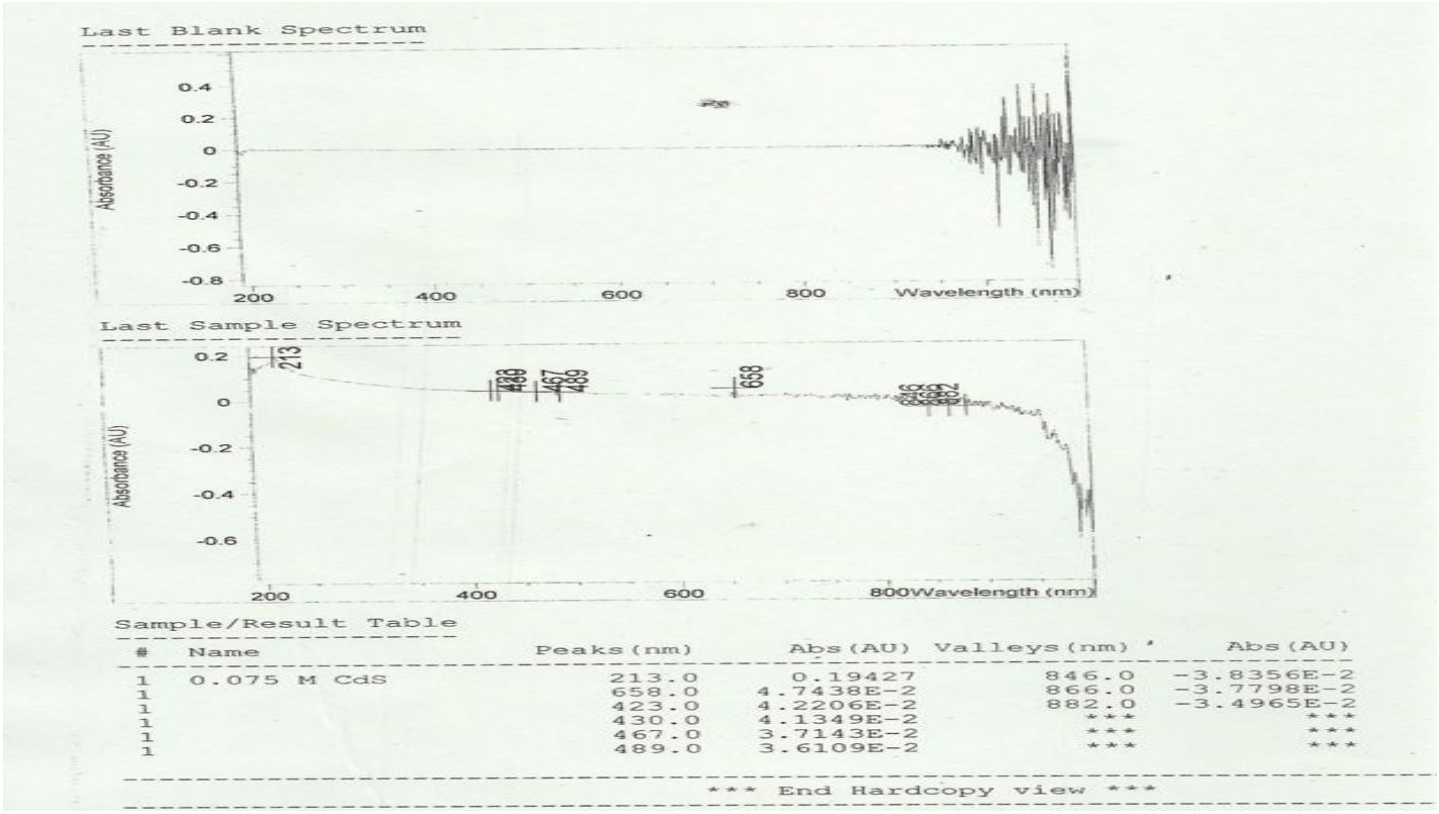


Figure 5: UV result showing the absorption peaks for CdS at concentration 0.10 M



Sample/Result Table

#	Name	Peaks(nm)	Abs(AU)	Valleys(nm)	Abs(AU)
1	0.075 M CdS	213.0	0.19427	846.0	-3.8356E-2
1		658.0	4.7438E-2	866.0	-3.7798E-2
1		423.0	4.2206E-2	882.0	-3.4965E-2
1		430.0	4.1349E-2	***	***
1		467.0	3.7143E-2	***	***
1		489.0	3.6109E-2	***	***

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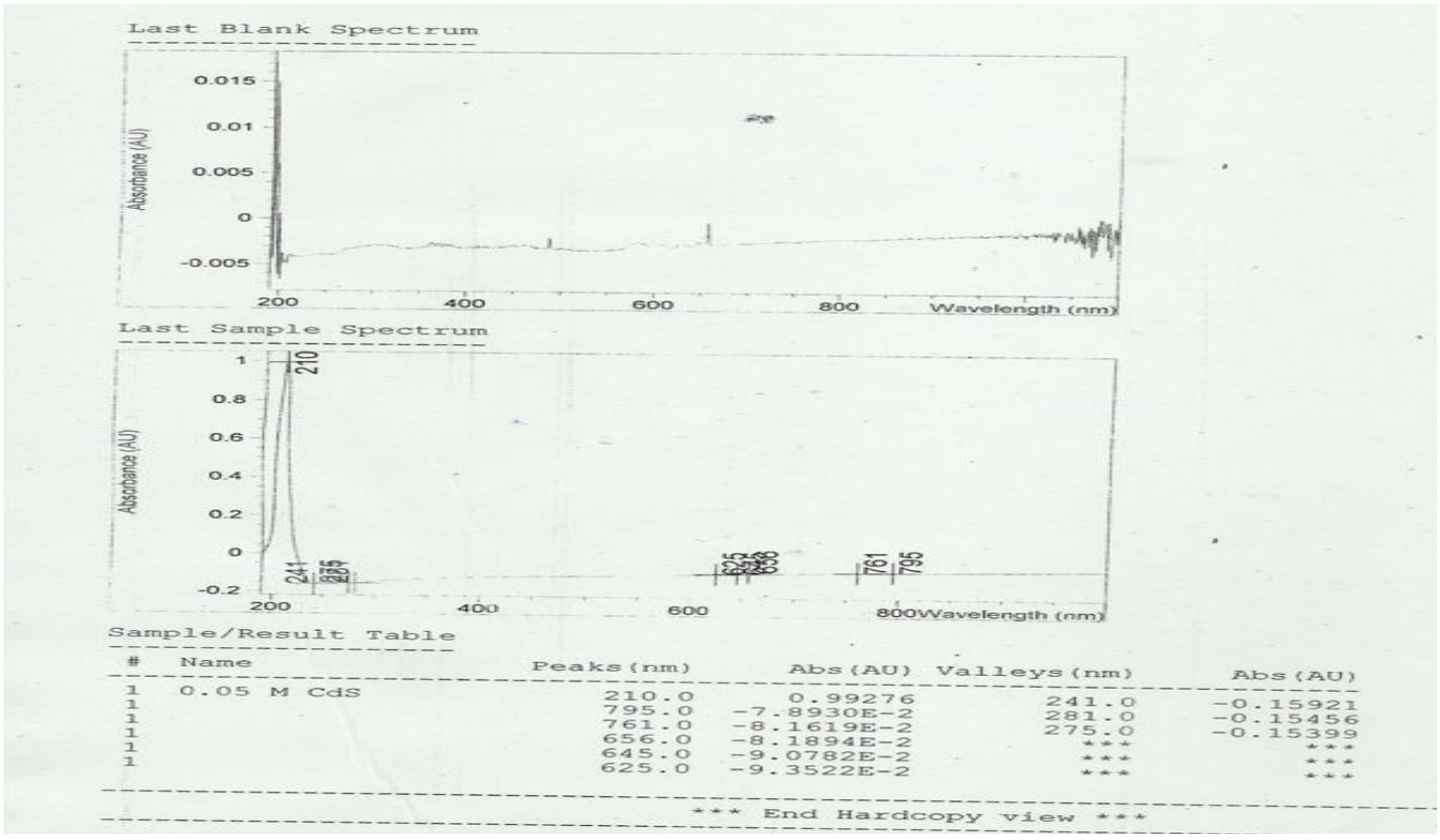
Figure 6: UV result showing the absorption peaks for CdS at concentration 0.075 M



Sample/Result Table

#	Name	Peaks(nm)	Abs(AU)	Valleys(nm)	Abs(AU)
1	0.05 M CdS	210.0	0.99276	241.0	-0.15921
1		795.0	-7.8930E-2	281.0	-0.15456
1		761.0	-8.1619E-2	275.0	-0.15399
1		656.0	-8.1894E-2	***	***
1		645.0	-9.0782E-2	***	***
1		625.0	-9.3522E-2	***	***

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Figure 7: UV result showing the absorption peaks for CdS at concentration 0.05 M

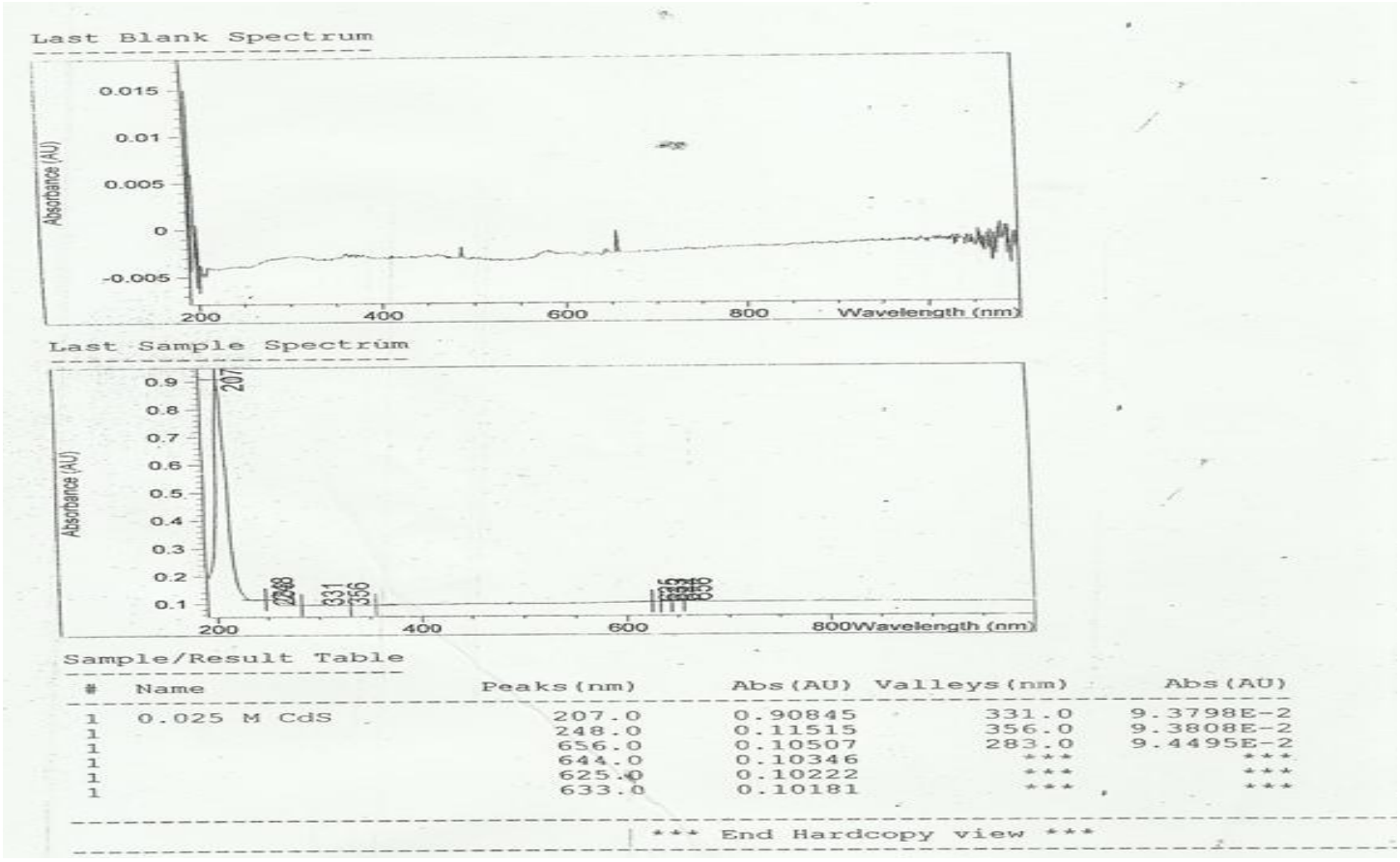

Figure 8: UV result showing the absorption peaks for CdS at concentration 0.025 M

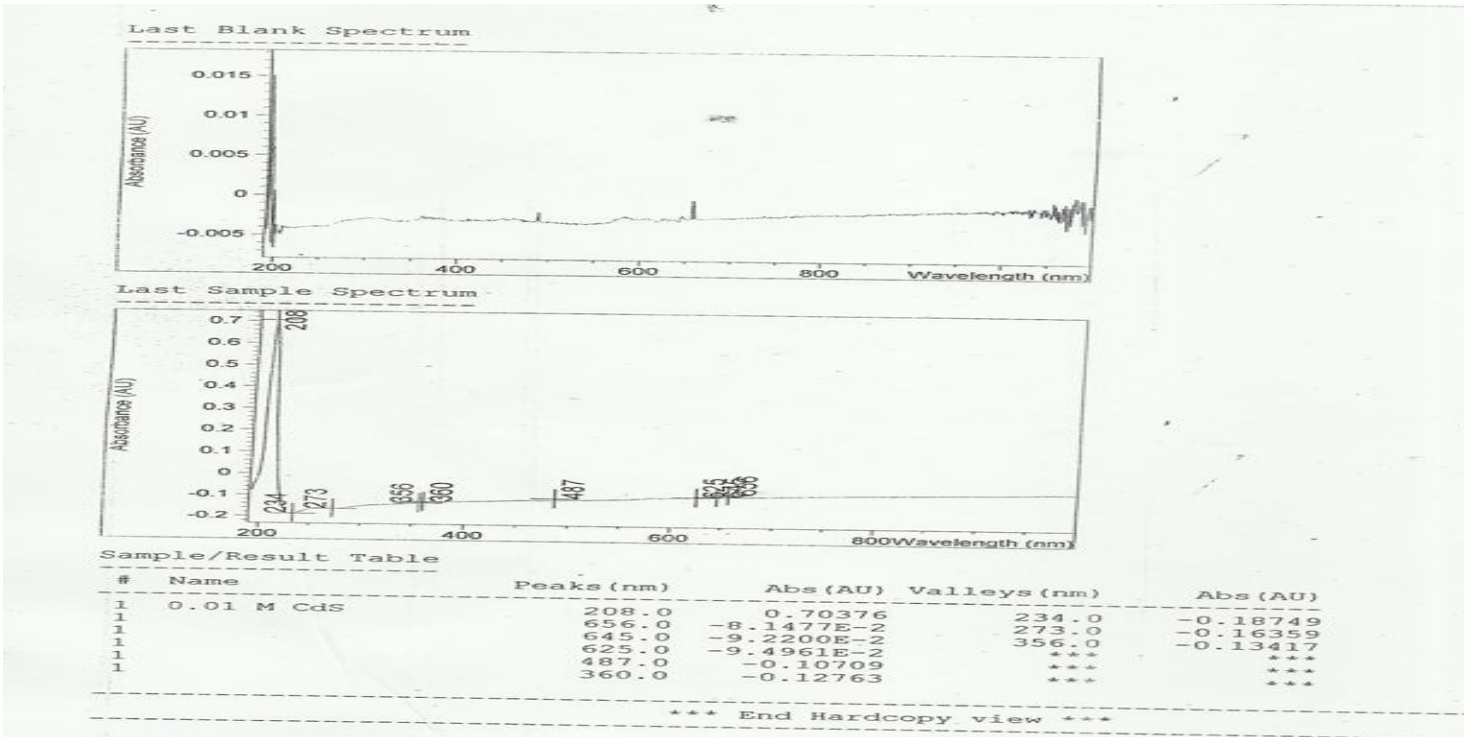

Figure 9: UV result showing the absorption peaks for CdS at concentration 0.01 M

X-ray Diffractometric Analysis

Structural analyses of synthesized CdS nanoparticles were studied using X-ray diffractometer. XRD pattern of the CdS nanoparticles illustrated in Figure 10-14 can be indexed as cubic and hexagonal structures of CdS (JCPDS 80-0019) and (JCPDS) respectively with prominent peaks corresponding to (200), (111), (101), (220) and (100) planes as reported by Lincot and Gary, (2006). The broadened peaks indicated that the particle size were in nano-range (Lincot and Gary, 2006). The average particle size of CdS nanoparticles calculated using Scherrer formula are 4.4 nm, 10.3 nm, 11.8 nm 18.8 nm and 40.24 nm (Lincot and Gary, 2006).

From the result, it was observed that the average size of the nanoparticles prepared calculated via Scherrer equation shows increase in size with decrease in precursor concentration. It has been reported that CdS nanoparticles were prepared via wet chemical method, characterized with XRD analysis and found out that the products are all within the nano-range, cubic and hexagonal phase were obtained also which conform with the work done by (Karl *et al*., 2002). Considering the size of the product obtained from XRD analysis, there was discrepancy between XRD results and that of UV-visible spectroscopy analysis carried out. Reason for discrepancy was not very clear and hence, it was recommended that more research work should be carried out at difference concentration (either below or above the concentrations used in this study) to further buttress the reason behind the discrepancy.

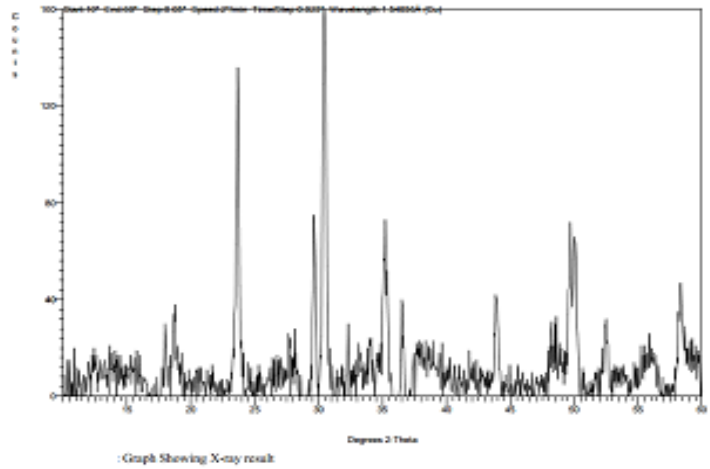

Figure 10: Result of XRD studies with XRD peaks for CdS prominent at 200 plane

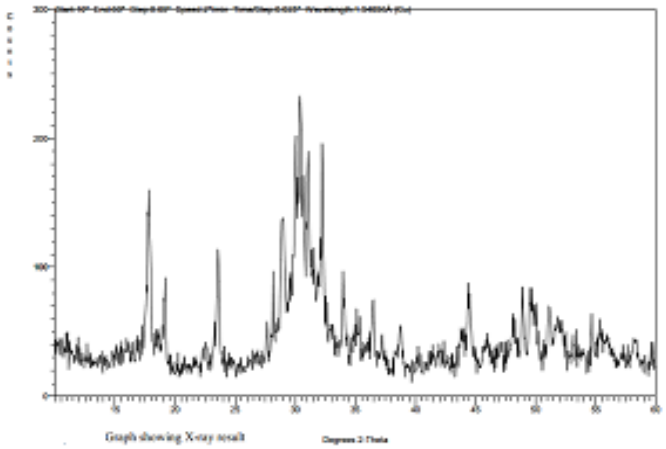

Figure 11: Result of XRD studies with XRD peaks for CdS prominent at 111 plane

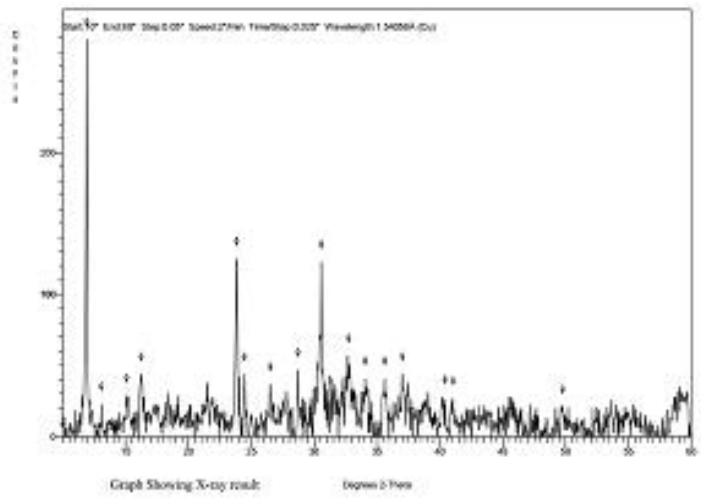

Figure 12: Result of XRD studies with XRD peaks for CdS prominent at 101 plane

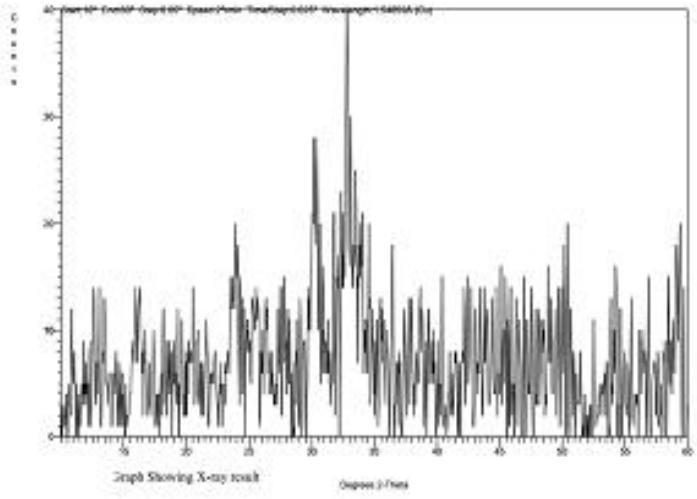

Figure 13: Result of XRD studies with XRD peaks for CdS prominent at 220 plane

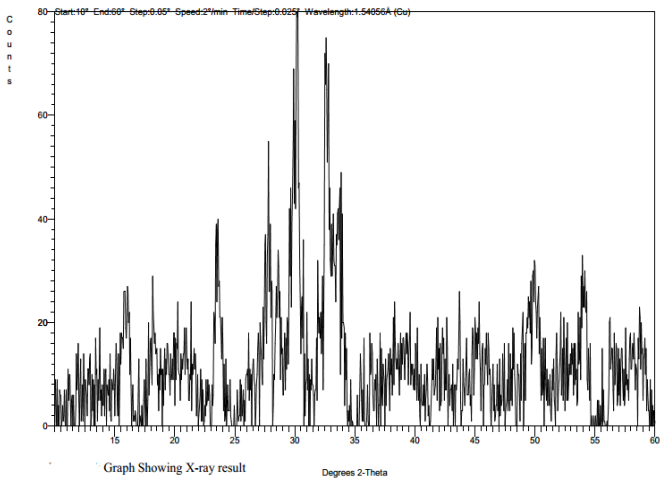

Figure 14: prominent at 101 plane XRD peaks for CdS prominent at 100 plane

CONCLUSION

The nanoparticle sizes of CdS nanoparticles obtained in this study ranged from 4.44nm to 40.24nm. XRD pattern of the CdS nanoparticles revealed the presence of both cubic and hexagonal phases. The mean size of the CdS nanoparticles estimated from the XRD analysis are found to fall within the nanoparticle range but increased with decrease in the precursor concentration. The UV-Visible absorption spectrum revealed the blue shift in absorption edge (high quantum confinement of nanoparticles). Owing to the blue shift in absorption edge seen in UV-Visible result and the nano ranges within which the size of the CdS nanoparticles prepared are found, one can conclude that wet chemical method of CdS nanoparticles preparation using methanol as capping agent is a suitable method of preparation, and the product stand a good chance of being used as suitable alternative in semiconductor devices.

It is recommended that more research work should be carried out at different concentration either below or above the concentration used in this study to further investigate the effect that change in concentration could have on the mean size of CdS nanoparticles and also to investigate the reason for discrepancy between the mean size calculated from XRD result and UV-visible result as obtained in this study.

CONFLICT OF INTEREST

None declared.

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