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**Faculty of Graduate Studies**

**Recycling CdS Thin Film Solar Cells  
Prepared by Chemical Bath  
Deposition**

**By**

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the Degree of Master of Chemistry, Faculty of Graduate Studies, An-  
Najah National University, Nablus, Palestine.**

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# Recycling CdS Thin Film Solar Cells Prepared by Chemical Bath Deposition

By

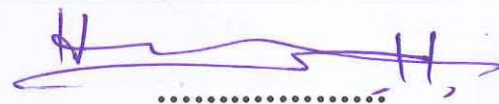
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III

## Dedication

*To my parents...*

*To my aunt Fathei Al Yamani*

*To my brothers .....*

*To those who are looking forward for more knowledge...*

## **Acknowledgements**

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*Suhaib Al Yamani*

## الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

## Recycling CdS Thin Film Solar Cells Prepared by Chemical Bath Deposition

أقر بأن ما اشتملت عليه هذه الرسالة إنما هي نتاج جهدي الخاص، باستثناء ما تم الإشارة إليه  
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**Recycling CdS Thin Film Solar Cells Prepared by Chemical Bath  
Deposition****By****Suhaib Mahyoub Muhammad Al Yamani****Supervisor****Prof. Hikmat S. Hilal****Co-supervisor****Dr. Ahed Husni Zyoud****Abstract**

CdS film electrodes deposited onto FTO/glass by Chemical Bath deposition (CBD) have been recycling here for the first time. Recycled films were examined by Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Photoluminescence Spectra (PL) and Electronic Absorption Spectra. Photo-electrochemical (PEC) characteristic were studied for various recycled films. Photo ( $J-V$ ) plots and conversion efficiency were studied.

The recycled film electrode properties were improved by annealing at 250°C and 300°C under nitrogen. The annealed films were cooled to room temperature slowly. Effects of cooling rate on physical and photo-electrochemical properties was studied.

The effect of preparation stirring on film properties was also studied .It was found that films prepared without stirring have better properties than those with stirring. The effect of deposition time preparation on characteristics of films was also studied. Film deposition in 45 min showed highest PL intensity, while those deposited in 60 min showed highest PEC conversion efficiency.

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The effect of annealing temperature on the characteristics of the prepared films was studied. The 250°C for (60 min) gave films with higher conversion efficiency than other higher or lower temperature.

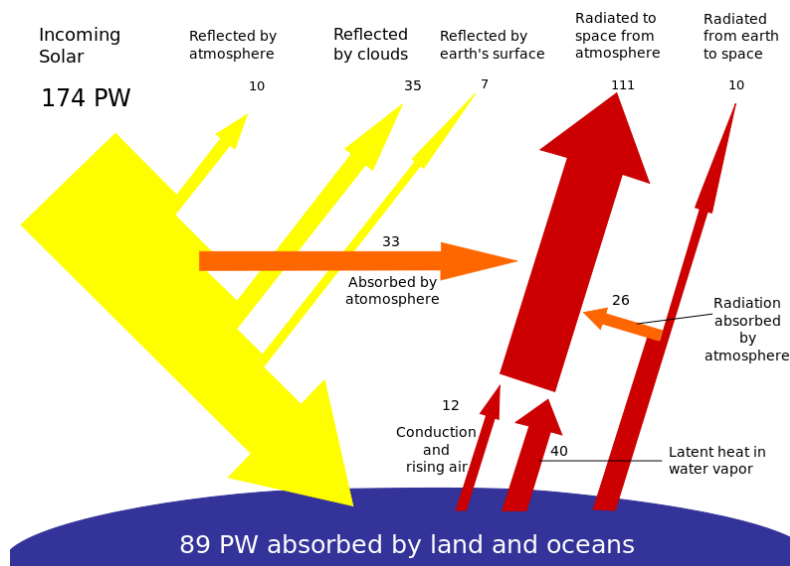
The study showed that semiconductor and electrode such as CdS can be recycled and reused, in making new PEC electrodes, without losing their characteristics. The aim of this study was successfully achieved.

# Chapter One

## Introduction

### 1.1 Introduction to Solar Energy

The sun is continuously beaming light and heat. All wind, fossil fuel, hydro and biomass energy are originally from sunlight. Solar energy was the first energy on the earth. It is now used in wide range of application technologies such as solar heating, solar photovoltaic, solar thermal electricity, solar architecture and artificial photosynthesis [1-4].



**Figure (1.1):** About half the incoming solar energy reaches the Earth surface[5]

There are two important facts about the solar energy as shown in Figure (1.1):

1. The earth receives 174 pet watts (PW) (1 pet watt =  $10^{15}$  watt) of incoming solar energy. Approximately 30% of solar energy is reflected in the upper atmosphere and goes back to space, absorbed by clouds, ocean, and landmasses

2. The sun emits radiation with a wide spectrum range, about 49% as heat and 46% as light. This includes visible, infrared and a small fraction of Ultra Violet. The total solar spectrum is shown in Figure (1.2).

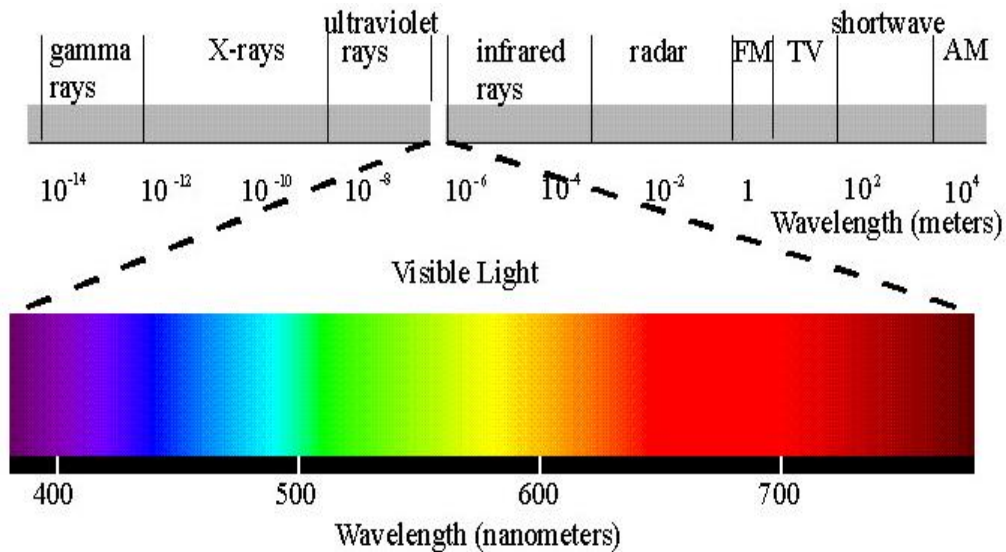


Figure (1.2): Sunlight spectrum[6]

## 1.2. Why Researchers are interested in Solar Energy?

Scientists are becoming more interested in solar power to avoid greenhouse effect. Here are a number of advantage for solar energy.

### 1.2.1 Advantages of Solar Energy

Solar energy has many advantages, such as

1. Clean and available energy
2. Financial saving
3. Better for the environment, although solar collectors and other equipment manufactured in factories cause some pollution
4. Free energy that comes directly from the sun

5. Can be used in remote areas
6. Can be used in many devices in life, such as calculators and other low power system.

### **1.2.2 Disadvantages of Solar Energy**

Solar energy has a number of disadvantages, such as

1. Can only be used in sunny day.
2. Solar collectors, panels and solar power stations are very expensive, compared with conventional power stations. Saving power devices, such as batteries, are needed which cost money.
3. Large areas of land are required to collect solar energy.
4. Some countries are poor in solar energy, such as the UK, with unreliable climate [1].

### **1.3. Semiconductors**

A semiconductor is a material with properties between metal and insulator having a degree of electronic conductivity. Semiconductors are crystals that in their pure state have mostly resisted. When the proper impurities are added by a process called doping in trace amounts (parts per billion), they display much lower resistance along with other interesting and useful properties. Depending on the impurities added, semiconductor materials are two electrically different types, p- and n- type semiconductors. Many modern devices are based on semiconductors such as quantum dots, solar cells, light-emitting diodes (LEDs) and transistors. A semiconductor has many properties, Such as variable conductivity, depletion, energetic electrons travel far, light emission, and thermal energy conversion



Semiconductors are normally found in Group IV of the periodic table. Compound groups III and V such as gallium arsenide GaAs [7], gallium phosphide GaP [8] and indium phosphide InP [9], and group II-VI compound cadmium sulfide CdS [10] and cadmium selenide CdSe [11], Organic semiconductors, made of organic compounds such as PPV (poly (phenylene vinylene ) [12], are known.

#### **1.4. Photovoltaic (PV) Systems**

A PV system is a system that converts light into direct electric current (DC) with type. To generate electrical power, semiconductors have been employed as solar panels so called photovoltaic materials (examples are monocrystalline silicon [13], amorphous silicon [14], copper indium gallium selenide [15] and cadmium sulfide. PV systems involve solid n-p junctions, which could be either with same material (called homo-junction photovoltaics, e.g. silicon cells) or with two different semiconductors (called hetero-junction photovoltaics, e.g. CdS for the n-type layer and CdTe for the p-type layer) [16].

The p-n junction is thus interfaces between n- and p- type semiconductors [17].

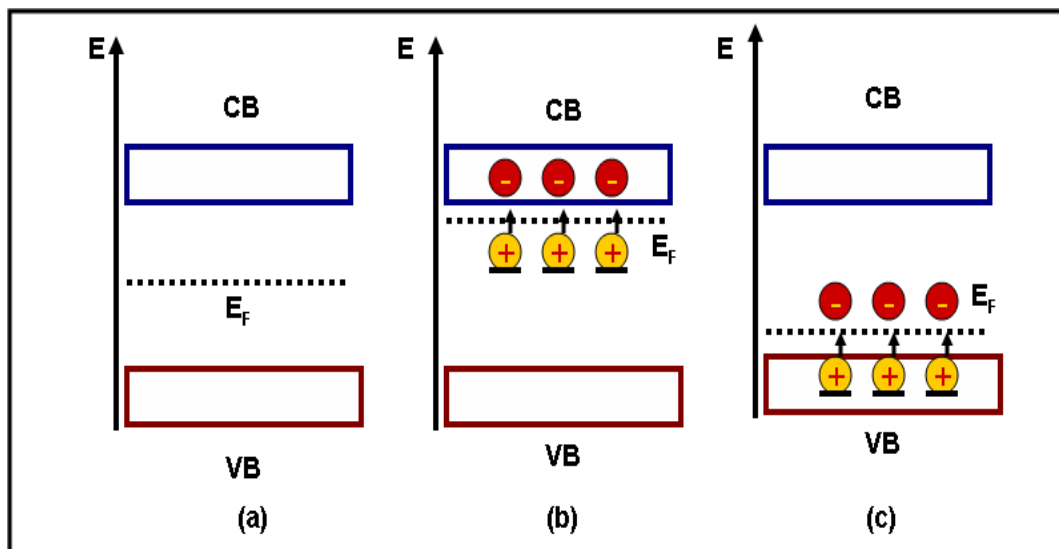
**The N-type semiconductor** is a Semiconductor type holes in the valence band are exceeded by electrons in the conduction band [17].

**The P-type semiconductor** is a Semiconductor type electrons in the conduction band are exceeded by holes in the valence band [17].

### 1.5. Photoelectrochemical (PEC) Systems.

PEC cells are based on semiconductor materials, and can be used in solar energy conversion into electrical power. Instead of the solid state p-n junction, PEC is another type of solar cells, where a semiconductor electrolyte junction is used. Such systems are called photoelectrochemical (PEC) cells[18].

The semiconductor surface is kept in contact with a suitable electrolyte solution. Space charge layer (SCL) occurs, and the Fermi level of semiconductor will go up or down to equal redox potential of the redox couple [19, 20] as shown in Figure (1.3).

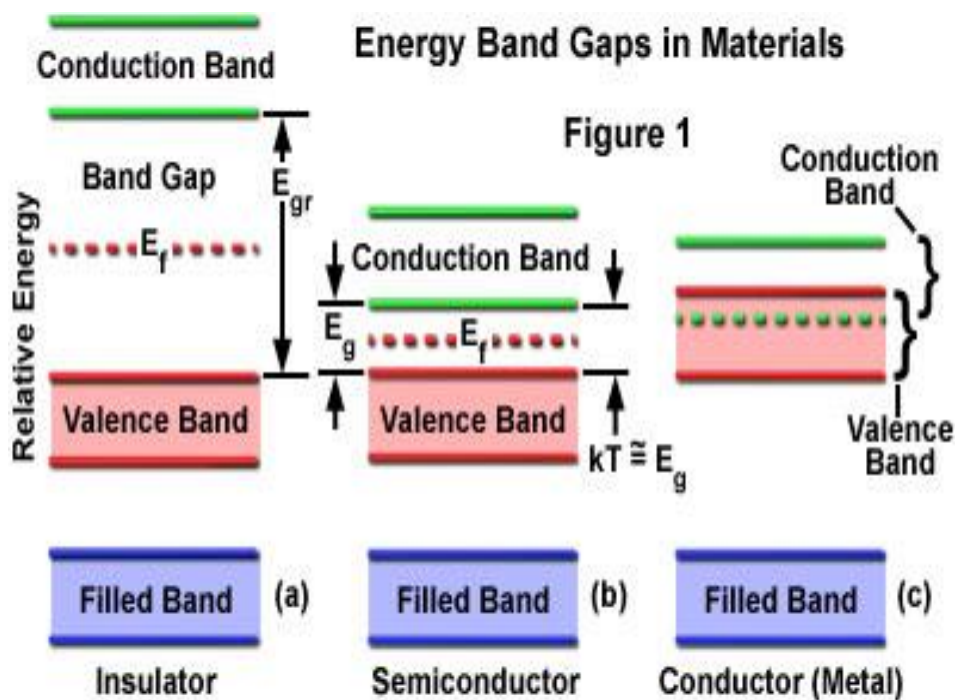


**Figure (1.3):** Fermi level diagram, a) intrinsic semiconductor, b) *n*-type semiconductor, c) *p*-type semiconductor.[21]

### 1.6. Energy Band Gap

The distance between the valence band (VB) and conduction band (CB) in a material is called band gap. The value of the band gap differs between

insulators, semiconductors and conductors. In insulators, high energy band gap exists, but in conductors no energy band gap exists, because overlap between valence band (VB) and conductive band (CB) occurs. Typically semiconductors have band gap values in the range 1.0 - 3.7 eV [22], as shows in Figure (1.4)



**Figure (1.4):** A schematic showing energy band gap for material a) insulator b) semiconductor c) conductor

## 1.7. Solar Panels

Solar cells are connected together to generate electricity from sunlight. The resulting electricity can be used in commercial and residential applications [23]. Each cell is rated by its direct current (DC) output power under standard test conditions (STC). Both current and potential are important parameters.

### **1.7.1 Efficiency**

Efficiencies for solar cells depend on type of semiconductors and on preparation quality. Some cells can generate electricity from a range of frequencies of sunlight 300 nm – 800 nm include ultraviolet, infrared and Ultra Vailot-visible [24].

### **1.7.2 Type of Solar Cell**

There are two types of solar cells inorganic and organic types.

#### **a) Inorganic Solar Cell**

Inorganic semiconductors can be used to make solar cells. Example are crystalline, multicrystalline, amorphous, and microcrystalline Si, the III A compounds and alloys, CdTe [25], the chalcopyrite compound  $\text{CuInS}_2$  [26] and alloys of the  $\text{CuInS}_2$ - $\text{CuGaS}_2$  [27], copper indium gallium diselenide (CIGS) [28], and Groups III and V such as gallium arsenide [29].

Some applications were developed in the last century using inorganic solar cells such as :

- a. Supplying power in remote location such as electronic communications.
- b. Supplying power for consumer products such as calculators.
- c. Supplying power for applications in space satellites [30].

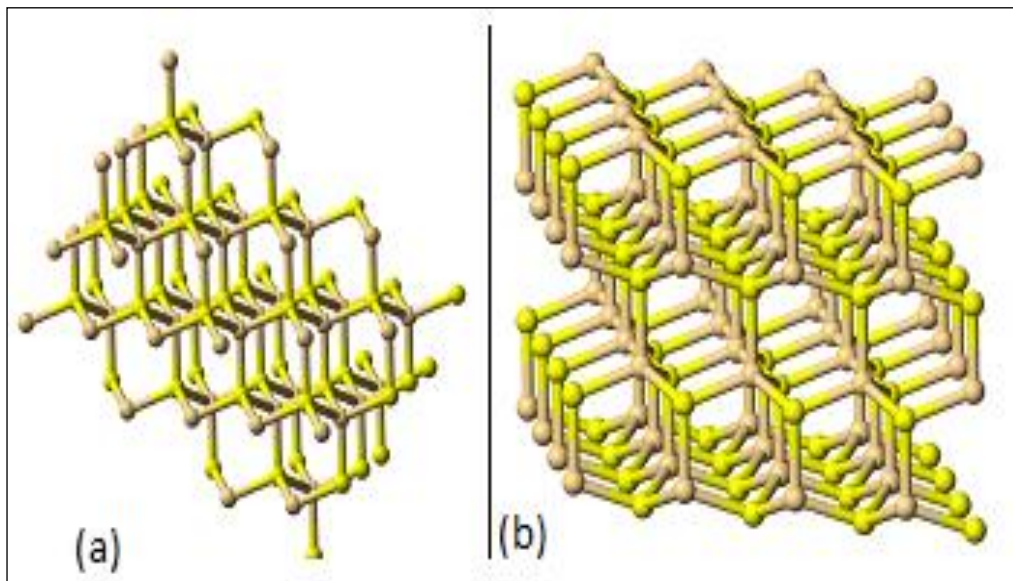
#### **b) Organic Solar Cell**

Organic systems, such as conductive organic polymers, or small molecular systems have been used as solar cells. Some organic

materials such as PPV (poly (phenylene vinylene) ), derivatized-PPV, polyacetylene and many other material are used [31, 32].

### 1.8. Cadmium Sulfide (CdS) Solar Cells

Cadmium Sulfide has been widely used in solar cells. Cadmium Sulfide is a yellow or orange solid depending on size of grown crystal. The yellow color changes to orange or brown by heating . CdS occur in nature with two different crystal structures as the rare minerals greenockite (hexagonal system ) and hawleyite ( simple cubic ) as show in Figure (1.5) , CdS has many commercial applications such as pigments and thin film solar cells [33, 34].



**Figure (1.5) :** Structures of CdS, a) Hawleyite-3D-balls b) Greenockite-3D-balls [35]

### 1.8.1 Cadmium Sulfide Properties

Some properties of cadmium sulfide are known, as shown in Table (1.1).

**Table (1.1): Properties of CdS**

Molecular formula	CdS
Molar mass	144.48 g mol <sup>-1</sup>
Appearance	Yellow-orange to brown solid. Exited absorbance 392nm. [36, 37]
Density	4.826 g/cm <sup>3</sup> , solid.
Melting point /Boiling point	1,750 °C at (10 MPa) /980 °C.
Solubility in water	Insoluble.
Solubility	Soluble in acid, e.g. 1.0M HCl.

### 1.8.2 Methods of Preparation for CdS

CdS can be prepared by a number of methods such as:

1. Sol gel techniques [38].
2. Chemical bath deposition [35]
3. Sputtering [39].
4. Spraying with precursor cadmium salt, sulfur compound and dopant [40].
5. Screen printing using a slurry containing dispersed CdS [41].
6. Electrochemical deposition [42] .
7. Combination of Chemical bath deposition and Electrochemical deposition [43].

Among these methods, Chemical Bath Deposition (CBD) is cheap in cost, high yield, good reproducibility and needs only one solution in the container. When manufacturing can be prepared by batch processing deposition or continuous processing deposition .When compared to the other methods, these methods demand don't need expensive equipment [44].

## **1.9. Thin Films**

Thin film modern technology is heavily used to produce a thin layer of semiconductor materials by deposition onto substrates (e.g. FTO and ITO), many semiconductors can be used as a thin film electrode in solar cells, such as ZnO, CdS, CdSe, CuS ,CuSe ,CdTe and others.

### **1.10. CdS Thin Films**

These are important semiconductors for application in solar cells and electronic device. CdS films have many advantages such as suitable energy bond gap  $\sim 2.3$  eV [45], important optical properties , high absorption coefficients and can be prepared by many different methods using starter materials. CdS thin films (n-type) [46] show good efficiency when mixed with CdTe (p-type) [47] compared to amorphous-Si. Unfortunately, Cadmium is toxic and costly to dispose of. Scientists are becoming interested in recycling CdS solar cells to avoid contamination with Cd<sup>2+</sup> ions .

### **1.11. Recycling of Solar Cells**

Mostly, solar panels are manufactured from aluminum and iron frames with the semiconductor as active material. Recycling possibilities depend on:

1. Silicon based modules: Aluminum and plastic frames are broken up manually at the beginning of the process. The module is then crushed in a mill and the different fractions are separated into their components [48]. More than 80% of the silicon can be recovered.
2. Non-silicon based modules: These materials require particular recycling in order to separate the different semiconductor materials and frames. In cadmium telluride [49], the regeneration process

begins with crushing the cell and subsequently separating the different parts. Up to 90% and 95% of the glass and the semiconductor materials, respectively, are recovered.

### **1.12. Objectives of this work**

The main goal of this work is :

1. Taking CdS thin films used in solar cells and recycling them into new CdS thin film electrodes.
2. Investigating the effect of many parameters such as temperature, time and stirring on conversion efficiencies of the recycled film electrode .

### **1.13. Hypothesis**

Recycling CdS solar cells will be valuable, because:

1. The  $\text{Cd}^{2+}$  ions will not be allowed to contaminate water and environment.
2. The newly recycled CdS solar cells will have comparable efficiencies with freshly prepared CdS. The process will have environmental and economic value in the future and will give new pathways to recycle other types of solar cells.

### **1.14. Novelty**

1. To our knowledge, complete recycling of CdS film based solar cells prepared by CBD has not been reported. Therefore, this work will be conducted here for the first time.
2. Other types of solar cells, such as those of Si, yield non-hazardous  $\text{SiO}_2$  after disposal, and do not necessarily need to be recycled. Solar cells with hazardous species, such as CdS, must be recycled. This reflects novelty and relevance of this proposed work.
3. Solar cells involving hazardous materials should always be recycled. This work is just one example for future technologies.



## Chapter Two

### Experimental

#### 2.1 Materials

Thiourea ( $\text{CS}(\text{NH}_2)_2$ ),  $\text{NH}_3$ ,  $\text{NaOH}$ , Pure  $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$  and,  $\text{Na}_2\text{S}$  were purchased from Aldrich, calculated  $\text{Cd}^{2+}$  from recovered.  $\text{HCl}$ ,  $\text{NH}_4\text{Cl}$  were purchased from Frutarom. Methanol was obtained from Riedel-DeHaën in a pure form. Highly conductive fluorine tin oxide FTO/Glass samples were kindly donated by Dr. Guy Campet of ICMCB, University of Bordeaux, France.

#### 2.2 Recovering the $\text{Cd}^{2+}$ ions:

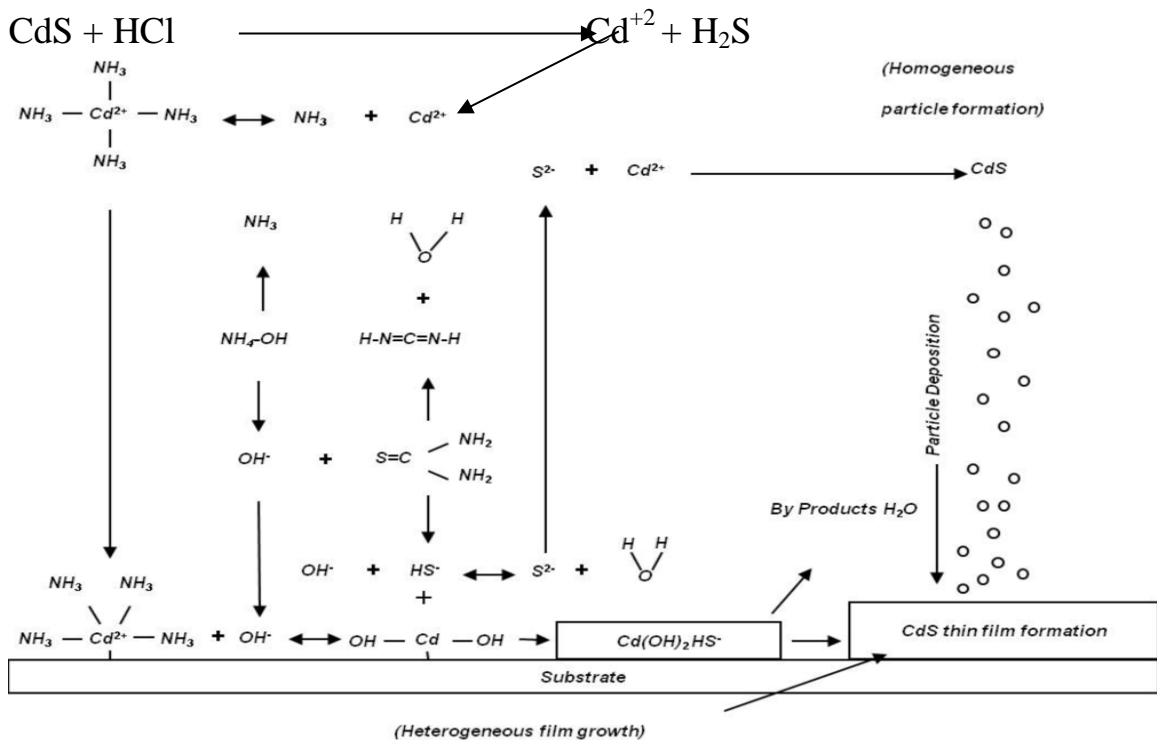
Earlier prepared CdS thin films were taken from previous student and immersed in  $\text{HCl}$  with different concentration (0.6, 0.8 and 1.0) M. The 1.0 M was more suitable and used all the time. Pre-used CdS Films and excess powders were placed in the  $\text{HCl}$  acid for 5 min.

#### 2.3 Pretreatment of FTO/Glass Substrate

In order to obtain uniformity and good adherence of deposit recycled CdS, films by chemical bath deposition (CBD) techniques, FTO/Glass was cleaned before recycling CdS film deposition process. The FTO/Glass slide recovered from CdS solar cells were used here again as substrates. The substrates further were treated with concentrated  $\text{HCl}$  for 60 min followed by methanol for 30 min in a sonicator. The substrates were treated again by immersion in dilute solution of  $\text{HCl}$  (10% v/v) for 5 second, rinsing with distilled water, immersing in methanol, rinsing again with distilled water, prior to use.

## 2.4 Preparation of CdS Film from Recovered Cd<sup>+2</sup> Ions

Film recycling was achieved by Chemical Bath Deposition (CBD), using Cd<sup>+2</sup> recovered from earlier prepared films. Atomic absorption spectroscopy (AAS) was used to determine resulting concentration of Cd<sup>+2</sup> obtained from the earlier prepared CdS thin films. Figure (2.1). shows the mechanism used to prepare CdS recycled thin film electrodes.

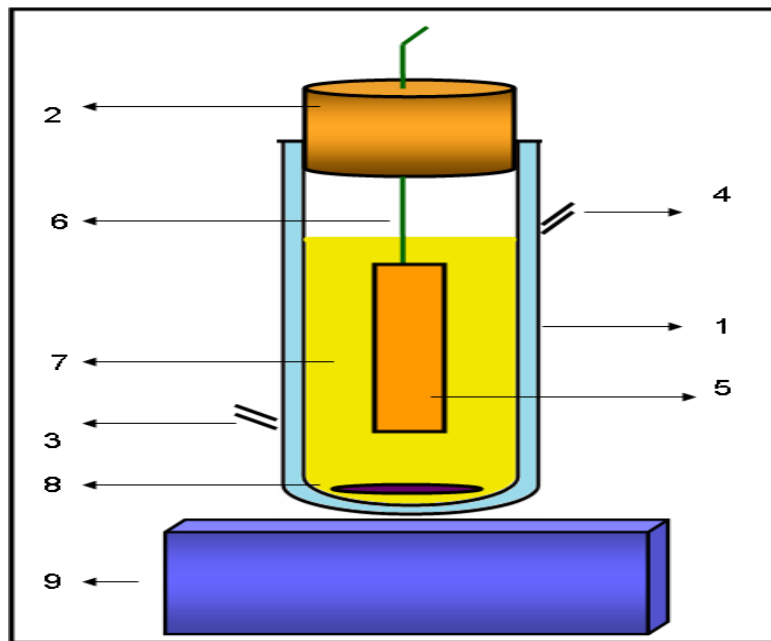


**Figure (2.1) :** Mechanism for production of CdS thin film electrodes [50]

### 2.4.1 Chemical Bath Deposition (CBD) Technique

Chemical bath deposited CdS thin films were prepared by classical method. The experimental arrangement is shown in Figure (2.2). The bath solution contained 25.0 mL of distilled water, 2.5 mL of 0.2 M Cd<sup>+2</sup> recycling, 10 ml of NH<sub>4</sub>Cl and 15.0 mL of 2.0 M NH<sub>4</sub>OH. In some cases, the

preparations were made with stirring while in other cases preparations were made without stirring for comparison. Temperature was kept at 80° C during the deposition process [37]. The held substrates were immersed in the solution. The system was closed with rubber sealing. Substrate holder was also isolated using covering plastic [43].



**Figure (2.2)** : Experimental arrangement for CBD-CdS film.

1) Beaker (60 ml), 2) rubber seal, 3) water bath input, 4) water bath output, 5) FTO/Glass substrate, 6) substrate holder, 7) solution containing (water, CdCl<sub>2</sub>, thiourea, NH<sub>4</sub>Cl, NH<sub>4</sub>OH and HCl), 8) magnetic stirrer, 9) magnetic stirrer plate [21]

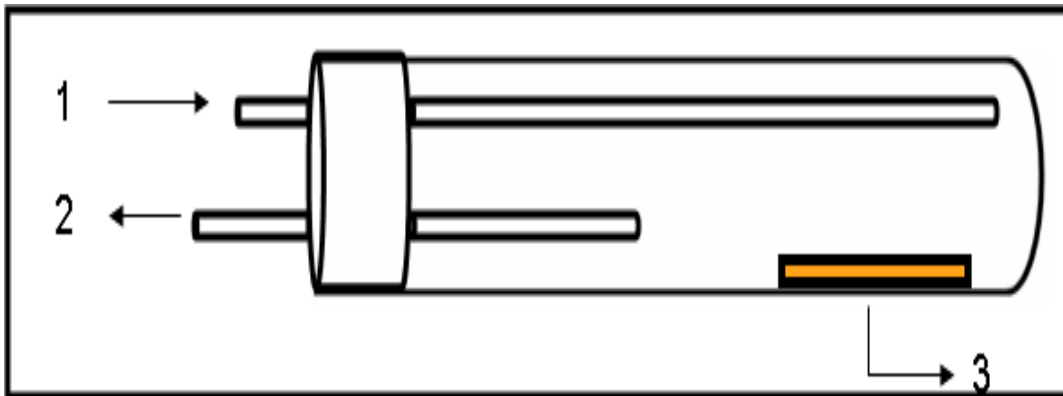
A syringe was used to add 2.5 mL of 0.6 M thiourea to the bath solution. The final pH value of the solution became ~ 10.3 [51]. The deposition process was continued for different times 30, 45 and 60 minutes.

## 2.5 Modification of CdS Thin Film

CdS thin film modification involved using different preparation times, stirring rate, cooling rate and annealing temperature at (250°C or 300°C).

### 2.5.1 Annealing Process

Annealing was conducted using a thermostated horizontal tube furnace, Figure (2.3) . The prepared CdS thin films were inserted in a 30 cm long Pyrex cylinder. The temperature was raised to the desired value (250°C, 300°C) under N<sub>2</sub> atmosphere. The 250°C was optimal temperature. The annealing process was continued for one hour at the constant temperature, as shown in Figure (2.3)



**Figure (2.3):** The annealing system, 1) nitrogen input, 2) nitrogen output, 3) CdS thin film [21].

### 2.5.2 Cooling Rate Control

After the annealing process, the furnace was turned off and left to cool slowly to room temperature under N<sub>2</sub> atmosphere. Cooling rate was 90°C /h on the average .

### **2.5.3 Time and Stirring**

Different CdS thin films were prepared by changing times, using stirring or no stirring. Different times (30, 45, and 60) minutes were used for comparison between them in their PEC characteristics, some samples were prepared with stirring, while others were prepared without stirring.

## **2.6 Film Characterization**

The prepared CdS thin films have been studied by following techniques.

### **2.6.1 Electronic Absorption Spectra**

The optical absorption spectra of solid state CdS thin films were studied at room temperature in the wavelength range 350-750 nm FTO/Glass was used as a blank. A Shimadzu UV-1601 spectrometer, was used to measure the spectra.

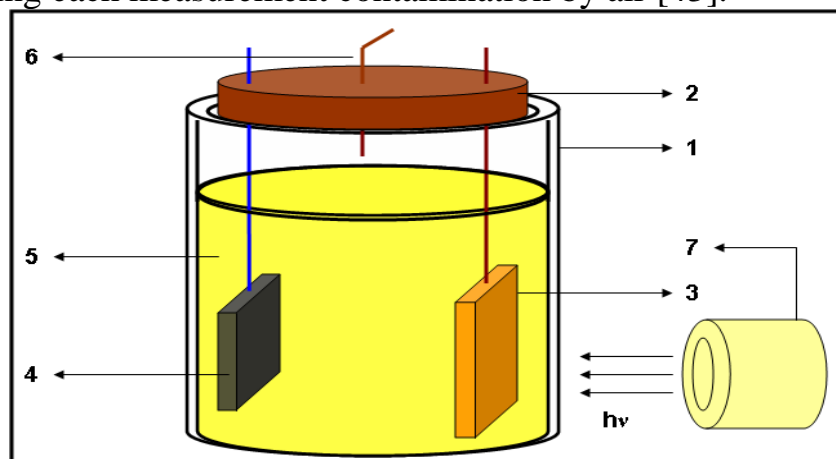
### **2.6.2 Fluorescence Spectrometer**

The emission fluorescence spectra for the prepared CdS thin films were measured to find the band gap of CdS using excitation at wavelength 392 nm. A Perkin-Elmer LS 50 luminescence spectrometer was used. In order to remove the undesired reflected shorter wavelengths, a cutoff filter (450 nm) was used.

### **2.6.3 Photoelectrochemical Cell**

CdS thin film electrode was used as working electrode in the PEC cell, and a platinum counter electrode was connected to the internal reference electrode, all in electrolytic solutions. As shown in Figure (2.4), using polysulfide  $\text{NaOH/S}^{2-}/\text{S}_x^{2-}$  system (0.10 M  $\text{Na}_2\text{S}$ , 0.10 M  $\text{NaOH}$ , 0.10 M  $\text{S}$ ) as electrolytic solution [43, 52]. High purity nitrogen (99.9999%) was

bubbled through the solution for at least 3 minutes to eject the dissolved oxygen before each measurement, and was then kept bubbling over the solution during each measurement contamination by air [43].



**Figure (2.4):** Two-electrode photo-electrochemical (PEC) cell. 1) Beaker (60 ml), 2) rubber seal, 3) CdS working electrode, 4) platinum counter electrode, 5) electrolytic solution, 6) nitrogen, 7) light source [21].

For illumination, a 50 Watt halogen spot lamp was used. The lamp has an intense convergent of wide spectral range between 450-800 nm with high stability. The lamp was placed at a defined distance from CdS working electrode and kept constant in all measurements. The illumination intensity on the electrode was measured by a LX-102 light meter and was 38000 lux (equivalent to  $0.0056 \text{ W.cm}^{-2}$ ) [43, 53].

#### 2.6.4 Plots of Current Density-Potential

The photocurrent experiments were conducted, using halogen spot lamp 50 watt. Measurements were done under nitrogen atmosphere, at room temperature. Using poly sulfide  $\text{NaOH/S}^{-2}/\text{S}_x^{-2}$  system (0.10 M  $\text{Na}_2\text{S}$ , 0.10 M  $\text{NaOH}$ , 0.10 M S) as electrolyte solution.

A computer controlled Princeton Applied Research (PAR) Model 263A Potential/ Galvanostat was used to measure the current density versus. Voltage ( $J$ - $V$ ) plots using the same PEC cell described formerly.

### **2.6.5 X-Ray Diffraction (XRD)**

Crystal structure and crystallinity was investigated by XRD-7000, SHIMADZU X-ray diffract meter (XRD), where  $\text{CuK}\alpha$  rays ( $\lambda = 1.5406 \text{ \AA}$ ) were used. XRD measurements were kindly conducted at ISAA Environment Consulting Co. Ltd, Chungju City, S. Korea.

### **2.6.6 Scanning Electron Microscope (SEM)**

SEM micrographs were recorded on a Field Emission Scanning Electron Microscope FE-SEM, JEOL JSM-6700F at ISAA Environment Consulting Co. Ltd, Chungju City, S. Korea, the same equipment was used for EDX measurements.

### **2.6.7 Atomic Absorption Spectroscopy (AAS).**

AAS was used to find the concentration of  $\text{Cd}^{2+}$  ions in solution A Thermo 50-60 Hz Type ICE 3500 AA system was used. The device was calibrated before use, with concentrations of 5, 10 , 20 and 50 ppm,  $\text{Cd}^{2+}$  ion concentrations in different solution were then measured using the AAS.

## Chapter Three

### Results and Discussion

Chemical bath deposition CBD preparation techniques were used in this work to prepare new CdS nano-sized thin films by recycling used ones. Different parameters were used to enhance the prepared film, including, deposition time (30, 45 and 60 min) and annealing CdS thin film deposition at different temperatures (250°C and 300°C) under a nitrogen atmosphere for 1 hour. The annealed films were slowly cooled to room temperature. Effect of stirring during the process of preparation has also been studied.

The main objective of this work is to take earlier prepared and used CdS thin films to recycle then to produce new CdS thin films. Finding best conditions to recycle films with preferred properties was another objective. The recycled film properties were studied in terms of short circuit current density ( $J_{sc}$ ), open-circuit photo potential ( $V_{oc}$ ), XRD, PL spectra, electronic absorption spectra, photo  $J$ - $V$  plots, efficiency enhancement, and value of short-circuit current. Atomic Absorption Spectroscopy (AAS), was used to calculate  $Cd^{2+}$  ion concentration. In all CdS films preparation solution of  $Cd^{2+}$  ion ( 2.5 mL, 42 ppm) were used. Remaining  $Cd^{2+}$  ions concentration after each preparation, was calculated by AAS. Table (3.1) shows the concentration of remaining  $Cd^{2+}$  ion after each preparation.

**Table (3.1) : Concentration of remaining  $Cd^{2+}$  ion after each preparation.**

Deposition time	Concentration of $Cd^{2+}$ ion of substrate	Concentration of $Cd^{2+}$ ion in solution and beaker
30 min	28 ppm	14 ppm
45 min	30 ppm	12 ppm
60 min	35 ppm	7 ppm



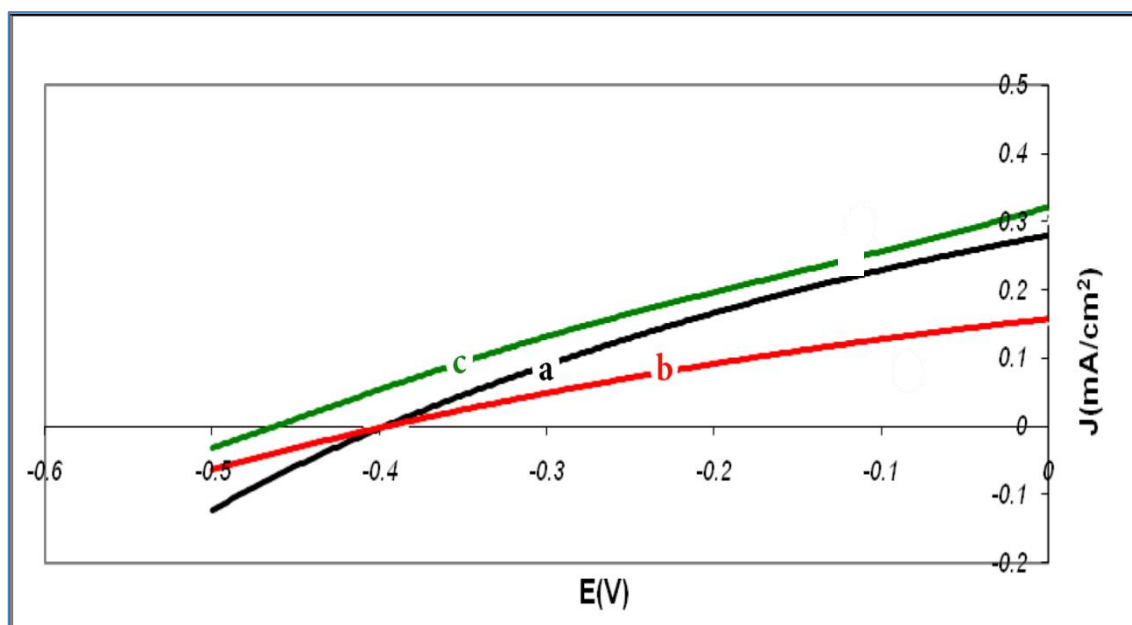
This chapter describes and discusses the effects of annealing temperature (250°C and 300°C), stirring, and deposition time (30, 45, 60 min) on characteristics of different types of recycled CdS thin film electrodes.

### 3.1 Effect of Deposition Time on Recycled CdS Electrode Characteristics (Annealed at 250°C With Stirring)

Effect of deposition time (30, 45 and 60 min) CBD-CdS recycled thin film electrode (annealed at 250 °C), was studied.

#### 3.1.1 Photo J-V of Recycled CdS Thin Film Electrodes

Photo J-V were measured for CdS thin film electrodes, deposited in different times (30, 45, 60 min) annealed at 250°C with stirring, Figure (3.1). The results are summarized in Table (3.2)



**Figure (3.1 ):** Photo *J-V* plot for annealed CBD-CdS recycling thin film electrodes (annealed at 250°C with stirring). a) 30 min b) 45 min c) 60 min. All measurements were conducted in aqueous  $S^{2-}/S_x^{2-}$  redox system at room temperature.

The  $V_{OC}$  values for both films deposited in 30 and 45 min were nearly the same. The 60 min film showed higher  $V_{OC}$  value. The film deposited in 60 min also showed higher  $J_{SC}$  value. It gives higher percentage conversion efficiency ( $\eta \sim 0.75541\%$ ) Table (3.2) summarizes PEC values for different films electrode. So the 60 min is best deposition time among the series. The study showed that the CdS deposited in 60 min was the best film. During the process cadmium sulfide particles were prepared with stirring, which speeds up deposition and yields particles. This may also causes inconsistency in the arrangement of the particles on the film surface.

**Table (3.2) Effect of deposition time on PEC characteristics of CdS thin film electrodes (Annealed at 250°C with Stirring)**

<i>Sample</i>	<i>Deposition time</i>	$V_{oc}$ (V) $\pm 0.0001$	$J_{SC}$ (mA/cm <sup>2</sup> ) $\pm 0.0001$	$^a \eta$ % $\pm$ 0.0001	$^b FF$ %
<b>a</b>	30 min	-0.400	0.298	0.6140	16.79
<b>b</b>	45 min	-0.397	0.150	0.3331	8.78
<b>c</b>	60 min	-0.474	0.314	0.7554	17.05

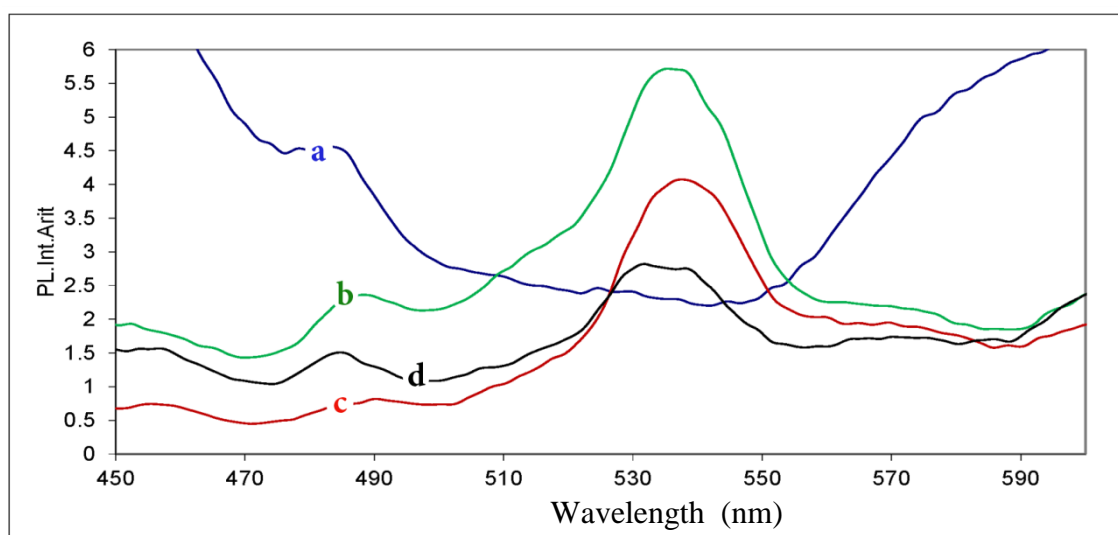
$^a \eta$  (%) = [(maximum observed power density)/ (reach-in power density)] $\times 100\%$ .

$^b FF$  = [(maximum observed power density)/  $J_{sc} \times V_{oc}$ ] $\times 100\%$ .

### 3.1.2 Photoluminescence (PL) Spectra for CdS Thin Film

Photoluminescence spectra were investigated for recycled CdS film electrodes, annealed at 250°C with stirring, deposited in different times (30, 45 and 60 min), Figure (3.2). The systems were excited at wavelength 392 nm. The Figure shows a peak at  $\approx 392$  nm in the UV region, and a second more intense peak at  $\approx 537.5$  nm, 539 nm and 538 nm for films

deposited in 30, 45, and 60 min, (showing band gap  $1240/537.5 = 2.31$  eV,  $1240/539 = 2.17$  eV and  $1240/538 = 2.30$  eV respectively). PL results show that with longer deposition times red shift occurs. This means that particle size of CdS increases giving smaller band gap. This is due to effect of time deposition on film thickness [35]. The results showed the film deposited in 45 min has more intensity arrangement than others, as it showed the higher PL intensity.

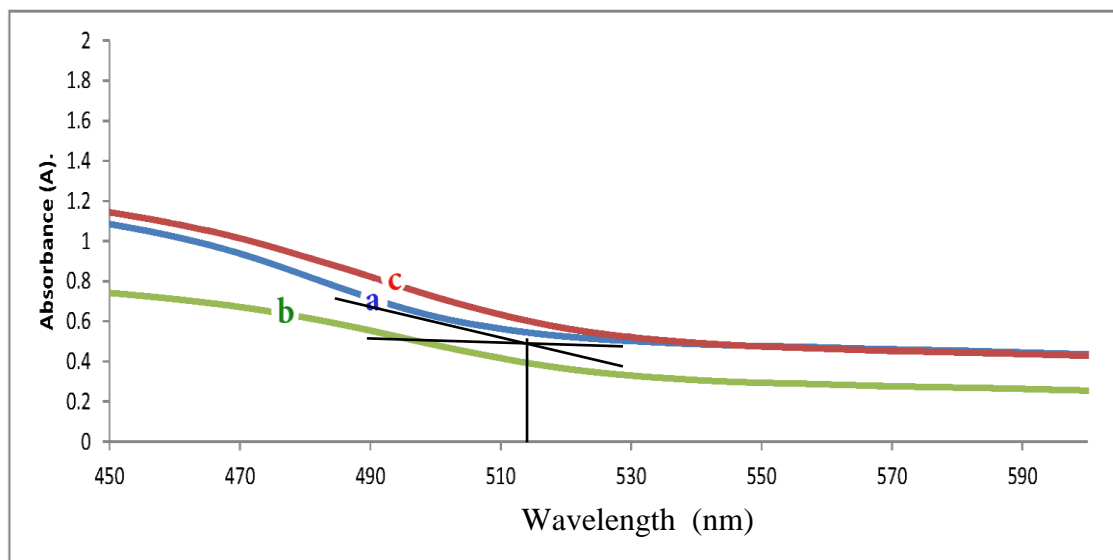


**Figure (3.2 ):** Photoluminescence spectra CBD-CdS recycling thin film electrodes which prepared different time, annealed at 250°C with stirring. a) FTO b) 30 min c) 45 min d) 60 min

### 3.1.3 Electronic Absorption Spectra for CdS Thin Film Electrodes

Effect of deposition time on the electronic absorption spectra was investigated for recycled CdS thin film electrodes prepared in different times (30, 45 and 60 min ), and annealed at 250°C, Figure (3.3). Absorption edge value 504, 508 and 512nm, with the band gaps 2.46, 2.44

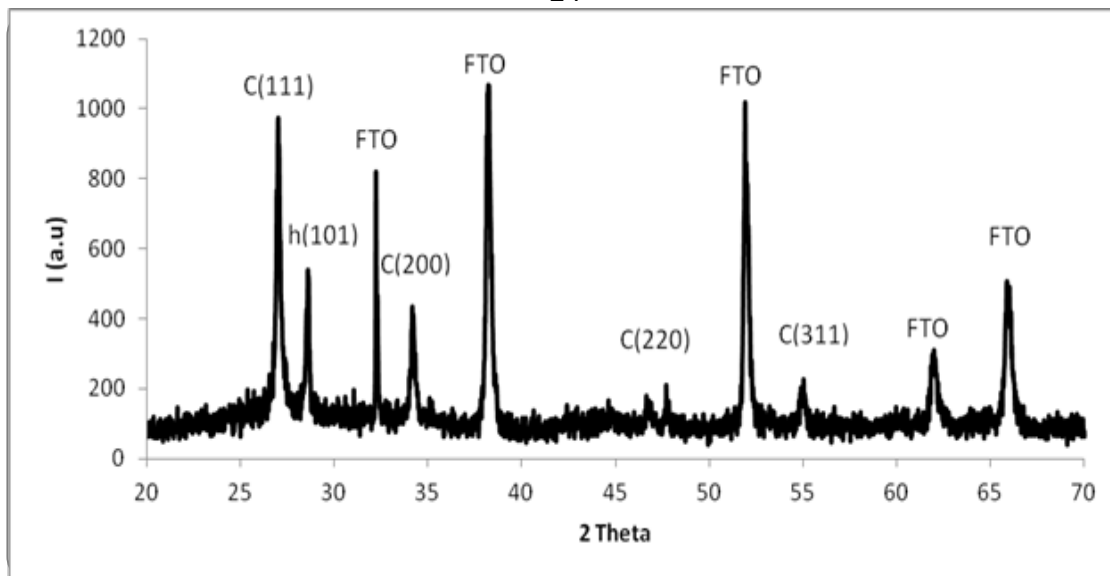
and 2.42 eV were observed for the prepared films, respectively. The film 45 min showed higher absorption intensity. This is because the 45 min deposition time gives the more uniform film than other two electrodes.



**Figure (3.3):** Electronic absorption spectra for the CdS thin film deposition different time, annealed at 250°C, with stirring a) 30 min b) 45 min c) 60 min.

### 3.1.4 XRD Spectra for CdS Thin Film Electrodes

X-ray diffraction measurements were obtained for recycled CBD-CdS thin film electrodes deposited in 60 min, after annealing. X-ray diffraction data showed that the annealed CBD-CdS films involved soundly crystalline particles. XRD patterns are shown in Figure (3.4). The films involved mixed hexagonal and cubic phases. The average grain size for recycled CBD-CdS particles were found in cubic phase with  $\sim 33$  nm, and in hexagonal phase with  $\sim 47.6$  nm, after annealing. Table (3.3) shows the positions of observed peaks and their planes.



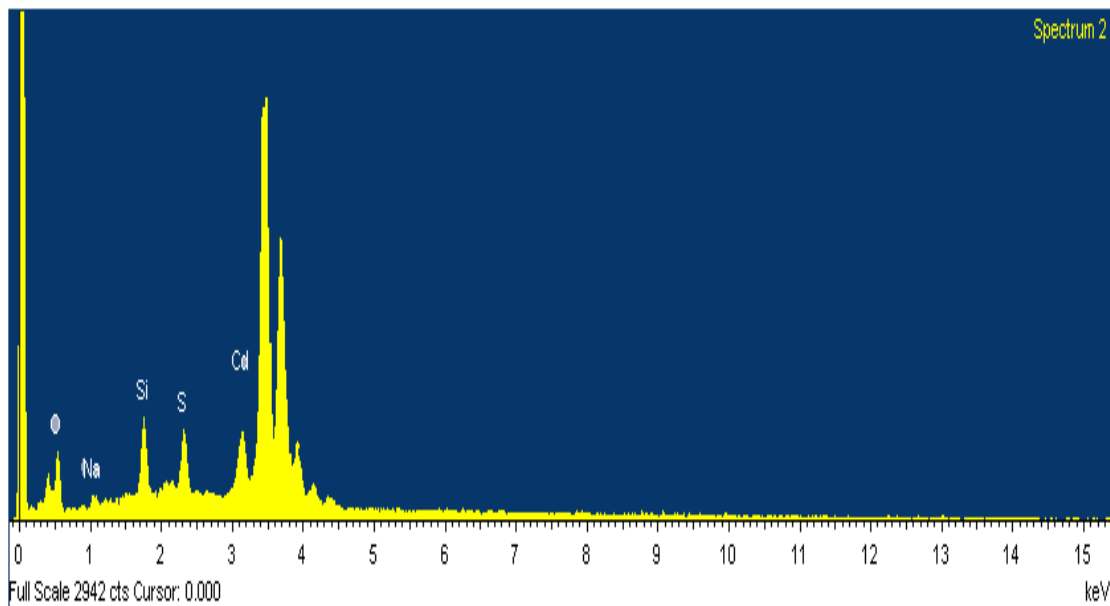
**Figure (3.4):** XRD of annealed at (250°C) recycled CBD-CdS film prepared in 60 min with stirring.

**Table (3.3):** XRD pattern results for annealed (at 250°C) recycled CBD-CdS thin film electrodes prepared in 60 min with stirring.

Position of observed peak (2 theta)	Planes	Reference
26.80	C (111)	[54]
28.40	C (101)	[55]
33.65	FTO sub.	[56]
34.74	C (200)	[57]
37.74	FTO sub	[56]
47.50	C (220)	[58]
51.44	FTO sub.	[56]
55.00	C (311)	[54]
61.58	FTO sub.	[56]
65.50	FTO sub.	[56]

### 3.1.5 EDX Spectra for CdS Thin Film Electrodes

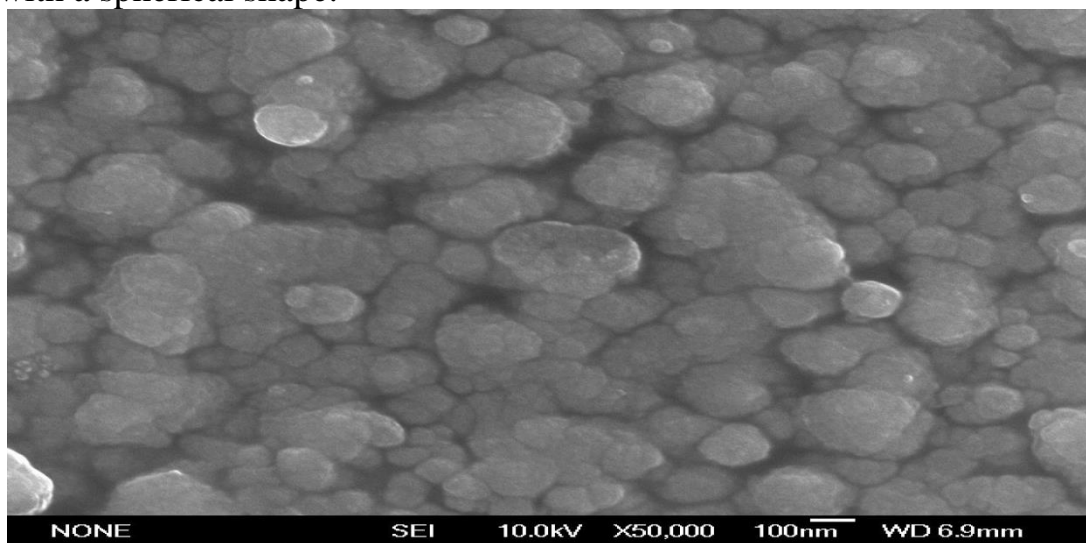
EDX measurements were obtained for recycled CBD-CdS thin film electrodes after annealing. EDX patterns are shown in Figure (3.5). The EDX analysis shows cadmium:sulfur with 1:1 atom ratio, as shown in Figure (3.5). This result confirms the formation of CdS.



**Figure (3.5):** EDX for recycled recycling CBD-CdS film in 45 min with Stirring after annealing at (250°C).

### 3.1.6 SEM Spectra for CdS Thin Film Electrodes

SEM images were obtained for recycled CBD-CdS thin film electrodes after annealing. SEM patterns are shown in Figure (3.6). The SEM images indicate agglomerates (38 nm – 400 nm) of nanoparticles (20 nm – 45 nm), with a spherical shape.



**Figure(3.6):** SEM of annealed at (250°C) recycled CBD-CdS film at 45 min with stirring.

Figure (3.1) and Table (3.2) show that deposition of cadmium sulfide deposited in 60 min is better than those deposited in 30 or 45 min, in terms of PEC efficiency, PL spectra. Figure (3.2), showed that deposition within 45 min gives higher PL intensity. The size of particle increased with deposition time, as Figure (3.2) showed through red shift [59]. The results of PEC are consistent with PL which showed that deposition within 60 min is the best, where the particle size has increased with minimum energy band gaps.

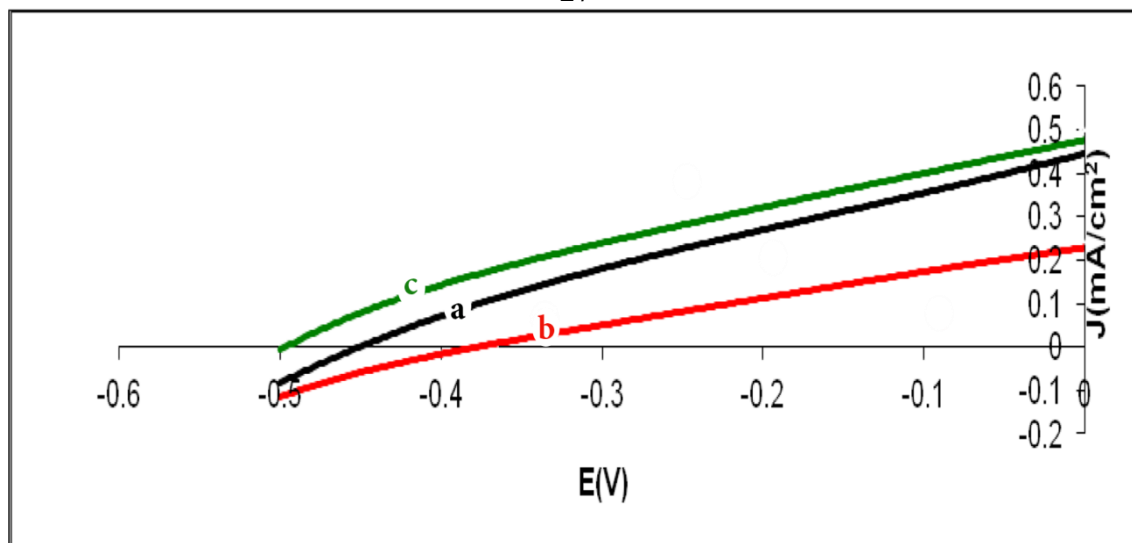
These results are consistent with Sahar Khudruj in terms of PL and electronic absorption. PEC efficiency in this work shows higher efficiency than Sahar Khudruj results using CBD-CdS reported earlier [53].

### **3.2 Effect of Deposition Time on Recycled CdS Electrodes (Annealed at 250°C without Stirring)**

Effect of deposition time on recycled CBD-CdS thin film electrodes, prepared at different times 30, 45 and 60 min without stirring, was studied after annealed at 250 °C.

#### **3.2.1 Photo J-V of Recycled CdS Thin Film Electrodes**

Photo J-V were measured for CdS thin film electrodes, deposited in different deposition times (30, 45 and 60 min) without stirring, annealed at 250°C, Figure (3.7). The results are summarized in Table (3.4),



**Figure (3.7):** Photo  $J$ - $V$  plot for annealed at 250°C CBD-CdS recycling thin film electrodes which prepared different times without stirring, a) 30 min b) 45 min c) 60 min. All measurements were conducted in aqueous  $S^{2-}/S_x^{2-}$  redox system at room temperature.

The film deposited in 60 min showed higher  $V_{oc}$  value and higher  $J_{sc}$  value than other films. It gives higher percentage conversion efficiency ( $\eta \sim 1.5940\%$ ), Table (3.4) summarizes PEC values for different films. The 60 min shows higher PEC values than 30 and 45 min films.

**Table (3.4) Effect of deposition time on PEC characteristics of CdS thin film electrodes (Annealed at 250°C without Stirring)**

<i>Sample</i>	<i>Deposition time</i>	$V_{oc}$ (V) $\pm 0.0001$	$J_{sc}$ (mA/cm <sup>2</sup> ) $\pm 0.0001$	<sup>a</sup> $\eta$ % $\pm$ <b>0.0001</b>	<sup>b</sup> $FF$ %
<b>a</b>	30 min	-0.450	0.410	1.0527	31.85
<b>b</b>	45 min	-0.382	0.240	0.3878	9.49
<b>c</b>	60 min	-0.500	0.500	1.5940	33.72

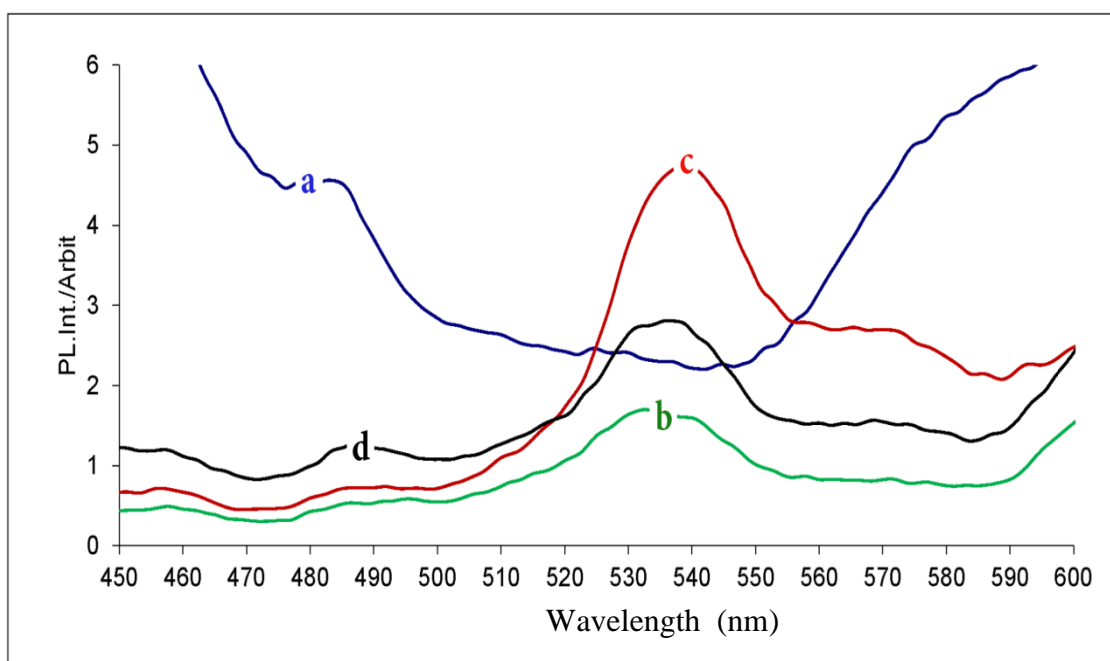
<sup>a</sup> $\eta$  (%) = [(maximum observed power density) / (reach-in power density)] $\times 100\%$ .

<sup>b</sup> $FF$  = [(maximum observed power density) /  $J_{sc} \times V_{oc}$ ] $\times 100\%$ .



### 3.2.2 Photoluminescence Spectra for CdS Thin Film

Photoluminescence spectra were investigated for recycled CdS thin film electrodes prepared in different time without stirring, (annealed at 250°C), Figure (3.8). The systems were excited at wavelength 392 nm. The Figure shows intense peaks at  $\approx 535$  nm, 536 nm and 537 nm for film deposited in 30, 45, and 60 min, respectively (with band gap  $1240/535 = 2.32$  eV,  $1240/536 = 2.31$  eV and  $1240/537 = 2.30$  eV ). The film deposited in 30 min shows higher intensity than the other films. This indicates that the 45 min deposition time gives particles with more than one ordering.

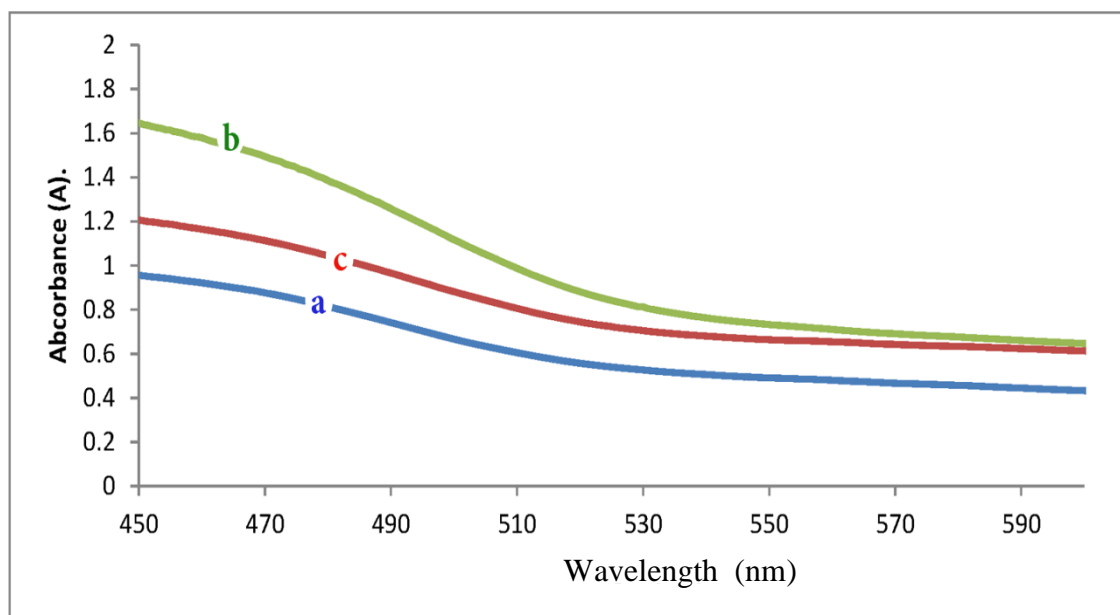


**Figure (3.8):** Photoluminescence spectra CBD-CdS recycling thin film electrodes which prepared without stirring in different times, annealed at 250°C. a) FTO b) 30 min c) 45 min d) 60 min

### 3.2.3 Electronic Absorption Spectra for CdS Thin Film Electrodes

Effect of deposition time on the electronic absorption was investigated for recycled CdS thin film electrodes prepared at different times (30, 45 and

60 min), and annealed at 250°C , Figure (3.9). Absorption edge values observed for deposition time 30, 45 and 60 min were  $\approx$  515 nm, 518 nm and 521 nm, (with band gap  $1240/515 = 2.40$  eV,  $1240/518 = 2.39$  eV and  $1240/521 = 2.38$  eV) were observed for the prepared films respectively. The film prepared in 30 min showed higher absorption intensity. This is because 30 min deposition time gives the more uniform film than other two electrodes.

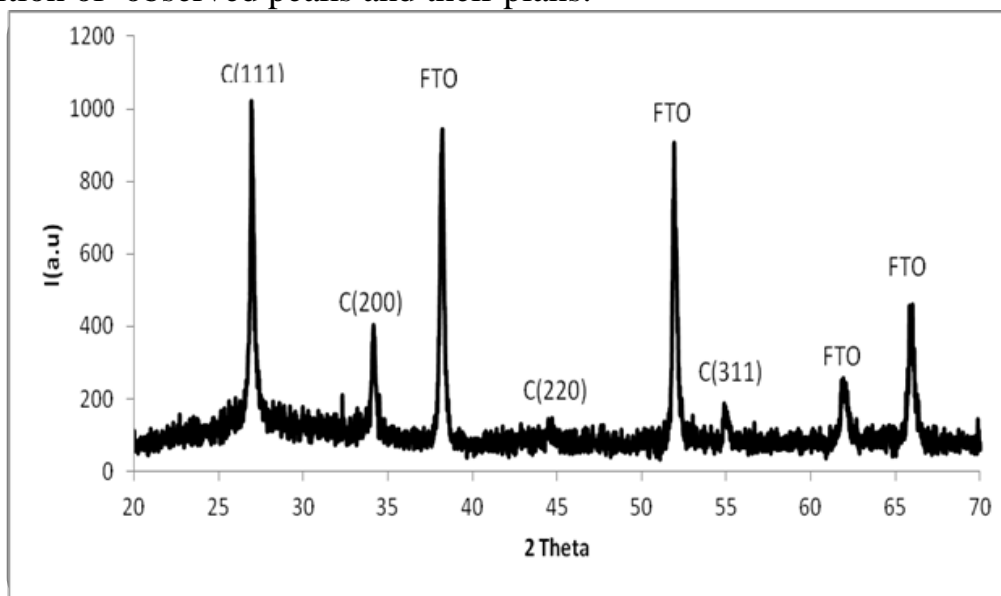


**Figure (3.9):** Electronic absorption spectra for the CdS thin film deposition different time, annealed at 250°C, without stirring a) 30 min b) 45 min c) 60 min.

### 3.2.4 XRD Patterns for CdS Thin Film Electrodes

X-ray diffraction measurements were obtained for recycled CBD-CdS thin film electrodes deposited in 60 min after annealing. X-ray diffraction data showed that annealed CBD-CdS films involved soundly crystalline particles. XRD patterns are shown in Figure (3.10). The average grain size for recycled CBD-CdS particles was found was  $\sim 20.3$  nm after annealing,

Figure (3.10). The films involved cubic phase only. Table (3.5) shows the position of observed peaks and their plans.



**Figure (3.10):** XRD pattern of annealed recycling CBD-CdS film prepared in 60 min without stirring (annealed at 250°C) .

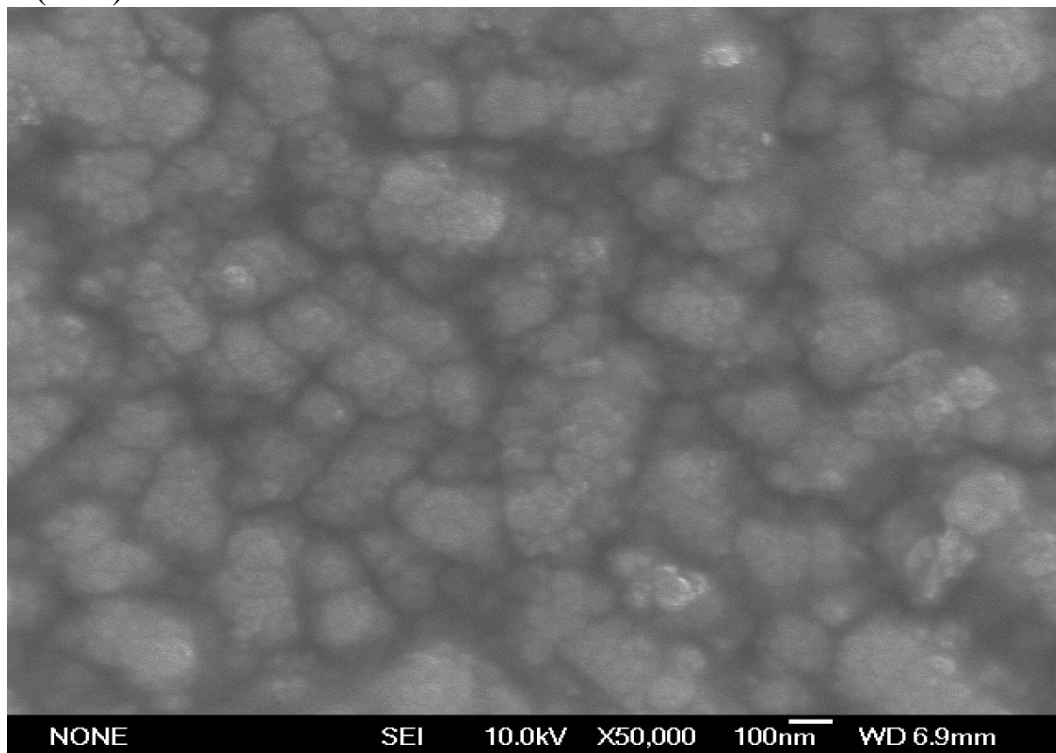
**Table (3.5 ):** XRD results for recycled CBD-CdS thin film electrodes deposition in 60 min without stirring after annealing.

Position of observed peak (2 theta)	Planes	Reference
26.80	C (111)	[54]
34.74	C (200)	[57]
37.74	FTO sub.	[56]
47.50	C (220)	[58]
51.44	FTO sub.	[56]
55.00	C (311)	[54]
61.58	FTO sub.	[56]
65.50	FTO sub.	[56]

### 3.2.5 SEM Images for CdS Thin Film Electrodes

SEM image was obtained for recycled CBD-CdS thin film electrodes after annealing. SEM patterns are shown in Figure (3.11). The SEM images indicate agglomerates (100 nm – 350 nm) nanoparticles (16 nm – 32 nm),

with a spherical shape. The film prepared without stirring shows more compactness than the one prepared with stirring, as shown in Figures (3.6) and (3.11).



**Figure (3.11):** SEM of annealed at ( 250°C) recycled CBD-CdS film in 45 min without stirring.

Based on Figures (3.4) and (3.11), it can be seen that the annealed at (250°C) film prepared without stirring exhibited the stable cubic structure, whereas the film prepared with stirring exhibited a mixed phase hexagonal and cubic.

We see from Figure (3.7) and Table (3.4) that a deposition of cadmium sulfide within 60 min is better than in 30 or 45 min in terms of PEC efficiency and PL intensity. Figure (3.8) shows that deposition within 45 min give a higher intensity for PL emission band. With longer time 30 or 45 min the size of particles was increased, Figure (3.8) shows a red shift.

So the results are consistent with Figure (3.9), where electronic absorption shows that deposition within 60 min is the best. This means particle size has increased with longer deposition time, causing the smaller band gap value.

Table (3.2) and (3.4) show that the value of  $\eta\%$  for films prepared without stirring is higher than those prepared with stirring. It is clear that without stirring films are better than stirred ones as shown in Figures ( 3.7, 3.8 and 3.9). PEC, PL and electronic absorption spectra also indicate same trend.

Tables (3.2) and (3.4) show a comparison between annealed films at 250°C with stirring and without stirring, and the non stirred films exhibited higher PEC characteristics

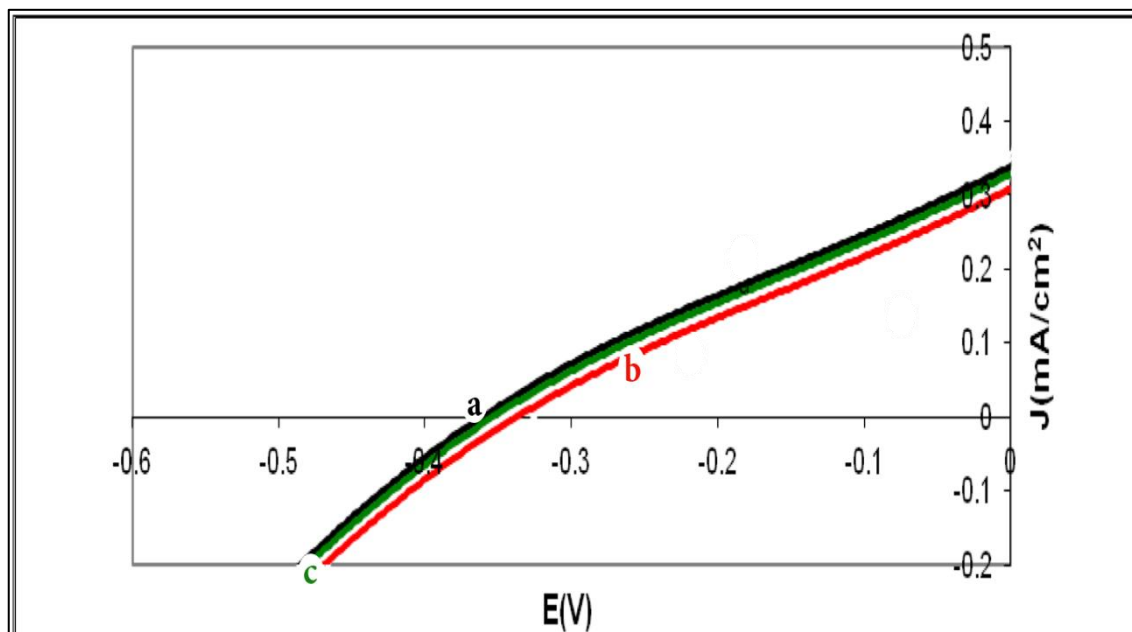
PL showed that the particle size of recycled CdS, film prepared with stirring is bigger than CdS film prepared without stirring and this is consistent with XRD and SEM Figure (3.2) and (3.8). CdS recycled thin film prepared without stirring showed better PEC characteristic than with stirring. This is due to the higher crystallization and uniformly film.

### **3.3 Effect of Deposition Time on Recycled CdS Electrodes (annealed at 300°C with stirring)**

Effect of deposition time on CBD-CdS recycled thin film electrodes prepared in different times 30, 45, 60 min (annealed at 300 °C, with stirring) was studied.

#### **3.3.1 Photo J-V of recycling CdS Thin Film Electrodes**

Photo J-V were measured for CdS thin film electrodes, deposited at different times (30, 45 and 60 min) and annealed at 300°C with the stirring, Figure (3.12). The results are summarized in Table (3.6).



**Figure (3.12):** Photo  $J$ - $V$  plot for annealed CBD-CdS recycling thin film electrodes which prepared in different times with stirring, annealed at 300°C. a) 30 min b) 45 min c) 60 min. All measurements were conducted in aqueous  $S^{2-}/S_x^{2-}$  redox system at room temperature.

The  $V_{oc}$  values for both films deposited in 30 and 60 min were nearly the same. The 45 min film showed lower  $V_{oc}$  value. The film deposited in 30 min showed also higher  $J_{sc}$  value than others. It gives higher percentage conversion efficiency ( $\eta \sim 0.6104\%$ ) Table (3.6) summarizes PEC values for different films. So, the 30 min is the best deposition time among the series.

**Table (3.6) Effect of deposition time on PEC characteristics of CdS thin film electrodes (Annealed at 300°C with Stirring)**

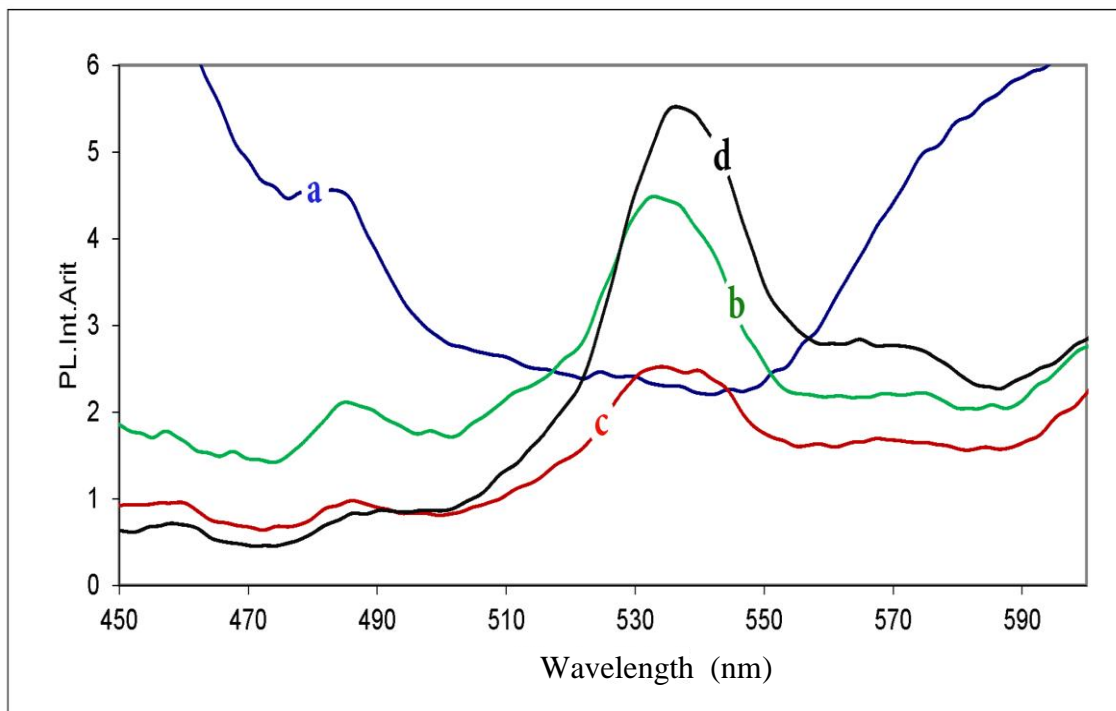
<i>Sample</i>	<i>Dopistion time</i>	$V_{oc}$ (V) $\pm 0.0001$	$J_{sc}$ (mA/cm <sup>2</sup> ) $\pm 0.0001$	$^a \eta$ % $\pm 0.0001$	$^b FF$ %
<b>a</b>	30 min	-0.360	0.360	0.6104	17.72
<b>b</b>	45 min	-0.340	0.330	0.5140	15.23
<b>c</b>	60 min	-0.358	0.350	0.5783	16.45

<sup>a</sup> $\eta$  (%) = [(maximum observed power density) / (reach-in power density)] $\times$ 100%.

<sup>b</sup>FF = [(maximum observed power density) /  $J_{sc} \times V_{oc}$ ] $\times$ 100%.

### 3.3.2 Photoluminescence Spectra for CdS Thin Film

Photoluminescence spectra were investigated for CdS recycled thin film electrodes, annealed at 300°C and prepared with stirring, Figure (3.13). The systems were excited at wavelength 392nm. The Figure shows intense peaks at  $\approx$  535.5 nm, 537 nm and 536 nm for film deposited in 30, 45, and 60 min, respectively (with band gap  $1240/535.5 = 2.31$  eV,  $1240/537 = 2.30$  eV and  $1240/536 = 2.31$  eV, respectively). The film deposited in 45 min shows higher intensity than the other 30 & 60 min films. PL results show that with longer deposition times the mean particle size of CdS increases. The Figure (3.13) shows the different shift spectra between film because of the different size.

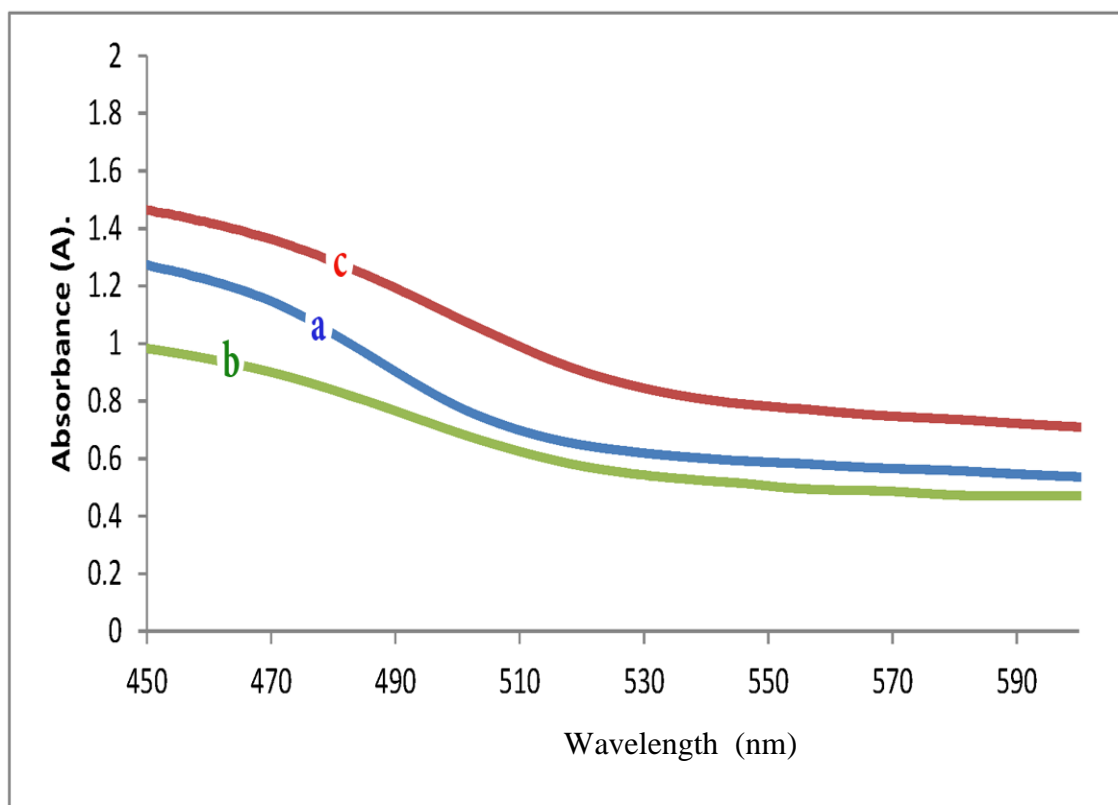


**Figure (3.13):** Photoluminescence spectra CBD-CdS recycling thin film electrodes which prepared different times with stirring, annealed at 300°C. a) FTO b) 30 min c) 45 min d) 60 min.

### 3.3.3 Electronic Absorption Spectra for CdS Thin Film Electrodes

Effect of deposition time on the electronic absorption spectra was investigated for recycling CdS thin film electrodes prepared in different times (30, 45 and 60 min), and annealed at 300°C, Figure (3.14). Values of absorption edges and band gaps for films deposited in 30, 45 and 60 min are 515 nm, 518 nm and 521 nm, and 2.40 eV, 2.39 eV 2.38 eV , respectively. The 45 min film showed higher absorption intensity. This is because 45 min deposition time gives more uniform than other two electrodes.

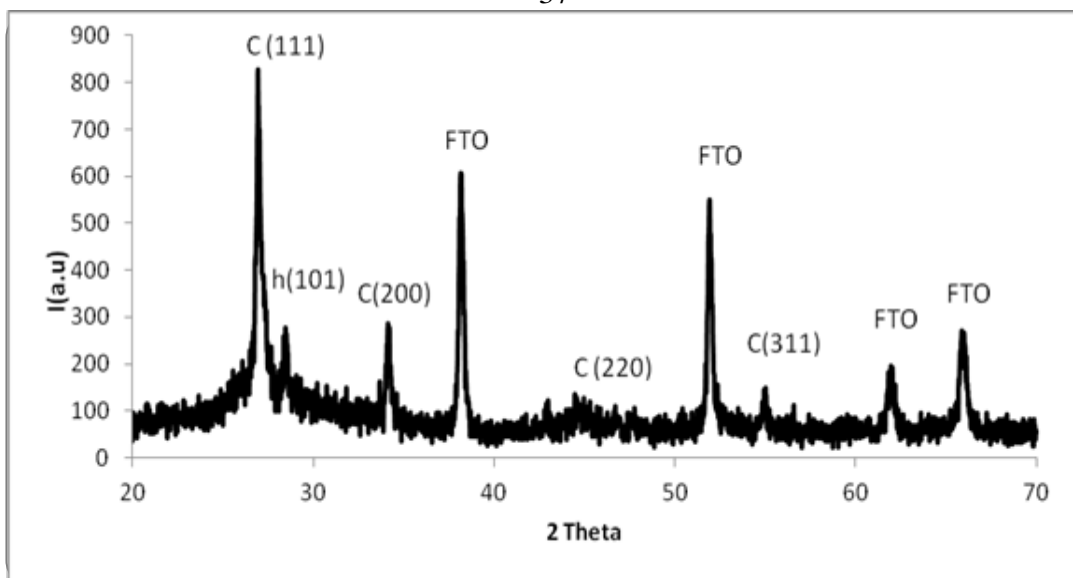




**Figure (3.14):** Electronic absorption spectra for the CdS thin film deposition different time, annealed at 300°C, with stirring a) 30 min b) 45 min c) 60 min.

### 3.3.4 XRD Spectra for CdS Thin Film Electrodes

X-ray diffraction measurements were obtained for recycled CBD-CdS thin film electrodes after deposition in 60 min with annealing at 300°C. X-ray diffraction data showed that annealed CBD-CdS, films involved soundly crystalline particles. XRD patterns in Figure (3.15) shows that the films involved mixed hexagonal and cubic phases. The average grain size for recycled CBD-CdS particles were found in cubic phase with ~ 19.5 nm size and in hexagonal phase with ~ 43.7 nm size after annealing, Figure (3.15). Table (3.7) shows the position of observed peaks and their planes.



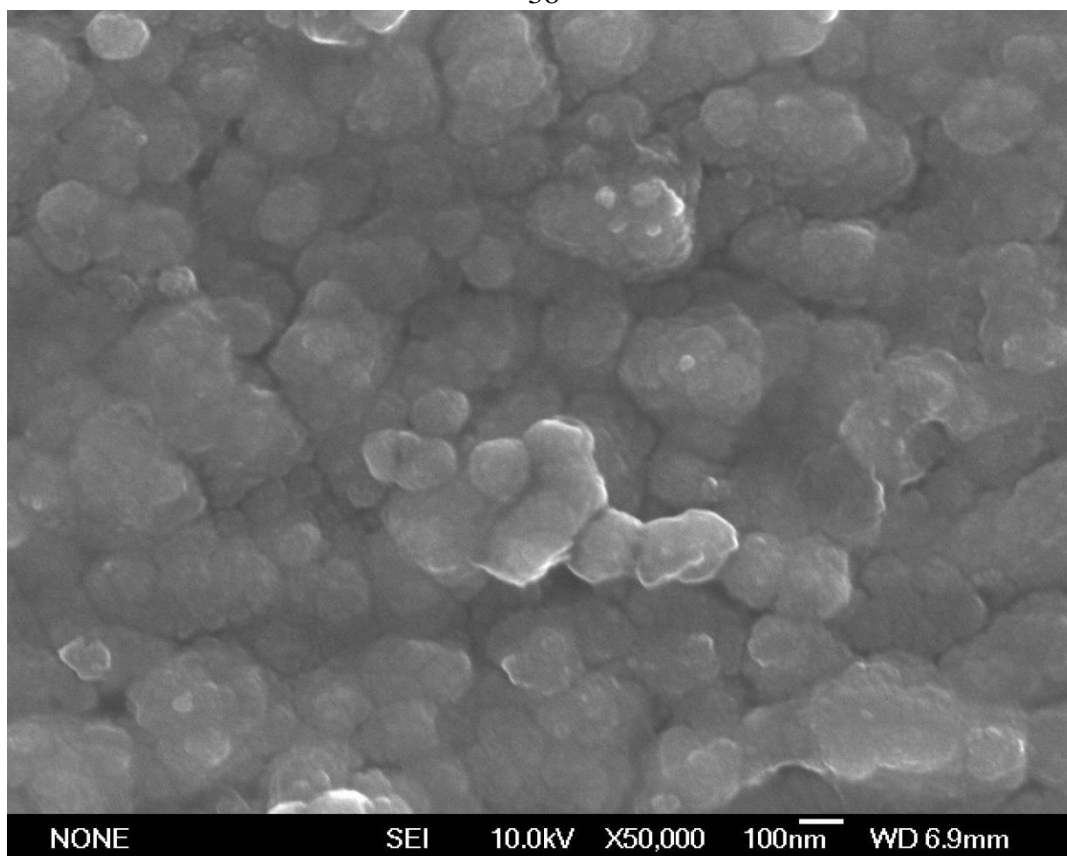
**Figure (3.15):** XRD pattern of annealed recycling CBD-CdS film at 60 min (annealed at 300°C with Stirring) .

**Table (3.7):** XRD results for recycled CBD-CdS thin film electrodes prepared with stirring, after annealing at 300°C

Position of observed peak (2 theta)	Planes	Reference
26.80	<b>C (111)</b>	[54]
28.40	<b>h(101)</b>	[55]
34.74	<b>C (200)</b>	[57]
37.74	FTO sub.	[56]
47.50	<b>C (220)</b>	[58]
51.44	FTO sub.	[56]
55.00	<b>C (311)</b>	[54]
61.58	FTO sub.	[56]
65.50	FTO sub.	[56]

### 3.3.5 SEM Spectra for CdS Thin Film Electrodes

SEM measurements were obtained for recycled CBD-CdS thin film electrodes after annealing. SEM patterns are shown in Figure (3.16). The SEM images indicate agglomerates (100 nm – 500 nm) nanoparticles (20 nm – 45 nm), with a spherical shape



**Figure(3.16):** SEM of recycled CBD-CdS film at 45 min with stirring, annealed at 300°C

In Figure (3.12) and Table (3.6) deposition of cadmium sulfide within 30 min is better than that within 45 or 60 min in terms of PEC efficiency. Figure (3.13), indicates that the PL intensity is higher for films deposited in 45 min. The size of particles decreased with deposition time showing blue shift. So the results are consistent with electronic absorption, which clarified that deposition within 30 min is the best. So the particle size decreased with longer time which led to maximum the energy band gap. By annealing at 300°C, the peak for h(101) showed lower intensity, as shown in Figure (3.15). This is due to transition of hexagonal phase in to the more stable cubic phase by annealing at 300°C. Similar results were reported [60].

Annealing the SCs is known to enhance the films homogeneity, PEC and structure [53, 61, 62]. Annealing reduces defects and removes surface roughness, All CdS contain defects and vacancies from which atoms are missing while treatment with temperature decreases defects or vacancies. These vacancies gradually spread through the film (from surface into the bulk). Vacancy concentration is lowered by diffusion of vacancy to grain boundaries or dislocation [63, 64]. Based on EDX data, Figure (3.5), showed Cd:S, 1:1 with no ( $\text{CdCl}_2$ ) traces. This is because heating at ( $250^\circ\text{C}$  and  $300^\circ\text{C}$ ) removed any possible unreacted  $\text{CdCl}_2$  [65].

Table (3.2) and (3.6) show comparison between annealed films at  $250^\circ\text{C}$  and that  $300^\circ\text{C}$  with stirring, annealing films at  $250^\circ\text{C}$  is better than those at  $300^\circ\text{C}$ .

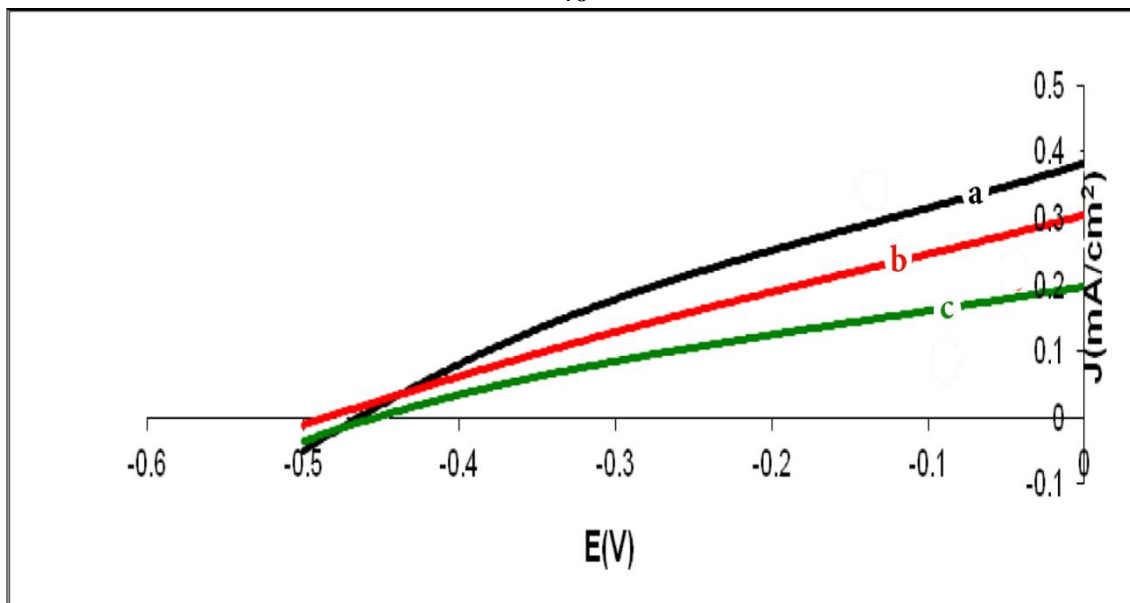
These results are consistent with Adawiya J. Haider for annealing CdS films at  $300^\circ\text{C}$  in terms of PL, XRD and particle size [60].

### **3.4 Effect of Deposition Time on Recycled CdS Electrodes annealed (at $300^\circ\text{C}$ without stirring)**

Effect of deposition time (30, 45 and 60 min) without stirring on CBD-CdS, recycled thin film electrode, (annealed at  $300^\circ\text{C}$ ), was studied.

#### **3.4.1 Photo J-V of recycling CdS Thin Film Electrodes**

Photo J-V plots were measured for CdS thin film electrodes, deposited in different time (30, 45 and 60 min) without stirring and annealed at  $300^\circ\text{C}$ , Figure (3.17). The results are summarized in Table (3.8).



**Figure (3.17):** Photo  $J$ - $V$  plot for annealed CBD-CdS recycling thin film electrodes which prepared different time, annealed at  $300^{\circ}\text{C}$  no stirring. a) 30 min b) 45 min c) 60 min. All measurements were conducted in aqueous  $\text{S}^{2-}/\text{S}_x^{2-}$  redox system at room temperature

The  $V_{oc}$  values for all film are similar, the film deposited in 30 min showed higher  $J_{sc}$  value than the other. It gives higher percentage conversion efficiency ( $\eta \sim 1.04\%$ ) Table (3.8) summarizes PEC values for different films. So 30 min is best deposition time among the series.

**Table (3.8):** Effect of deposition time on PEC characteristics of CdS thin film electrodes (Annealed at  $300^{\circ}\text{C}$  without stirring).

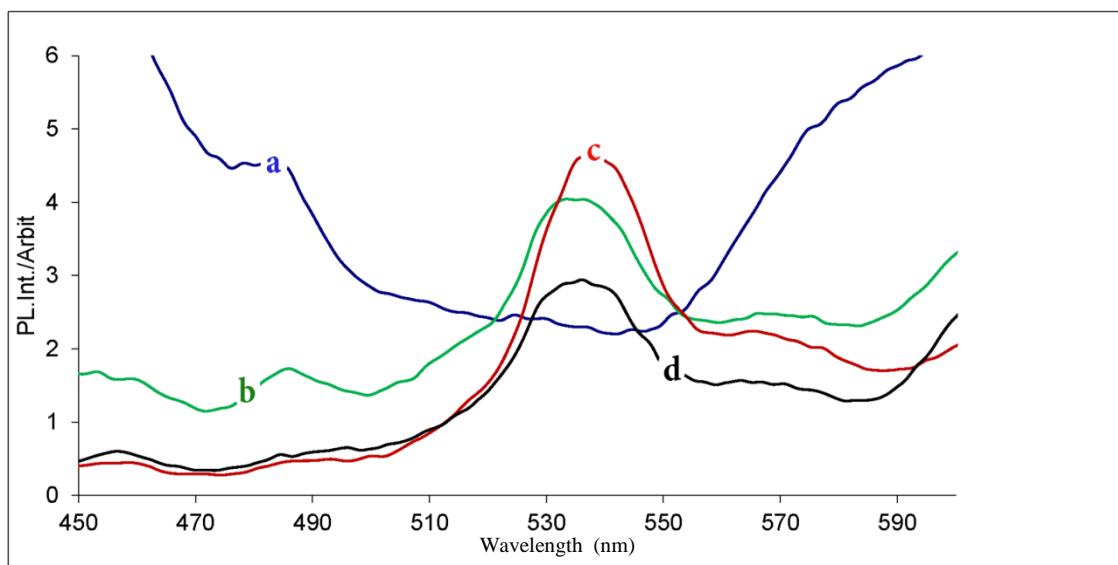
<i>Sample</i>	<i>Deposition time</i>	$V_{oc}$ (V) $\pm 0.0001$	$J_{sc}$ ( $\text{mA}/\text{cm}^2$ ) $\pm 0.0001$	$^a\eta$ % $\pm 0.0001$	$^bFF$ %
<b>a</b>	30 min	-0.498	0.380	1.0400	30.88
<b>b</b>	45 min	-0.494	0.260	0.7849	18.52
<b>c</b>	60 min	-0.490	0.190	0.4819	14.58

$^a\eta$  (%) = [(maximum observed power density) / (reach-in power density)] $\times 100\%$ .

$^bFF$  = [(maximum observed power density) /  $J_{sc} \times V_{oc}$ ] $\times 100\%$ .

### 3.4.2 Photoluminescence Spectra for CdS Thin Films

Photoluminescence spectra were investigated for recycled CdS thin film electrodes, annealed at 300°C, deposited at different times (30, 45 and 60 min) without stirring, Figure (3.18). The systems were excited at wavelength 392nm. The Figures show peak intense peaks at  $\approx$  535 nm, 536 nm and 538 nm for film deposited in 30, 45, and 60 min, respectively (with band gap  $1240/535 = 2.32$  eV,  $1240/536 = 2.31$  eV and  $1240/538 = 2.30$  eV, respectively). The film deposited in 60 min shows higher intensity than the other films. The PL intensity increased with deposition time. A red shift also occurred with increased deposition time. This is due to larger particle size, which is known to cause a red shift [59, 66].

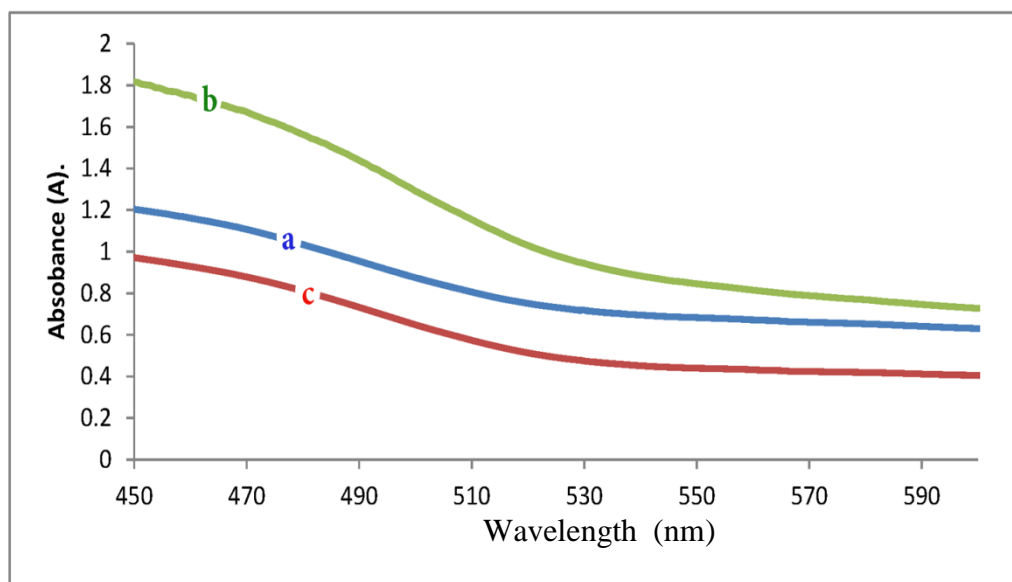


**Figure (3.18):** Photoluminescence spectra CBD-CdS recycling thin film electrodes which prepared different times without stirring, annealed at 300°C. a) FTO b) 30 min c) 45 min d) 60 min

### 3.4.3 Electronic Absorption Spectra for CdS Thin Film Electrodes

Effect of deposition time on the electronic absorption spectra was investigated for recycled CdS thin film electrodes prepared at different

times (30, 45 and 60 min) annealed at 300°C, Figure (3.19). Absorption edge values deposition time 30, 45 and 60 min  $\approx$  504 nm, 509 nm and 517 nm, (with band gap  $1240/504 = 2.46$  eV,  $1240/509 = 2.43$  eV and  $1240/517 = 2.39$  eV, respectively), were observed for the prepared films respectively. The film 60 min showed higher absorption intensity. This is because the 60 min deposition time gave more uniform film than other two electrodes.

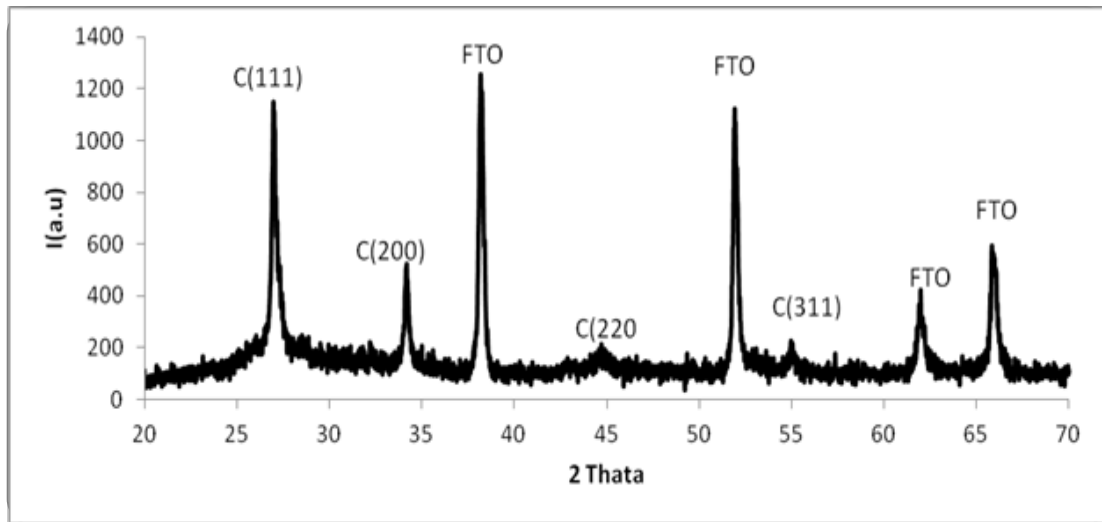


**Figure (3.19):** Electronic absorption spectra for the CdS thin film deposited in different time, annealed at 300°C, with stirring a) 30 min b) 45 min c) 60 min.

#### 3.4.4 XRD Spectra for CdS Thin Film Electrodes

X-ray diffraction measurements were obtained for recycled CBD-CdS thin film electrodes deposited in 60 min after annealing. X-ray diffraction data showed that annealed CBD-CdS films involved soundly crystalline particles. XRD patterns are shown in Figure (3.20). The average grain size

for recycled CBD-CdS particles was found to be  $\sim 32.5$  nm after annealing, Figure (3.20). The films involved cubic phase only. Table (3.9) shows positions of observed peaks and their planes.



**Figure (3.20):** XRD pattern of annealed recycling CBD-CdS film at 60 min (annealed at 300°C, without Stirring) .

**Table (3.9): XRD results for (annealed at 300°C) recycled CBD-CdS thin film electrodes deposited in 60 min without stirring.**

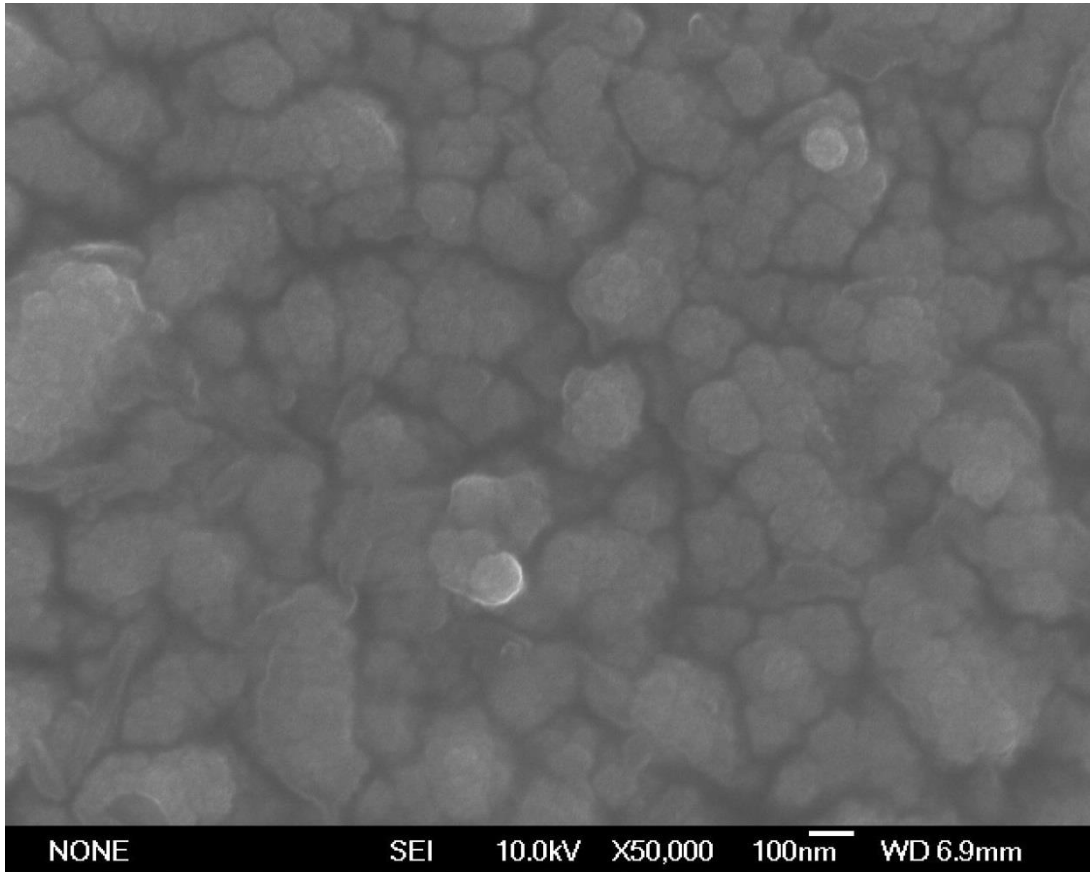
Position of observed peak (2 theta)	Planes	Reference
26.80	<b>C (111)</b>	[54]
34.74	<b>C (200)</b>	[57]
37.74	FTO sub.	[56]
47.50	<b>C (220)</b>	[58]
51.44	FTO sub.	[56]
55.00	<b>C (311)</b>	[54]
61.58	FTO sub.	[56]
65.50	FTO sub.	[56]

### 3.3.5 SEM Spectra for CdS Thin Film Electrodes

SEM measurements were obtained for recycled CBD-CdS thin film electrodes after annealing. SEM patterns are shown in Figure (3.21). The



SEM image indicates agglomerates (50 nm – 400 nm) nanoparticles (16 nm – 32 nm), with a spherical shape



**Figure(3.21):** SEM of annealed recycling CBD-CdS film at 45 min without stirring annealed at 300°C .

Figure (3.17) and Table (3.8) showed that the deposition of cadmium sulfide within 30 min is better than that within 45 or 60 min in terms of PEC efficiency, Figure (3.18 ), indicates that the PL intensity is higher for films deposited in 60 min. The size of particles increased with time and showed a red shift, so that the results are consistent with electronic absorption, which clarified that deposition within 60 min is the best. So the

size particles have increased with longer deposition time, causing the smaller band gap value.

From Table (3.6) and (3.8) We can see that the value  $\eta\%$  for films annealed at 300°C is higher for the film prepared without stirring. It is clear that without stirring films are better than stirred ones as shown in Figure (3.17, 3.18 and 3.19). PEC, PL and electronic absorption spectra also indicate same trend. The facts are explained by kinetics. Stirring increases reaction rate, and yield particles with smaller size due to quick formation of more nuclei [67]

Table (3.2) and (3.6) show comparisons between annealed films at 250°C and at 300°C in stirring, and from these two tables, we note that deposition of annealed films at 250°C is better than those at 300°C. The 250°C temperature is the optimal annealing temperature. This is consistent with the literature [68, 69]

Table ( 3.6 ) and ( 3.8) also show that deposition of annealed films at 300°C without stirring is better than those at 300°C with stirring [70].

Films prepared in 60 min deposition time with stirring, followed by annealing at 250°C, give cubic phase only. When annealed at 250°C without stirring as shown Figure (3.4), the films give only cubic phase.

Figures (3.13) and (3.18) show that the film prepared without stirring has larger size than the one prepared with stirring, both being annealed at 300°C. This indicates that without stirring, high crystallinity is expected.

**Conclusions:**

1. CdS film electrode based solar cells can be recycled by simple techniques described in this work.
2. Chemical bath deposition can be used to deposit CdS film electrodes from  $\text{Cd}^{2+}$  solution, recovered by recycling used CdS cells with mineral acid.
3. Effect of deposition time (30, 45 and 60 min) on PEC characteristics was studied. The longer 60 min deposition time gives best PEC, with annealing at  $250^{\circ}\text{C}$ . Annealing at  $300^{\circ}\text{C}$  showed better PEC characteristics for 30 min film.
4. Stirring may effect PL intensity electronic absorption and PEC characteristics of recycled electrodes .
5. CdS recycled thin film annealed at  $250^{\circ}\text{C}$  and  $300^{\circ}\text{C}$  without stirring involved nanoparticles with only cubic phase.

**Suggestion for Future Work:**

1. Recycling of CdS film using other different techniques (ECD and ECD/CBD).
2. Recycling of other types of semiconductors (CdSe, CuS and many others).
3. Coating the recycled film electrode with electro-active matrices.
4. Doping the recycled CdS film with different dopants.

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جامعة النجاح الوطنية  
كلية الدراسات العليا

## اعادة تدوير الخلايا الشمسية المكونة من الافلام الرقيقة لمركب CdS والمحضر بالترسيب الكيميائي

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قدمت هذه الأطروحة استكمالاً لمتطلبات الحصول على درجة الماجستير في الكيمياء بكلية الدراسات العليا في جامعة النجاح الوطنية في نابلس، فلسطين.

2014

ب

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### الملخص

تم تدوير و اعادة استخدام اقطاب CdS المثبتة على FTO/Glass بواسطة حمام الترسيب الكيميائي (CBD). وتم فحص هذه التقنية اعادة التدوير هنا للمرة الاولى. وتم استخدام المجهر الالكتروني (SEM) وحيود الاشعة السينية (XRD)، وأطياف لمعان الضوئي (PL) وأطياف الامتصاص لدراسة الافلام المختلفة المدورة. و تم دراسة الخصائص الكهروكيميائية (PEC) للافلام المختلفة المدورة ، مثل منحنيات التيار والجهد وكفاءة التحويل . وتمت دراسة (XRD) و (SEM) وتأثيرها بطريقة تحضير الافلام.

تم تحسين خصائص الافلام بتسخينها على درجة حرارة 250°C و 300°C تحت نيتروجين. وتم اجراء التبريد على الافلام بعد تسخينها الى درجة حرارة الغرفة ببطء . حيث تم دراسة تأثير التسخين على صفات الافلام الفيزيائية والكهربائية.

تم كذلك دراسة تاثير التحريك اثناء تحضير الافلام على خصائصها الفيزيائية والكهربائية، حيث وجد ان الافلام المحضرة بدون تحريك لها خواص افضل من الافلام المحضرة مع التحريك . وتم ايضا دراسة تاثير زمن ترسيب التحضير على خصائص الافلام حيث لوحظ ان الزمن الافضل كان 45 دقيقة من اجل زيادة شدة الوميض ، اما الوقت 60 دقيقة اعطى افلام اعلى كفاءة في تحويل الضوء الى كهرباء.

تمت دراسة تأثير درجة حرارة التسخين على صفات الافلام المدورة، ف لوحظ ان درجة التسخين 250°C لمدة 60 دقيقة اعطت افلاما لها كفاءة تحويل اعلى من غيرها.

ت

بينت الدراسة أنه يمكن إعادة تدوير و استخدام اقطاب اشباة الموصلات من نوع الافلام CdS المستخدمة في عمليات التحويل الفوتو كهربائي بدلا من تركها ، دون ان تنقص كفاءتها و صفتها وهذا محور اهداف هذه الدراسة.