



Effect of cooling rate of pre-annealed CdS thin film electrodes prepared by chemical bath deposition: Enhancement of photoelectrochemical characteristics

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ARTICLE INFO

Article history:

Received 1 December 2008

Accepted 29 December 2008

Available online 15 January 2009

Keywords:

CdS films
Annealing
Cooling rate
Efficiency
Stability

ABSTRACT

Thin films of CdS, deposited by chemical bath deposition (CBD) onto films of fluorine-doped tin oxide/glass (glass/FTO) substrates were prepared and investigated for photoelectrochemical conversion (PEC) of light into electricity. Knowing the hazardous nature of CdS, the focal theme of this work was to modify the electrodes by simple economic ways to maximize their conversion efficiency and minimize their degradation under PEC conditions. This was to avoid leaching out of hazardous Cd²⁺ ions. Different parameters have been investigated for this purpose. Multi-deposition preparation, redox couple, and electrode etching affected electrode PEC characteristics. Consistent with earlier literature, annealing the electrode enhanced its conversion efficiency and stability. On the other hand, effect of cooling rate of pre-annealed CdS electrodes, prepared by CBD, on their PEC characteristics has been investigated here for the first time. Controlling the cooling rate was one major factor that affected CdS surface morphology, conversion efficiency and stability under PEC conditions. The major recommendation coming out here is that PEC characteristics of CdS thin film electrodes can be significantly enhanced by pre-annealing the electrode at ~250 °C followed by its slow cooling.

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1. Introduction

The emergence of thin film semiconducting (SC) materials, as replacement for mono-crystalline counterparts, is well justified. Compared to mono-crystalline SC electrodes, thin films are easy to prepare under mild conditions with no special demand for high cost techniques, such as special vacuum, pressure, . . . , etc. [1–52]. Metal chalcogenide thin films, such as those of CdS, are one important example of film SC electrodes. Both CBD and Electrochemical Deposition techniques have been widely described to prepare FTO/CdS electrodes for the purpose of photoelectrochemical (PEC) applications [1–14]. Investigating the CdS film electrodes from different points of view, such as short-circuit enhancement, open-circuit potential enhancement, SEM surface studies, absorption spectra and photoluminescence (PL) spectra, are known. Effects of multiple deposition, redox couple nature, and other parameters, are reported [13–15]. However, despite the widespread interest in CdS, it is very hazardous in nature. Under PEC conditions, it degrades into soluble Cd²⁺ ions, which are terribly hazardous and environmentally unfriendly. This has been confirmed in a recent study

conducted earlier [16]. Such hazards would limit the use of CdS as a future large scale material for SC electrode manufacturing, unless its characteristics are modified. The most demanding characteristic modifications are light-to-electricity conversion efficiency (short-circuit current density, J_{SC} , open-circuit photopotential, V_{OC} , quantum yield, fill factor, FF) and electrode stability to degradation. Should economic techniques, to improve CdS electrode efficiency and stability be developed, the future applicability of such systems would be boosted.

Just like other cadmium chalcogenides, we have been interested in CdS thin films, prepared by CBD technique, onto glass/FTO substrates. We wish to utilize simple economic techniques to simultaneously improve both efficiency and stability of CdS electrodes under PEC conditions. In earlier reports [17–19], a number of techniques were suggested to enhance both the efficiency and stability of mono-crystalline n-GaAs and n-Si SC electrodes. Pre-annealing and controlled cooling rate showed enhanced J_{SC} , V_{OC} and stability at the same time.

Thin film characteristic enhancement by annealing is widely reported in literature [1,5,14,22–30]. Different characteristics of thin films, prepared by different techniques including CBD, such as PL spectra, crystallite size, conductivity, PEC characteristics and others were modified by annealing. The annealing was performed under air, under nitrogen or under vacuum.

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Reports, dealing with effect of cooling rate on different characteristics, of mono-crystalline and thin film materials, such as PL spectra, absorption spectra, crystallite size, conductivity and others are known [27,32–35,46–47]. Some reports dealing with PEC characteristics enhancement of SC thin films, prepared by spray pyrolysis, sputtering or chemical vapor techniques, are available [22,25,48–52]. Despite the widespread studies on CdS films prepared by CBD [1,5,14,22–30], no earlier comprehensive studies, dealing with effect of cooling rate onto PEC characteristics of such CBD-prepared CdS thin films, were performed. To the best of our knowledge, the effect of cooling rate on both efficiency and stability of such systems under PEC conditions has not been reported. Due to the promising nature of such systems, and the concurrent above-mentioned environmental limitations, it is necessary to find out simple techniques to enhance both efficiency and stability of such systems. The present communication is mainly devoted to show, for the first time, how cooling rate of pre-annealed CdS thin film electrodes, prepared by CBD, can simultaneously affect their efficiency and stability. Combination of such techniques with other experimental parameters, such as etching and redox couple are also included.

2. Experimental

2.1. Chemicals

LiClO₄, KOH, K₃Fe(CN)₆, K₄Fe(CN)₆, CdCl₂, thiourea (CS(NH₂)₂), NH₄Cl, HCl and NH₃ were all purchased from either Aldrich or Frutarom. All organic solvents (methanol, dichloromethane, DMF) were obtained from Riedel-DeHaën in pure form. Highly conductive FTO/glass samples were kindly donated by Dr. Guy Campet of ICMCB, University of Bordeaux, France.

2.2. Equipment

A PC controlled Princeton Applied Research (PAR) Model 263A potentiostat was used for *J* vs. *V* study. A 50 W solar simulator Xe lamp was used as a light source [20]. Light intensity was measured with Lutron-LX 102 light meter and calibrated with a Kipp & Zonen CM11 pyranometer (W m⁻²) [15].

SEM measurements, obtained here, were conducted in Institut d'Etudes Françaises (IEF) laboratories of the Université Paris XI, France. Solid state electronic absorption spectra, for the CdS films, were measured on a Shimadzo 1601 spectrophotometer.

2.3. CdS film preparation and annealing

CdS films have been grown using CBD technology on FTO/glass. The choice of deposition parameters has been guided by kinetic studies carried out earlier [12–14]. Preparation was conducted in a chemical bath containing cadmium chloride, ammonium chloride, ammonium hydroxide and thiourea in suitable proportions. The bath was maintained at 80 °C in a constant-temperature oil bath and under constant stirring during deposition. This was prepared by adding into the beaker containing 25 ml of stirred deionized water at 80 °C, 2.5 ml of 0.12 M CdCl₂, 10 ml of 0.20 M NH₄Cl, and 15.0 ml of

2.00 M NH₃. Pre-cleaned FTO/glass substrates (1 cm × 5 cm), held by special holders, were then partially immersed in the solution (keeping 1 cm × 1 cm of the substrates out of the solution). The system was firmly closed using a rubber seal to prevent ammonia evaporation, and to keep pH under control. This was also to prevent Cd(OH)₂ deposition along with CdS. Finally thiourea (2.5 ml of 0.60 M) was syringed inside the beaker. The total volume of the bulk solution was 55 ml, and the pH level was in the range 10–11. Preparation conditions are described in Table 1.

In order to obtain good adherence and film uniformity, the glass/FTO substrates were pre-cleaned prior to deposition. The multi-step cleaning involved the following: (i) washing with Liquinox soap, (ii) washing with distilled water, (iii) washing with methanol, (iv) washing again with distilled water, (v) soaking in dilute HCl (10%, v/v) for 5 s, (vi) washing with distilled water, (vii) washing with methanol, (viii) washing with deionized water, (ix) drying with nitrogen stream. Deposition time was 30 min, during which the solution color changed from pale yellow to yellow within 4 or 5 min and finally to bright orange. After each deposition, the coated substrate was cleaned in distilled water and dried in nitrogen atmosphere and preserved from surface contamination. Multi-deposition was performed using the same glass/FTO/CdS samples as substrates for further deposition. Multi-deposition yielded CdS films with thickness enough to show semiconduction character. Thinner films, prepared by mono-deposition, were not thick enough to show semiconduction, instead they showed only conduction behaviors. Film thickness study and control was performed earlier [12–14].

Annealing of glass/FTO/CdS system was conducted using a thermostated horizontal tube furnace. The prepared glass/FTO/CdS samples were inserted in the middle of a long Pyrex cylinder. The furnace temperature (150, 250 or 350 °C) was kept constant for 30 min under air. The heater was then switched off and left to cool, as desired, either slowly or by quenching.

Slow cooling was performed as follows: After annealing, the furnace setting temperature was lowered stepwise, 50 °C each, and left for 20 min interval. This was repeated until room temperature was reached. Total cooling time varied from 2 to 7 h, depending on the annealing temperature.

Quenching was performed as follows: After annealing was complete, the annealing system (Pyrex cylinder and film substrate) was taken out of the furnace and left to cool, from the annealing temperature to room temperature, under continuous flow of air within 2 min.

2.4. The PEC experiment

The prepared electrodes of CdS were pre-etched prior to use in PEC experiments. The electrode was immersed in the dilute HCl (10%, v/v) solution for 5 s and then rinsed with distilled water. The above procedure was repeated for two or three times to obtain a shiny film surface. The electrode was then rinsed with distilled water and methanol, and dried with nitrogen.

The clean CdS film electrode was incorporated as a working electrode into a three-electrode one-compartment photoelectrochemical cell, with a platinum counter electrode and a reference

Table 1
Chemical bath composition and PEC characteristics.

Exp. #	CdCl ₂ (M)	Thiourea ^a (M)	Temperature (°C)	Time (min)	<i>J</i> _{sc} (mA cm ⁻²)	<i>V</i> _{oc} (V)
1	0.12	0.60	80	30	0.18	-0.42
2	0.12	0.60	80	15	0.05	-0.22
4	1.00	1.00	80	30	0.09	-0.28
5	1.00	1.00	80	15	0.11	-0.3

^a Final added reactant.

saturated calomel electrode (SCE). J - V plots were constructed using a PAR 63A Potentiostat. Two types of redox couples were used in this study. The first was: KOH/ $\text{Fe}(\text{CN})_6^{3-/4-}$ (1.00 M KOH, 0.05 M $\text{K}_3\text{Fe}(\text{CN})_6$, and 0.05 M $\text{K}_4\text{Fe}(\text{CN})_6$) as a redox couple in distilled water (pH 6.5), with 0.10 M LiClO_4 used as supporting electrolyte [15]. The second was: $\text{NaOH}/\text{S}^{2-}/\text{S}_x^{2-}$ (Using 0.10 M Na_2S , 0.10 M NaOH and 0.10 M S) as a redox couple [21]. The solution was stirred at the beginning, and was stopped as PEC experiment started.

High purity nitrogen gas (99.999%) was bubbled through the solution for at least 5 min before each experiment, and was kept to bubble above the solution during the experiment to minimize contamination with air. The solar simulator illumination intensity on the electrode was 0.035 W cm^{-2} .

3. Results

During PEC experiments, CdS degraded into Cd^{2+} ions readily, as witnessed by polarographic analysis of the solutions [16]. Under neutral or acidic conditions, degradation was almost complete. To lower the degradation, high pH values were used unless otherwise stated.

Effect of different parameters (multi-deposition, annealing, cooling rate, etching and redox couple) on J - V plots were investigated. Stability testing was studied by constructing J_{SC} vs. time plots.

3.1. Effect of deposition conditions and multi-deposition

Effects of bath concentrations and deposition time on CdS cell efficiency were studied. Table 1 shows the different chemical bath compositions performed in a set of four representative samples, together with measured short-circuit currents and open-circuit voltages in KOH/ $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple systems. The table shows that the film prepared using chemical bath of (0.12 M CdCl_2 , 0.20 M NH_4Cl , 2.00 M NH_3 and 0.60 M thiourea) at 80°C for 30 min has the best J_{SC} and V_{OC} . Therefore, unless otherwise stated, these

bath conditions were used to prepare CdS film electrodes throughout this work.

The effect of multi-deposition of CdS on its efficiency was studied. Fig. 1 shows J - V plots obtained using different depositions. Mono-deposition samples did not show semiconductor behaviors. Instead they showed only normal conductivity associated with FTO, since the CdS layer was too thin to screen the FTO. Thicker films could be made using mono-deposition only if higher reactant concentration is used. However, this was not followed, because the deposition rate becomes very fast yielding films with undesired characteristics. Multi-deposition strategy was therefore followed here. Among the different samples prepared, the triply deposited CdS system showed best J - V plots with higher allowed output power.

The influence of multi-depositions and annealing on the absorption spectra of prepared films were investigated. Fig. 2A and B shows the electronic spectra of untreated mono-deposition and multi-deposition CdS electrodes. While the absorption edge for mono-deposition films is not well defined, Fig. 2A, a sharp absorption edge, at about 525 nm corresponding to a band gap of approximately 2.36 eV, can be observed for triply deposited film, Fig. 2B.

3.2. Effect of annealing

Annealing the CdS electrode affects its PEC characteristics. Fig. 3A and B shows that the J - V plots of CdS change by pre-annealing the electrode. Among the different temperatures, the 250°C gave electrodes with best J - V plots [5]. The tendency was apparent with both slowly cooled samples, Fig. 3A, and quenched samples as well, Fig. 3B. This is a direct evidence in favor of electrode pre-annealing at 250°C .

Effect of annealing on film stability was studied using aqueous (KOH/ $\text{Fe}(\text{CN})_6^{3-/4-}$) systems under illumination. Plots of J_{SC} vs. time were measured for untreated electrodes and for pre-heated ones using slow and rapid cooling from 250°C . Fig. 4 summarizes these findings. In each case, the J_{SC} vs. time plots started with very small

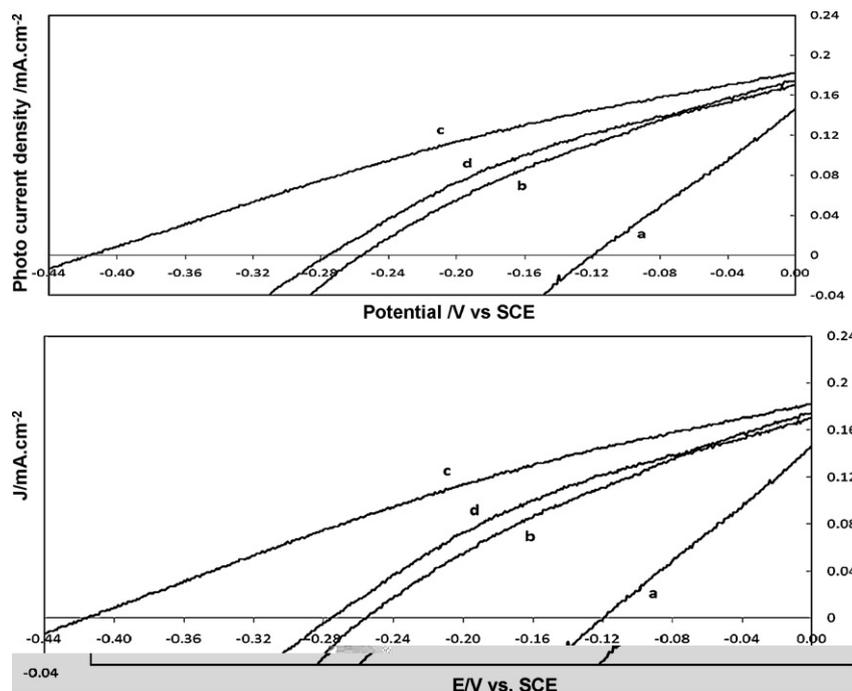


Fig. 1. Effect of deposition times on CdS electrode J - V characteristics. Photo J - V plots for deposited CdS electrodes from 0.12 M CdCl_2 , 0.20 M NH_4Cl , 2.0 M NH_3 and 0.60 M thiourea chemical bath at 80°C for 30 min. (a) One deposition, (b) two depositions, (c) three depositions and (d) four depositions. All measurements were conducted in aqueous KOH/ $\text{K}_4\text{Fe}(\text{CN})_6$ / $\text{K}_3\text{Fe}(\text{CN})_6$ at 25°C .

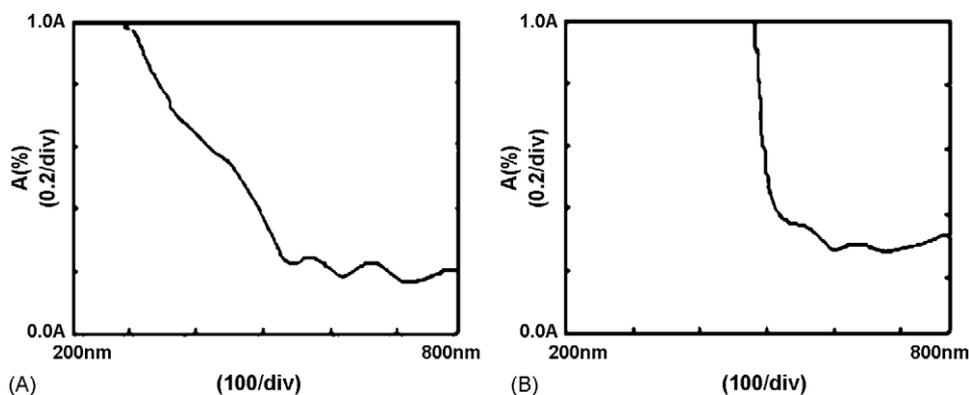


Fig. 2. Solid state absorption spectra of deposited CdS electrodes from 0.12 M CdCl₂, 0.20 M NH₄Cl, 2.00 M NH₃ and 0.60 M thiourea, CBD, at 80 °C for 30 min. (A) Untreated CdS electrode prepared from one deposition and (B) untreated CdS electrode prepared from three depositions.

J_{SC} values, which increased with time, leveling at almost a steady value for more than 240 min. This indicates the relative stability of CdS thin films under PEC conditions. As expected, the preheated CdS electrodes show higher J_{SC} values than untreated counterparts. Quenched CdS electrode from temperature 250 °C has a value of J_{SC} five-fold than their untreated counterpart. Slowly cooled CdS electrode from temperature 250 °C shows a rather higher value of J_{SC} , seven-fold, than their untreated counterpart.

3.3. Effect of cooling rate

The effect of cooling rate, of pre-annealed electrodes at different temperatures, was investigated. Slowly cooled samples, from 250 °C, gave a J_{SC} value ($\sim 0.8 \text{ mA cm}^{-2}$) higher than the quenched counterpart one (0.4 mA cm^{-2}) as shown in Fig. 3A and B. Value of V_{OC} for the slowly cooled electrode was also more negative ($\sim -0.58 \text{ V}$) compared to that for the quenched counterpart

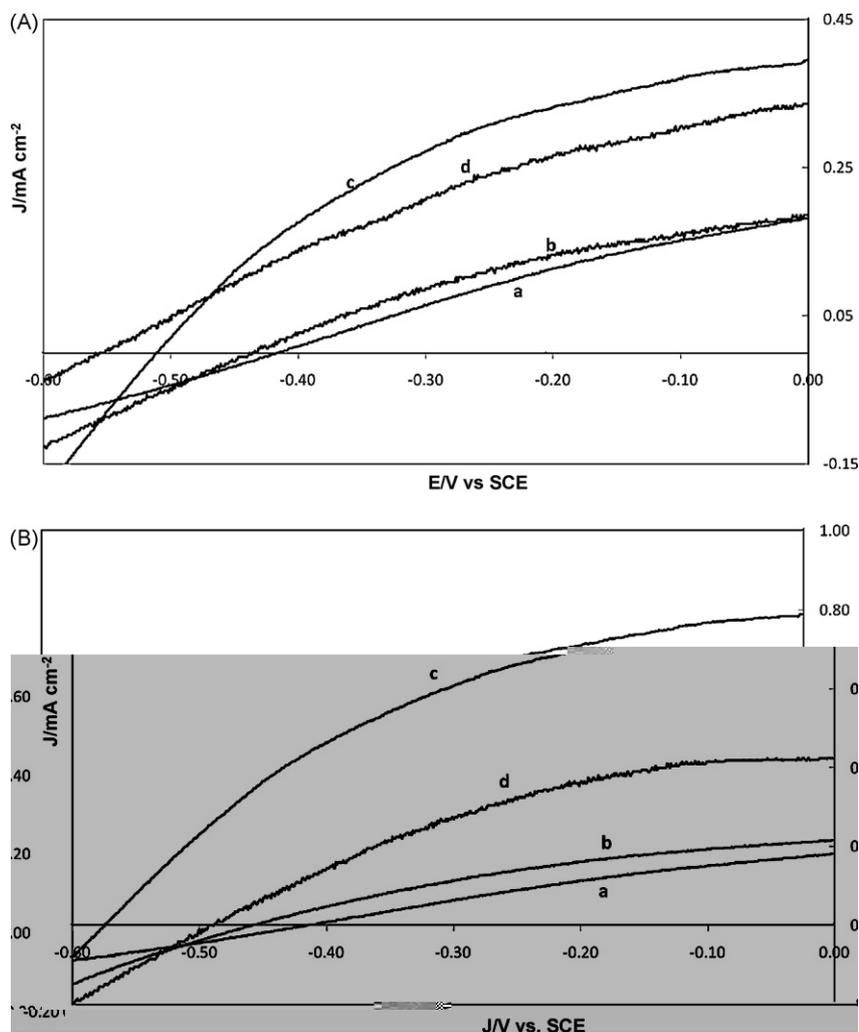


Fig. 3. Effect of cooling rate on CdS electrode J - V characteristics. (A) Photo J - V plots for (a) unheated CdS electrode, and quenched CdS electrodes from (b) 150 °C, (c) 250 °C, and (d) 350 °C. (B) Photo J - V plots for (a) unheated CdS electrode, and slowly cooled CdS electrodes from (b) 150 °C, (c) 250 °C, and (d) 350 °C. All measurements were conducted in aqueous KOH/K₄Fe(CN)₆/K₃Fe(CN)₆ at 25 °C.

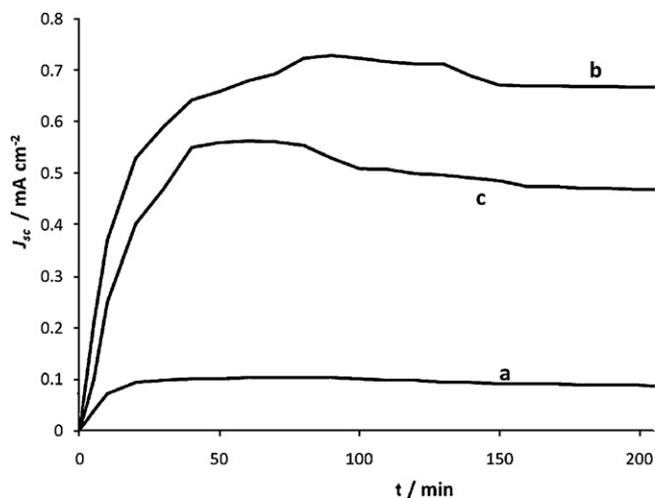


Fig. 4. Short-circuit current density vs. time measured for CdS thin film electrodes: (a) untreated, (b) slowly cooled from 250 °C, and (c) quenched from 250 °C. All measurements were conducted in aqueous KOH/K₄Fe(CN)₆/K₃Fe(CN)₆ at 25 °C.

(~ -0.52 V). The maximum output power for the slowly cooled electrode is higher than that for the quenched electrodes. The measured percent efficiency, η (%) (maximum observed power density divided by radiation reach-in power density, multiplied by 100%) for the slowly cooled electrode was 1.3% compared to that for the quenched electrode (0.6%).

Slowly cooled electrodes showed higher stability than the quenched counterparts. Plots of J_{SC} values vs. time, Fig. 4b and c, indicate about 40% enhancement in J_{SC} for slowly cooled electrodes compared to quenched counterparts. This indicates a higher stability for the slowly cooled electrode.

Values of electrode percentage conversion efficiencies, η %, and fill factor, FF, values were calculated for different electrodes. Table 2

Table 2

Effects of annealing and cooling rates on PEC characteristics.

Entry number	Annealing temperature (°C)	Cooling method	V_{OC} (V)	J_{SC} (mA cm ⁻²)	η (%) ^a	FF (%) ^b
1	Room temperature	–	–0.42	0.18	0.21	21
2	150	Quenched	–0.44	0.19	0.23	35
3		Slow	–0.46	0.22	0.28	30
4	250	Quenched	–0.51	0.4	0.6	41
5		Slow	–0.58	0.79	1.3	42
6	350	Quenched	–0.56	0.34	0.54	33
7		Slow	–0.49	0.42	0.55	41

All measurements were conducted in aqueous KOH/K₄Fe(CN)₆/K₃Fe(CN)₆ at 25 °C.

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

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

summarizes data on η %, V_{OC} , J_{SC} and FF. The results indicate that slowly cooled CdS electrodes, from different temperatures 150, 250 and 350 °C, gave higher efficiency than quenched counterparts. This tendency was more profound in case of 20 °C annealing. Among different systems, maximum values of efficiencies were obtained by slow cooling of preheated CdS samples from temperature 250 °C, Table 2, entry 5.

Parallel to its effect on J – V plot and stability, the cooling rate affected the surface structure of the CdS films. Fig. 5A and B shows SEM photographs for two CdS film electrodes pre-annealed at same temperature, and cooled differently. The quenched electrode apparently has dark spots indicating deep holes in the CdS film. The slowly cooled films show a more uniform CdS matrix with better sintering.

3.4. Effect of electrode pre-etching

The effect of CdS film electrode etching on PEC characteristics was studied. Triply deposited CdS electrodes, slowly cooled from 250 °C, were etched by dilute HCl (10%, v/v) solution. Etching of CdS electrode surface did not enhance the photo J – V plots. Fig. 6 shows the photo J – V plots of etched electrodes and unetched counterparts.

The effect of etching on stabilizing the CdS electrode surface was studied while using aqueous (KOH/Fe(CN)₆^{3–/4–}) systems under PEC conditions. Fig. 7 shows the effect of etching on untreated and pre-annealed/pre-cooled CdS electrode stabilization. The J_{SC} values of CdS films increase with etching, reaching 1.5-fold the unetched counterparts throughout the 240 min exposure period.

3.5. Effect of type of redox couple

The effect of the nature of redox couple on electrode efficiency and stability was studied. In addition to the KOH/Fe(CN)₆^{3–/4–} redox couple system described above, polysulfide (S^{2–}/S_x^{2–}) redox couple was investigated.

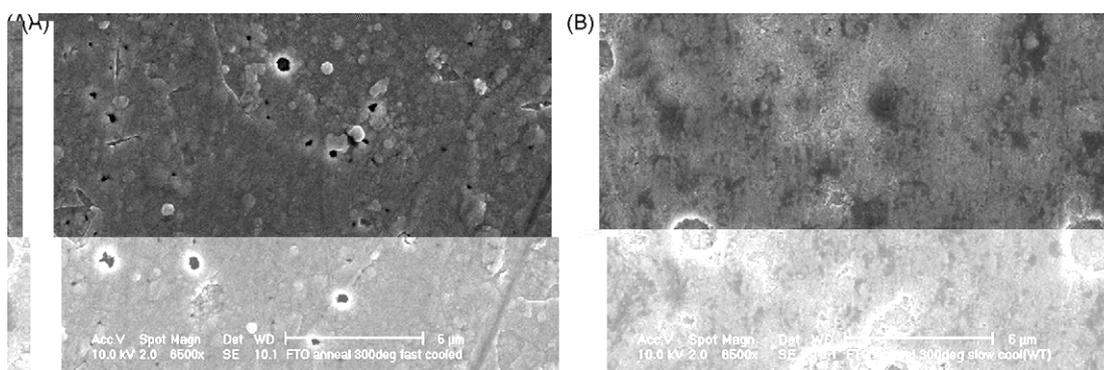


Fig. 5. Effect of cooling rate on CdS film surface texture. SEM micrographs measured for pre-annealed CdS at 300 °C, (A) quenched and (B) slowly cooled.

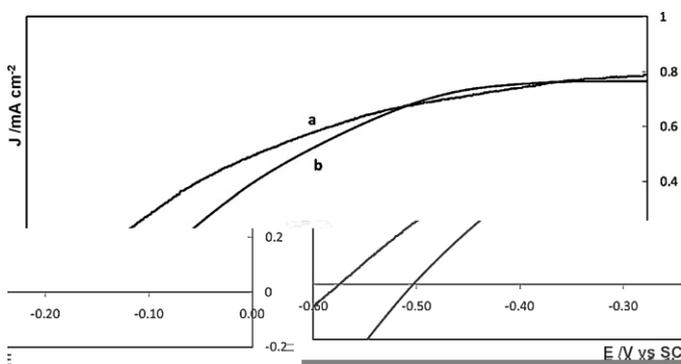


Fig. 6. Effect of etching on CdS electrode. Photo J - V plots of slowly cooled CdS electrodes from 250 °C (a) unetched and (b) etched in HCl (10%, v/v). All measurements were conducted in aqueous KOH/ $K_4Fe(CN)_6/K_3Fe(CN)_6$ at 25 °C.

In polysulfide redox couple, with higher nominal concentrations of Na_2S (1.00 M) and S (1.00 M), the electrode was highly unstable even under highly basic conditions (1.00 M KOH). The CdS film completely degraded under PEC conditions, leaving naked FTO and causing a short-circuit error in the system. Direct contact between the FTO layer and the solution occurred due to CdS removal. Lower polysulfide system concentrations, Na_2S (0.10 M) and S (0.10 M), gave higher stability even at lower KOH concentrations (0.10 M). Therefore, polysulfide redox couple concentrations involved the system NaOH (0.10 M), Na_2S (0.10 M) and S (0.10 M).

Photo J - V plots of CdS electrode slowly cooled from 250 °C in two different redox couple systems are shown in Fig. 8. The KOH/ $Fe(CN)_6^{3-/4-}$ redox couple system gives better photo J - V plot than S^{2-}/S_x^{2-} redox system. When slowly cooled CdS electrode was studied inside polysulfide redox couple system; it showed significant enhancement in J - V plots, compared to non-annealed counterpart in the same redox couple, Fig. 9. Similar results were observed using the KOH/ $Fe(CN)_6^{3-/4-}$ redox couple, Fig. 3B. The results confirm electrode efficiency enhancement by slow cooling of pre-annealed samples in either redox couple, although values of J_{SC} and V_{OC} in the KOH/ $Fe(CN)_6^{3-/4-}$ redox system show superiority as compared to polysulfide redox couple.

The effect of type of redox couple on the CdS electrode stability was investigated. Values of J_{SC} vs. time (at applied potential 0.0 V vs. SCE) were measured using polysulfide and (KOH/ $Fe(CN)_6^{3-/4-}$) systems. Untreated CdS electrodes showed better J_{SC} vs. time plots, when studied using low concentration polysulfide NaOH

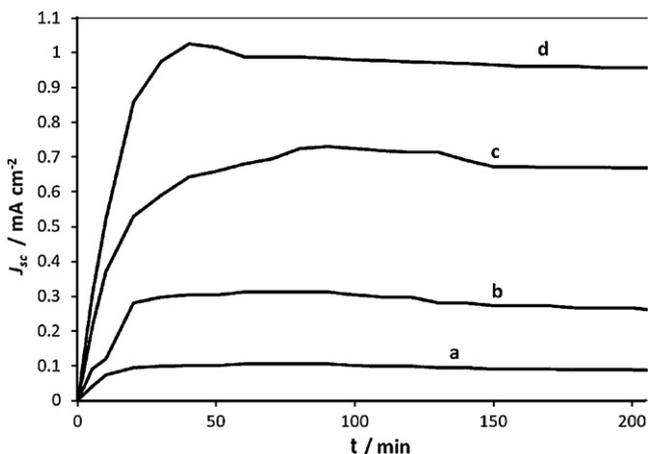


Fig. 7. Short-circuit current density vs. time measured for CdS thin film electrodes: (a) untreated unetched, (b) untreated etched in HCl (10%, v/v), (c) unetched slowly cooled from 250 °C, and (d) slowly cooled from 250 °C etched in HCl (10%, v/v). All measurements were conducted in aqueous KOH/ $K_4Fe(CN)_6/K_3Fe(CN)_6$ at 25 °C.

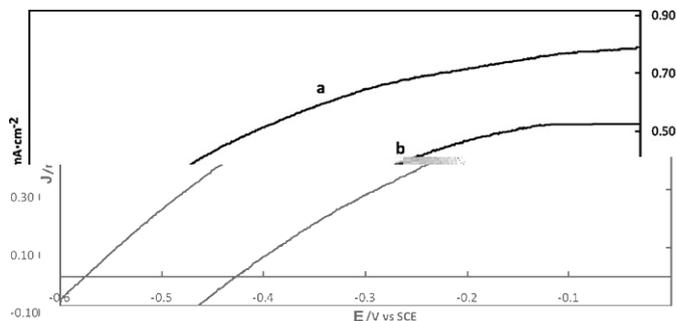


Fig. 8. Effect of redox couple system. Photo J - V plots for slowly cooled from 250 °C CdS electrode in (a) aqueous KOH/ $Fe(CN)_6^{3-/4-}$ redox system and (b) aqueous S^{2-}/S_x^{2-} redox system.

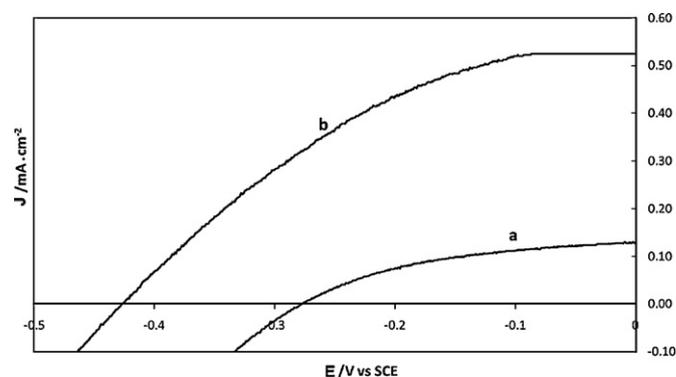


Fig. 9. Photo J - V plots for (a) untreated CdS electrode and (b) slowly cooled from 250 °C CdS electrode. Both J - V measurements were conducted in aqueous S^{2-}/S_x^{2-} redox system.

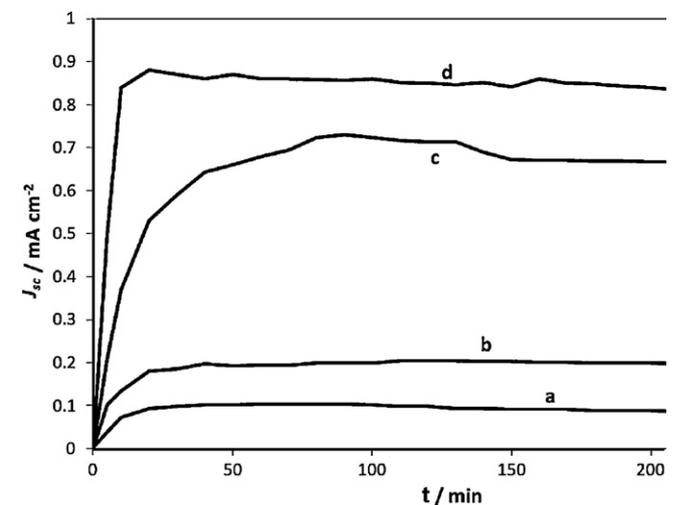


Fig. 10. Short-circuit current vs. time for CdS thin film electrodes (a) untreated in KOH/ $Fe(CN)_6^{3-/4-}$ aqueous solution, (b) untreated in S^{2-}/S_x^{2-} aqueous solution, (c) slowly cooled from 250 °C in KOH/ $Fe(CN)_6^{3-/4-}$ aqueous solution, and (d) slowly cooled from 250 °C in S^{2-}/S_x^{2-} aqueous solution.

(0.10 M)/ Na_2S (0.10 M)/ S (0.10 M) redox couple than when using (KOH/ $Fe(CN)_6^{3-/4-}$) counterparts. Moreover, the preheated CdS electrodes showed higher J_{SC} values when using polysulfide redox couple than when using (KOH/ $Fe(CN)_6^{3-/4-}$) counterparts, Fig. 10.

4. Discussion

Films of CdS exhibit n-type semiconductivity [1]. The PEC characteristics of CdS films were affected by different parameters such

as, deposition times, bath concentration and multiple depositions. CdS films prepared from a bath of low concentrations (0.12 M CdCl₂ and 0.60 M thiourea) have a shiny surface and a better photo *J*-*V* plot than films prepared from a bath of high concentrations (1.00 M CdCl₂ and 1.00 M thiourea). This is due to kinetic reasons. With lower bath concentrations, the deposition rate is expected to be lower and consequently allows more uniform crystals with less imperfection. With multiple depositions, the best film performance was obtained from films with three depositions.

It is worthwhile to know why multi-deposition is needed, knowing that a single deposition from heavily concentrated bath may yield enough thick films. As discussed above, higher reactant concentrations yield faster deposition rates with lower quality crystals. Therefore, to get reasonable film thicknesses without scarifying crystal quality, it is necessary to follow multi-deposition techniques using lower bath concentrations. Literature supports such discussions [4,12,13]. Photoluminescence, optical, electrical and photoelectrochemical characteristics of deposited films are affected by bath concentrations. Structure, crystal type and defect density are known to vary with bath concentrations. Optical absorption coefficient of the films decreases by increasing the thickness. This effect can be explained by proposing that the thicker film has larger crystallites. The fact that the triply deposited films showed best PEC characteristics is thus evident. Films with fourth deposition were presumably very thick with higher resistance. This affected their PEC characteristics. The optimal films were thus obtained with triple depositions.

Electrode characteristics, such as *J*-*V* plots, efficiency and stability were all enhanced by pre-annealing the CdS films. Consistent with earlier report [15,23–24], annealing of CdS thin films enhances their surface and improves the stability of the electrodes. Annealing increases the grain size (by sintering) and removes defects in the deposited films. Consequently, there is an increase in minority carrier diffusion to electrolyte solution in PEC solar cell, which prevents electrode photocorrosion normally associated with hole accumulation in the space charge layer (SCL). It should be noted that annealing at higher temperature may give negative effect by increasing imperfections and causing unnecessary surface oxidation, thus increasing surface state density. Therefore, the 250 °C was the optimal annealing temperature, which is consistent with literature [1,26–30].

Effect of cooling rate has been reported earlier for mono-crystalline SC electrodes [17–19], but not for CdS film electrodes prepared by CBD. Cooling rate affected PEC characteristics of the CdS electrodes herein studied. SEM study also showed better film texture for the slowly cooled films, Fig. 5. The slowly cooled samples showed better surface quality with a cross-linked surface that was free of dark islands, aggregates, or cracks. The quenched surface showed special dark holes which may be associated with peeling out of CdS from FTO surface due to irreversible shrinkage. Slowly cooled counterparts, Fig. 5, did not show any similar dark holes. While heating, imperfections increase in the film. In case of quenching, fast contraction of the film allows shrinkage to occur. In case of slow cooling contraction occurs uniformly throughout the film matrix. Moreover, in case of slow cooling, meta-stable constituents of the crystallites will have the chance to return to their stable positions, giving more crystal uniformity. In quenched samples, meta-stable constituents lose their kinetic energy, by quenching, before being able to return to their original stable positions, giving highly disordered crystallites. Similar discussions were reported for mono-crystalline SC electrodes [17–19]. Thus slowly cooled CdS film electrodes have better crystallite uniformity and better matrix inter-grain cross-linkage. Parallel to mono-crystalline electrodes [31–37], PEC characteristics for the slowly cooled film electrodes are expected to be better than those for quenched counterparts.

The *J*-*V* plots support this discussion. In each case, the CdS thin film electrodes were enhanced by heating. Furthermore, the slowly cooled samples showed better *J*-*V* plots than their quenched counterparts. Moreover, the *J*_{SC} vs. time plots also indicated higher stability for the slowly cooled electrodes.

Etching of CdS thin film enhances the film surface and improves the surface roughness of the electrode. Consequently, etching removes recombination centers (surface states) at the surface, reduces surface impurity and changes surface morphology [38]. In this study, etching the CdS thin films with dilute HCl (10%, v/v) solution enhanced their *J*_{SC} vs. time plots. Etching removes recombination centers at the surface, reduces surface impurity and changes surface morphology.

Different redox couples affected PEC characteristics of thin film CdS electrodes. Two different redox couples, S²⁻/S_x²⁻ and KOH/Fe(CN)₆^{3-/4-}, were studied here. The PEC system with S²⁻/S_x²⁻ was more stable than PEC system with KOH/Fe(CN)₆^{3-/4-} redox electrolyte, Fig. 10, whereas, the latter system has better photo *J*-*V* plots, Figs. 8 and 9. This can be explained as follows: the CdS film decomposes under PEC conditions [16,39]. In case of S²⁻/S_x²⁻ redox couple, the resulting Cd²⁺ ions recombine with solution S²⁻ ions to yield microcrystals of CdS, as very thin layer on the top of the original CdS film. This thin layer is responsible for stabilizing the CdS film. However, CdS microcrystalline extra layer increases cell series resistance and consequently decreases the photocurrent density and quantum yield. This discussion accounts for earlier literature reports. Literature demonstrated that using S²⁻/S_x²⁻ increases the CdS film stability [6–7,40–42], whereas the KOH/Fe(CN)₆^{3-/4-} system gives higher efficiency [40–45].

5. Conclusion

PEC characteristics, of CBD-prepared CdS thin films widely described in literature for light-to-electricity conversions, can be modified using a number of simple practices. Using optimal preparation conditions affects cell efficiency. Pre-annealing enhances efficiency and stability of the thin film electrode. The KOH/Fe(CN)₆^{3-/4-} redox couples give higher efficiency, whereas the S²⁻/S_x²⁻ couple enhances stability. Slow cooling of pre-heated CdS thin film electrodes greatly enhances their surface structure morphology, conversion efficiency and stability at the same time.

Acknowledgements

Thanks are extended to Mrs. Elisabeth Dufour-Gergam, Institut d'Etudes Françaises (IEF) laboratories, Université Paris XI, France, for help with SEM measurements. Donation of free FTO/glass samples, by Dr. Guy Campet of ICMCB, University of Bordeaux, France, is acknowledged.

Many thanks are due to the teaching and technical staff of the laboratories of the department of Chemistry at An-Najah N. University. Research equipment donated by French-Palestinian University Cooperation program is acknowledged.

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