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# Enhanced PEC characteristics for CdSe polycrystalline film electrodes prepared by combined electrochemical/chemical bath depositions

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### Abstract

Polycrystalline CdSe films have been deposited onto fluorine doped tin oxide (FTO/glass) substrates by three different techniques, electrochemical deposition (ECD), chemical bath deposition (CBD) and, for the first time, combined ECD and CBD (ECD/CBD). The films were comparatively characterized by photoluminescence spectra (PL), electronic absorption spectra, scanning electron microscopy (SEM) and X-ray diffraction (XRD). The SEM micrographs show that the films involved rod shaped agglomerates with various lengths and widths. XRD patterns show that the three systems involved nano-sized CdSe particles with cubic type crystals. Based on Scherrer's equation, the ECD film showed larger particle size than the CBD film, while the ECD/CBD film showed largest particles among the series. Similarly, the band gap values varied for different films as CBD > ECD > ECD/CBD. Photo-electrochemical (PEC) characteristics, including photo-current density vs. voltage (J-V) plots, conversion efficiency ( $\eta$ ), fill factor (FF) and stability were all studied for different film electrodes. The films exhibited n-type behaviors with direct band gaps. The new ECD/CBD-CdSe electrode exhibited higher conversion efficiency ( $\eta$ % ~ 4.40) than other counterparts. The results show the added value of combining ECD and CBD methods in enhancing PEC characteristics of CdSe film electrodes, even with no additional treatment.

Key Words: CdSe film electrodes; Electrochemical Deposition; Chemical Bath Deposition; Combined Electrochemical/Chemical Bath Deposition; Photo-electrochemistry; Conversion Efficiency Enhancement; Stability Enhancement

### 1. Introduction

Like other metal chalcogenides, polycrystalline cadmium selenide (CdSe) film electrodes, with nano-size particles, gained great attention in material research and technology. With their suitable band gap in the range 1.7-2.2 eV, CdSe polycrystalline films have been heavily studied from different aspects [1-4]. The band gap is suitable for solar spectrum and should yield efficient photo-conversion processes [5]. CdSe thin films are prepared by different methods, such as thermal evaporation, electrochemical deposition (ECD) , spray pyrolysis , successive ionic layer adsorption (SILA), chemical vapor deposition (CVD) and chemical bath deposition (CBD) [6]. Among those ECD and CBD depositions are convenient, non-costly and demand no advanced technology. The ECD process yields CdS films with high surface uniformity and good adherence to the FTO substrate while the CBD yields films with sound thicknesses suitable for PEC applications [7].

CdSe films prepared by either ECD or CBD have not been widely described for PEC processes. Polycrystalline CdSe films, prepared by CBD or ECD, are unstable under PEC conditions. This may explain why they are not widely used for photo-conversion. The monolithic CdSe electrodes are reported to yield conversion efficiency values up to 7% [8, 9]. Coating the CdSe monolithic electrodes with organometallic polymers may enhance their PEC characteristics such as the short-circuit current density [10]. In a recent study, we showed that CdSe film electrodes degrade under PEC conditions to yield the hazardous  $Cd^{2+}$  ions, and the as-prepared film exhibited immeasurably low conversion efficiency. After modification with electro-active complexes, embedded inside polysiloxane matrices, the CBD prepared CdSe films showed a measurable conversion efficiency of 0.24%. Higher conversion efficiency (1.1%) was observed by pre-annealing the film prior to coating [2, 11]. Annealing followed by etching CdSe films, electrodeposited onto titanium substrates, enhances their PEC conversion efficiency from 0.8 to 3.45% as reported earlier [11]. Therefore, it is worth looking for new methods to improve PEC characteristics of CdSe film electrodes.

In our search to enhance metal chalcogenide based film electrode PEC conversion efficiency and stability, a new simple technique has been examined for CdS film electrodes [12]. The method was based on combining the advantages of both CBD (suitable film thickness) and ECD (good adherence with FTO) preparations together, namely by using ECD to deposit a thin layer, followed by depositing a thicker layer by CBD. Enhanced PEC characteristics have been observed by the combined preparation. While literature showed conversion values of 0.049% for the CBD prepared CdS film [13], a value of 0.29% has been observed by the combined preparation method [12]. The conversion efficiency has thus been improved by 6 fold when using the combined preparation method in CdS film electrodes.

The combined ECD/CBD preparation method will be employed here to enhance CdSe film electrodes in PEC processes for the first time, keeping an eye on its conversion efficiency and stability. It is assumed that the ECD/CBD film will exhibit higher conversion efficiency than either ECD or CBD films prepared separately. The ECD layer will have good adherence to the

FTO surface [7], while the CBD layer will have the preferred thickness [14-16]. Effect of annealing on PEC characteristics of the CdSe films will also be studied.

### 2. Experimental

#### 2.1 Starting materials:

(CdCl<sub>2</sub>.2H<sub>2</sub>O, Na<sub>2</sub>S.XH<sub>2</sub>O and elemental sulfur, NH<sub>4</sub>Cl, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, HCl) were all purchased in pure form from Sigma-Aldrich or from (SDFCL). Transparent (~80% for wavelengths longer than 330 nm) highly conductive (~7  $\Omega^{-2}$ ) Glass/FTO substrates were purchased from Aldrich. Organic solvents were purchased from Sigma-Aldrich in analytical grade purity.

#### 2.2 Equipment:

Solid CdSe film electronic absorption spectra were measured on a Shimadzu UV-1601 spectrometer at room temperature, in the range 400-800 nm. Baseline correction was performed using pre-cleaned glass/FTO substrates. Solid state photoluminescence (PL) spectra were measured on a Perkin-Elmer LS 50 spectrometer with a cut-off filter to exclude reflected 500 nm and shorter wavelengths). The excitation wavelength was 385 nm.

A Hitachi, Model S-4300, Field Emission Scanning Electron Microscope in *Korea Institute* of Energy Research, Korea, was used for SEM measurement. The X-ray diffraction patterns were measured on a PANalytical X'Pert PRO X-ray diffractometer (XRD), using a CuKa ( $\lambda$ =1.5418 Å) at the *Pukyong National University, Korea*. Current density vs. potential (*J-V*) plots were measured on a PAR 261A Potentiostat/Galvanostat.

#### 2.2 CdSe film electrode preparation

CdSe thin films were prepared by electrochemical deposition ECD, chemical bath deposition CBD, and combined ECD/CBD.

#### 2.2.1 ECD method:

The ECD preparation is based on literature [3, 17], with some modification. FTO/ glass substrates (dipped area 2 cm X 1 cm) were used as working electrodes. A platinum sheet was used as a counter electrode. The counter electrode was also connected to the cell internal reference electrode (which was pre-calibrated vs. Ag/AgCl). The electrodes were dipped inside a solution which involved CdCl<sub>2</sub>.H<sub>2</sub>O (0.008 M) and Na<sub>2</sub>SeO<sub>3</sub> (0.005M). The Na<sub>2</sub>SeO<sub>3</sub> solution was prepared as described earlier [18]. An aqueous solution of sodium sulfite was prepared by dissolving Na<sub>2</sub>SO<sub>3</sub> (40.00 g) in distilled water (200 mL). The selenium powder (4.00 g) was then added and the system was refluxed at 90°C for 15 hr. The Na<sub>2</sub>SeSO<sub>3</sub> solution was then filtered and stored.

Cadmium chloride solution (1.60 mL, 0.50 M) was first mixed with  $Na_2SeSO_3$  solution (2.00 mL, 0.25 M) in a beaker and transferred into 100 ml volumetric flask. The volume was adjusted with distilled water to the mark with mixing. The solution was transferred to the deposition bath cell. Ammonium solution (2-3 drops) was added to control the solution pH to ~11. Nitrogen gas (99.999%) was bubbled inside the solution prior to deposition for 5 minutes to remove any dissolved O<sub>2</sub>. The nitrogen flow was continued above the solution during deposition with gentle stirring. The deposition potential was fixed at a constant voltage (- 1.0 volt vs. Ag/AgCl) using

DC stripping. Thin films were deposited in different periods of time, 15, 30 and 45 min. The film annealed in 15 min showed preferred characteristics, and unless otherwise stated all ECD films described were prepared in 15 min. The samples were taken out, washed with distilled water, dried by blowing nitrogen and stored in desiccator. The average film thickness value measured by gravimetry (assuming a density of 5.42 g/cm<sup>2</sup>) as described earlier [19] and by electrochemical calculations using the Faraday Law, was ~900 nm. Conductivity was calculated across the CdSe film by plotting the current density (A/cm<sup>2</sup>) vs. applied potential and by 4-probe, and was ~1.5X10<sup>-4</sup> ( $\Omega$ .cm)<sup>-1</sup>.

#### 2.2.2 CBD method:

The CBD procedure is based on earlier literature [2, 20, 21], with some modification. Two complexing agents were used here, triethanolamine and ammonia. The chemical bath involved CdCl<sub>2</sub> (5.00 mL, 0.50 M), triethanolamine (TEA) (5.00 mL, 7.4 M), NH<sub>3</sub> (2.50 mL, 13.4 M), Na<sub>2</sub>SeSO<sub>3</sub> (8.00 mL, 0.25 M) prepared as described above, and distilled water (20 mL). The materials were added to the reaction container in this order. The pH value of the solution was ~11. Pre-cleaned FTO/glass substrates were then vertically inserted in the solution. The deposition was allowed to proceed at 70°C for 4 h with continuous stirring. The system was tightly closed with rubber sealing. The solution color changed from colorless to pale yellow to bright orange and finally to red wine during the process. The coated substrate was then taken out, washed well with distilled water and allowed to dry in a desiccator. The average film thickness value, calculated gravimetrically was ~47 µm. The thickness for the CBD layer observed here is higher than that reported earlier for CBD prepared film [2]. The difference is due to difference in preparation method. The film conductivity was ~7.5X10<sup>-4</sup> ( $\Omega$ .cm)<sup>-1</sup>.

#### 2.2.3 Combined ECD/CBD method:

The procedure started with preparing the ECD-CdSe films on FTO/glass substrates, followed by CBD deposition as described above. The average value for the film thickness was 53  $\mu$ m, and the conductivity was ~9X10<sup>-4</sup> ( $\Omega$ .cm)<sup>-1</sup>. The ECD/CBD film electrode is shown in Scheme I.





#### 2.3 Annealing procedure:

A controlled-temperature horizontal tube furnace was used for CdSe film annealing purposes. The temperature was raised to the desired setting by a control unit. The prepared films, which were placed inside a Pyrex cylinder through which nitrogen gas was allowed to flow, were then inserted inside the tube furnace at the desired temperature. Annealing was continued for one hour. Cooling was performed by two ways, slow cooling and fast cooling. In slow cooling, the cylinders were kept inside the furnace which was allowed to cool slowly to room temperature in a course of 2 h, with average cooling rate equal to 2 °C/min. In fast cooling, the cylinders were taken out of the furnace and left to cool under  $N_2$  atmosphere to room temperature in less than15 minutes.

#### 2.4 The PEC experiment:

PEC experiments were conducted inside a quartz cell. The CdSe film electrodes were used as working electrodes. A platinum sheet was used as a counter electrode, and was connected to the potentiostat internal cell reference electrode. The internal cell was calibrated with Ag/AgCl reference electrode, and its reference was the same for NHE. Therefore, all used potentials are thus measured vs. NHE reference. The electrodes were dipped in a poly-sulfide (NaOH/S<sup>-2</sup>/S<sub>x</sub><sup>-2</sup>) redox couple solution, which involved Na<sub>2</sub>S (0.10 M), S (0.10 M) and NaOH (0.10 M). High purity nitrogen (99.9999%) was bubbled through the solution for 5 minutes to remove oxygen before each experiment. The nitrogen flow was then kept bubbling above the solution during each experiment. The photo J-V plots were measured under illumination with the 50 Watt

halogen spot lamp. The light intensity at the electrode surface was  $61 \text{ W/m}^2$  as measured by a model LX-102 digital light meter, pre-calibrated with a Kipp & Zonen CM11 pyranometer. The dark J-V plots were measured in complete dark by covering the system with a thick blanket.

Film stability under PEC conditions was studied for the three different films by keeping the working electrode under constant illumination  $(0.02 \text{ W/cm}^2)$  at 0.00 V applied bias (vs. NHE reference), at room temperature. The value of short- circuit current density was plotted vs. time.

### 3. Results and discussion

#### 3.1. CdSe film characterization:

CdSe films, prepared by different methods, have been comparatively characterized by electronic absorption spectra, PL emission spectra, SEM and XRD. Figure (1) shows plots  $(\alpha hv)^{1/2}$  vs. hv for the ECD and the CBD films, assuming direct band gap behavior [22]. The ECD/CBD film is not shown because it was too thick to study by electronic absorption spectra. Both ECD and CBD films exhibited direct band gap behavior, with band gap energies 2.09 and 2.20 eV, respectively. Therefore, as the CBD films have smaller particles than those in the ECD film, value of the band gap should be higher. It is known that the band gap value of a given semiconductor increases as particle size decreases [3]. Further evidence is presented by XRD patterns below.



**Figure (1)** Optical properties measured for CdSe thin films prepared by a) ECD technique, b) CBD technique.

The PL spectra measured for non-annealed ECD, CBD and combined ECD/CBD-CdSe films are shown in Figure (2). The PL spectra show that ECD, CBD and ECD/CBD films have emission bands with maximum intensities at 588 nm (2.11 eV), 578 nm (2.14 eV) and 599 (2.07 eV) respectively. The emission wavelengths are longer than other literature values observed for CBD prepared CdSe films with smaller nano-particles, in the range 3.67 - 6.92 Å [23]. The band gap values obtained from PL spectra are consistent with those obtained from electronic absorption spectra. The spectral results are also consistent with particle size values for different films. As discussed below, the particle sizes for different films vary as CBD < ECD < ECD/CBD. As particle size increases, the band gap value decreases and the emission wavelength becomes longer. Such behavior is known in films with nano-size particles [23].

The PL spectra showed different intensity values for different films, in the order CBD < ECD < CBD/ECD. The PL intensity variations are due to differences in crystallinity and imperfection density [15, 24]. With larger particle size, lower imperfection is expected, and the ECD/CBD film should have highest PL intensity. The lower PL intensity in CBD film is due to its smaller particle sizes, which cause higher relative number of surface atoms and higher imperfection. The intensity values thus indicate that surface states density is highest in the CBD film, and lowest in the ECD/CBD film.



Figure (2): Photo-luminescence spectra measured for CdSe thin films prepared by: a) ECD,b) CBD, c) combined ECD\CBD technique.

SEM images for ECD, CBD and ECD/CBD films are shown in Figure (3). The SEM micrographs resemble earlier SEM micrographs reported for CdSe prepared by CBD, in terms of agglomerate structures and sizes [5, 23, 25]. The Figure shows that all films involved agglomerates of smaller nano-sized CdSe particles. In case of CBD film, the agglomerates are rod shaped with ~200 nm in diameter and ~400 nm in length. The ECD film involved rod shaped

agglomerates with ~300 nm in diameter and ~400 nm in length. The ECD is clearly more compact with more inter-particle connections. The ECD/CBD film involves agglomerates with different shapes and sizes from other counterparts.

As the CBD layer is deposited onto the pre-deposited ECD layer, two layers may be expected, as reported earlier for CdS films [12]. Figure (4) shows that the ECD/CBD film involves one type of agglomerates that differ from either ECD or CBD films. A closer look at the large agglomerates (~1000 nm) indicates that they involve combinations of smaller rod-shaped agglomerates that are firmly welded together. The large agglomerates are also strongly interconnected together yielding a compact network in the film with no separate layers. This explains the higher ECD/CBD film conductivity compared to other counterparts. The importance of all these features in PEC study will be discussed again, *vide infra*.

In all films, the agglomerates are composed of smaller nano-size particles. Due to their small sizes, the nano-size particles could not be clearly observed for different films by the SEM microscopy.



Figure (3): SEM images for CdSe films prepared by (a) ECD, (b) CBD and (c) ECD/CBD methods.

XRD patterns for different films are shown in Figure (4). By comparison with earlier reports [6, 26, 27], the XRD patterns show that all films involved cubic type polycrystalline CdSe materials. The three characteristic bands at  $25.39^{\circ}$  (111),  $42.19^{\circ}$  (220) and  $49.74^{\circ}$  (311) [28] are observed here. The peaks at 27, 29.90, 34.09, 38.16, 38.80 and 51.80° are due to the FTO films present in the Glass/FTO substrates. The FTO peak at  $27^{\circ}$  appears only as a small shoulder in Figure 4c due to the relatively thick CuSe film on the substrate.

Despite its lower stability, compared to the hexagonal structure, the cubic structure dominates in the present study as preparations were made at relatively low temperatures, in accordance with literature [29]. The XRD patterns with their broad bands indicate that the CdSe films involve nano-size particles. The nano-size nature of CBD prepared CdSe films is well documented by XRD study in earlier literature [5, 23, 30]. This is consistent with the SEM results, discussed above, which confirm the nano-size nature of the particles present inside larger agglomerates. Based on Scherrer's equation, the average particle size values were 6.9 nm for ECD film, 4.5 nm for CBD film and 7.4 nm for ECD/CBD film. The particle size values are consistent with other values reported earlier [23]. The XRD results show that the particle size varied for different films as CBD < ECD < ECD/CBD. The XRD results, together with the optical spectra and the SEM micrographs, indicate that the CdSe films differ in value of particle size in the order CBD < ECD < ECD/CBD.



**Figure (4):** XRD patterns measured for CdSe thin films prepared by a) ECD, b) CBD, and c) ECD/CBD methods.

#### 3.2 PEC characteristics

PEC studies were performed for the different CdSe films. Dark J-V plots, photo J-V plots, conversion efficiency ( $\eta$ ), short-circuit current density ( $J_{sc}$ ), open circuit potential ( $V_{OC}$ ), fill-factor (FF) and stability under PEC conditions were all studied. Dark J-V plots were inconclusive and are excluded here due to occurrence of leakage current.

Photo J-V plots are shown in Figure (5), which shows that the CdSe films have n-type behavior. Positive values for  $J_{SC}$  and negative values for  $V_{OC}$  confirm the n-type nature of the three prepared film electrodes. The Figure shows that the measured values of both  $J_{SC}$  and  $V_{OC}$  varied for different films in the order ECD < CBD < ECD/CBD.



**Figure (5):** Photo *J-V* plots for CdSe thin film electrodes prepared by *a*) ECD, *b*) CBD and c) ECD\CBD. All measurements were conducted in aqueous  $S^{2-}/S_x^{-2-}$  redox system at room temperature.

The Figure results are summarized in Table (1) below. The Table shows that the combined ECD/CBD film electrode exhibited higher PEC characteristics, namely  $V_{oc}$ ,  $J_{sc}$ , and  $\eta$ , than other two counterparts. The results prove the basic hypothesis of this work where the ECD/CBD film is anticipated to combine the advantages of both ECD (good adherence to FTO surface) and CBD (suitable thickness) together. This is consistent with earlier study on CdS thin film electrodes [12].

The PEC characteristics for different film electrodes follow same variation trends observed in spectral results, SEM micrgraphs and XRD patterns, discussed above. The conversion efficiency of different electrodes varied as CBD < ECD < ECD/CBD. The ECD film shows higher conversion efficiency than the CBD electrode, because it has higher adherence [7] to the FTO, and higher crystallinity and uniformity than the CBD electrode, as evident from PL emission

spectra and XRD patterns. On the other hand the CBD film shows higher FF value than the ECD film electrode, which is attributed to its higher thickness, as shown in Sections 2.2.1 and 2.2.2 above. PEC characteristics can be enhanced by thicker film electrodes as reported earlier for other semiconductor film electrodes [14-16].

The table shows that the new ECD/CBD film shows the about 3.7 and 2.6 fold efficiency enhancement compared to the CBD and ECD electrodes, respectively. The ECD/CBD film higher efficiency is due to enhanced crystallinity as observed by XRD and PL emission spectra. The higher inter-agglomerate connectivity in the ECD/CBD film observed from SEM micrographs further enhances the conversion efficiency. This is evident from the value of ECD/CBD film conductivity being highest among the series as shown in Section 2.2 above. The higher  $J_{SC}$  value is due to higher carrier mobility across the ECD/CBD film compared to other counterparts. This is evident from values of conductivity for different electrodes described in Section 2.2 above, where the ECD/CBD electrode showed highest value. With its lower thickness, the ECD is less conductive than the CBD film, as shown in Section 2.2. Despite that, the higher crystallinity of the ECD film balances off the lower conductivity and yields higher efficiency than the CBD film.

Film Number	Preparation	$V_{OC}(\mathbf{V})$	$J_{SC}$ (A/cm <sup>2</sup> )	η%	<sup>b</sup> FF%
	method				
Α	ECD	-0.45	0.91×10 <sup>-3</sup>	1.72	20.7
В	CBD	-0.38	0.27×10 <sup>-3</sup>	1.16	42.8
С	ECD/CBD	-0.49	0.98×10 <sup>-3</sup>	4.40	40.2
t	ECD/CBD	-0.49	0.98×10	4.40	40.2

Table (1): Summary of PEC characteristics for different CdSe as-prepared film electrodes

The conversion efficiency of 4.4% is higher than other reported values for polycrystalline film electrodes of CdSe [2, 11] or CdS [13] prepared by ECD or CBD methods separately. The combined ECD and CBD technique is thus advantageous in yielding film electrodes with soundly high conversion efficiency, a feature that is commonly known for monolithic electrodes [7, 12, 31-34]. The observed conversion efficiency value for the ECD/CBD electrode is about 63% that of monolithic CdSe electrodes reported earlier [8, 9]. Therefore, the combined deposition technique yields film electrodes that may potentially compete with monolithic electrode systems.

Attempts to further enhance PEC characteristics for the ECD/CBD CdSe film electrode by annealing showed no value. Table (2) shows that the as-prepared ECD/CBD film electrode exhibited higher values for  $\eta$  and FF than other ECD/CBD electrodes annealed at 150, 250 or 350°C (entries **a** through **g**). Controlling cooling rate of the annealed film did not enhance the as-prepared CdSe film electrode.

The Table shows that electrodes annealed at different temperatures, while using same cooling method, exhibited different values for  $\eta$ , in the order 350 < 250 < 150 °C. The results show that

annealing at higher temperature may lower PEC characteristics of the ECD/CBD electrodes. Moreover, for each annealing temperature, slow cooling shows higher conversion efficiency value than the quickly cooled counterpart.

The results show that the PEC characteristics of the ECD/CBD film are lowered by annealing. Annealing is believed to have two opposing effects on the ECD/CBD film layers. Annealing is expected to increase disorder in the originally more crystalline ECD layer, and to increase crystallinity in the more disordered CBD layer. Similar results were reported for different film electrode systems [7, 12].

Entry	Annealing	Cooling	V <sub>OC</sub>	$J_{SC}$	η%	FF%
	Temperature	Rate	(V)	$(A/cm^2)$		
	(°C)					
А	Non-		-0.49	0.98×10 <sup>-3</sup>	4.40	40.2
	annealed					
В	150	Slow	-0.44	0.83×10 <sup>-3</sup>	1.58	22.9
С	150	Fast	-0.44	0.56×10-3	1.22	30.4
D	250°C	Slow	-0.47	$0.40 \times 10^{-3}$	1.14	24.46
Е	250°C	Fast	-0.34	$0.41 \times 10^{-3}$	0.93	31.5
F	350°C	Slow	-0.31	0.34×10 <sup>-3</sup>	0.62	36.1
G	350°C	Fast	-0.32	0.36X10 <sup>-3</sup>	0.50	26.5

Table (2): Summary of PEC characteristics for ECD/CBD-CdSe film electrodes annealed at different temperatures.

The as-prepared CdSe film electrode stability under PEC conditions was investigated. Figure (6) shows  $J_{SC}$  values measured for different film electrodes under continued exposure to a radiation intensity of 0.0061 W/cm<sup>2</sup> at zero applied potential using S<sup>2-</sup>/S<sub>x</sub><sup>2-</sup>/KOH redox couple. The radiation intensity used in stability experiments was intentionally lower than that used in J-V study, to avoid heating the electrode by long time exposure to radiation. The difference in values of  $J_{SC}$  between Figures (5) and (6) is thus due to difference in radiation intensity. Figure (6) shows that the  $J_{SC}$  values (~4x10<sup>-5</sup> - 5x10<sup>-5</sup> A/cm<sup>2</sup>) for both ECD and CBD film electrodes continue to decrease with time. This indicates the low stabilities of these two films under PEC conditions. The results are consistent with earlier reports on CBD prepared CdSe film electrodes, despite the difference in preparation procedure [2]. The J<sub>SC</sub> value for the ECD/CBD film electrodes and CBD films. The Figure thus indicates that the ECD/CBD is more stable than the ECD and CBD films. The induction period observed in the ECD/CBD film, which showed a small J<sub>SC</sub> value at the beginning, is due to contaminants at the electrode surface. With continued irradiation, the contaminants are removed and the electrode reaches steady state. Such behavior has been reported in other different film electrodes [2, 15, 35-37].



**Figure (6):** Plots of  $J_{SC}$  vs. time for non-annealed CdSe/FTO/glass thin film electrodes: a) ECD b) CBD, c) ECD/CBD. All measurements were conducted in aqueous  $S^{2-}/S_x^{2-}$  redox system at room temperature.

The results show for the first time that preparing CdSe film electrodes, by ECD followed by CBD, yields a new system with enhanced PEC characteristics. Compared to the ECD and the CBD film electrodes, the new film shows higher conversion efficiency and stability even with no further modification. More study is underway to further enhance PEC characteristics for the new ECD/CBD-CdSe films by combining annealing, cooling rate control and coating with electro-active materials.

### 4. Conclusion:

CdSe film electrodes have been prepared by electro-deposition followed by chemical bath deposition. The resulting film electrodes combine the advantages of both electro-deposition and chemical bath deposition methods. The new film electrode showed enhanced photoelectrochemical characteristics, with enhanced short-circuit current density, open circuit potential, conversion efficiency and stability, with no need for further treatment such as annealing. The combined preparation technique can be further considered for other metal chalcogenides film electrodes with known low stability.

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#### Graphical Abstract

