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# Combined electrochemical/chemical bath depositions to prepare CdS film electrodes with enhanced PEC characteristics

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ABSTRACT

A new method to prepare CdS film electrodes, based on electrochemical deposition (ECD), followed by chemical bath deposition (CBD), is described. The ECD/CBD-CdS film electrodes combine the advantages of both ECD-CdS film (good adherence to FTO/glass substrate) and CBD-CdS film (suitable film thickness) together. The new ECD/CBD electrode showed higher photo-electrochemical (PEC) efficiency and stability than either ECD- or CBD-CdS film electrodes, especially after annealing. Inter-particle connection and uniformity of the ECD/CBD-CdS film were further enhanced by annealing. Consequently, the electrode PEC conversion efficiency and stability were enhanced. The combined preparation technique, followed by annealing, is potentially useful for future manufacturing of CdS and other film electrode systems.



## 1. Introduction

CdS film electrodes, with nano-sized particles, deposited onto fluorine-doped tin oxide (FTO)/glass substrates, have many features such as suitable band gap, ~2.4 eV, and effective absorption coefficient, that make them good candidates for solar energy applications [1–4]. Glass/FTO/CdS film electrode systems can be prepared by a number of techniques, the most convenient of which are the conventional ECD and the CBD processes [5]. Each process has its own advantages and shortcomings. ECD process electrodes exhibit high uniformity and good adherence to the FTO surface, but suffer the shortcoming of being too thin. This explains the lack of interest in such electrodes by researchers, as very few reports have been described using such electrodes in PEC processes [5]. On the other hand, CBD process electrodes have relatively higher thickness and are more suitable for PEC applications [6,7]. However, CBD electrodes have lower uniformity and have shortcomings under PEC conditions [6]. The low stability for CBD-CdS electrodes is a major concern as they degrade and yield hazardous $Cd^{2+}$ ions under PEC conditions [8,9].

Combining the advantages of both ECD and CBD processes together is worth to investigate, and ECD/CBD-CdS films could thus be alternative systems. It is assumed that starting with ECD process; a uniform very thin CdS film that adheres well to the FTO surface will be prepared. The resulting ECD film can then be used as substrate for an additional CBD-CdS film. The combined ECD/CBD-CdS film may involve two different CdS stacks, which could be easily homogenized by thermal annealing. The resulting film should then combine the advantages of good adherence and uniformity of ECD process with controllable thickness of CBD process.

In order to test these assumptions, new ECD/CBD film electrodes have been prepared here for the first time. The resulting electrodes have been annealed to homogenize the resulting films and to increase inter-particle connections, without affecting particle sizes. Comparison of ECD/CBD-CdS film electrodes with earlier ECD- and CBD-CdS counterparts, in terms of morphology, crystallinity and PEC characteristics (conversion efficiency and stability) is described. Effect of annealing on film electrode characteristics is also discussed.

## 2. Experimental

### 2.1. Chemicals

All starting materials were purchased from Aldrich, Frutarom or Friedel de Haen in pure forms. Highly conductive FTO/glass substrates were kindly donated by Moulki Hakeem, ICMCB, University of Bordeaux.

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### 2.2. Equipment

Solid CdS film electronic absorption spectra were measured on a UV-1601 spectrophotometer, in the range 400–800 nm. Baseline correction was performed using pre-cleaned glass/FTO substrates. Photoluminescence (PL) spectra were measured for the CdS films on a Perkin-Elmer LS 50 spectrometer, using A 400 nm cut-off filter to exclude reflected wavelengths. The excitation wavelength was 392 nm.

AFM morphological analysis was performed at Al-Quds University, Abu-Dies, using a tapping mode-AFM system and WSxM software designed by Nanotec Electronica (Madrid, Spain) to acquire and analyze the Data. Soft, non-conductive, rectangular, commercial $Si_3N_4$ cantilevers (NSG 10, NT MDT Co., Ltd.) with spring constants of 5.5–22.5 N $m^{-1}$ and resonance frequencies in the range 190–325 kHz were employed.

XRD measurements were conducted in the ICMCB, University of Bordeaux, France, on a Philips XRD X'PERT PRO diffractometer equipped with Cu Kα ($\lambda$ 1.5418 Å). XRD patterns were compared with earlier literature.

### 2.3. CdS film electrode preparation

The ECD/CBD-CdS film layer was deposited onto glass/FTO substrates in a two-step procedure, starting with the ECD process then with the CBD process.

#### 2.3.1. The ECD process

The ECD-CdS film was prepared, onto pre-cleaned and pre-etched glass/FTO substrates (~4.0 × 1.0 $cm^2$), electrochemically at 90 °C as described earlier [5,10–13]. Solutions of $CdCl_2$ (10.00 ml, 0.20 M), $Na_2S_2O_3$ (10.00 mL, 0.05 M) and $LiClO_4$ (trace amount) and distilled water (30 mL) were thoroughly mixed. To control the pH value to ~2.5, dilute solutions of HCl and NaOH were added drop-wise. A thermostated oil bath was used to control reaction mixture temperature. Cathode electrode (glass/FTO) and anode electrode (platinum sheet) were used with special insulations to avoid direct contact of copper wiring with solution. Nitrogen flow was used to eliminate air contact with solution. The applied potential (−0.7 V wrt Ag/AgCl) on the working electrode was controlled with A 264B Polarograph, using a DC stripping mode, for 100 min. Water drops were added to keep the reaction solution volume constant. The resulting glass/FTO/CdS film was then rinsed with distilled water and dried under nitrogen. The average film thickness, calculated by gravimetry, was ~400 ± 60 nm.

#### 2.3.2. CBD CdS film layer

The preparation method followed earlier procedures [3,5,6,14–19]. Pre-cleaned glass/FTO/CdS substrates (~4.0 × 1.0 $cm^2$) described above were immersed inside a bath containing a solution of $CdCl_2$ (2.5 mL, 0.12 M), $NH_4Cl$ (10.0 mL, 0.20 M) and $NH_3$ (15.0 mL, 2.00 M). Thiourea (2.50 mL, 0.60 M) was added to the chemical bath. The total volume was made 55.0 mL by adding distilled water, and the pH was 10.3. The chemical bath was continuously stirred for 30 min at constant temperature (80 °C). The resulting ECD/CBD-CdS film was then rinsed with distilled water and dried with nitrogen. The value of film thickness was gravimetrically calculated to be about 1600 nm.

#### 2.3.3. CdS film annealing

The ECD/CBD-CdS films were annealed under nitrogen at 250 °C using a thermostated horizontal tube furnace [6]. The films were then slowly cooled to room temperature in a course of 2 h, with cooling rate of 2 degrees per min.

### 2.4. The PEC experiments

Current density vs. voltage (*J–V*) plots were measured using a computer-controlled Princeton Applied Research (PAR) Model 263A Potentiostat/galvanostat, as described earlier [5]. The glass/FTO/CdS electrodes were used as working electrodes in a one-compartment three-electrode cell, with platinum as counter electrode. The experimentally used reference electrode was Ag/AgCl, and unless otherwise stated the recorded potential values were recalculated to be with respect to SHE. An aqueous polysulfide redox couple NaOH (0.10 M)/$Na_2S$ (0.10 M)/S (0.10 M) was used [6,20]. The solution was first purged with $N_2$ gas (99.99999%) with continuous stirring for 5 min. Stirring and nitrogen bubbling were then terminated, keeping the nitrogen flow steadily above the solution.

Control experiments were conducted to check for dark *J–V*, as described earlier [5,20,21]. The applied voltage was scanned while measuring the resulting negative valued dark current. Photo *J–V* measurements were similarly performed under illumination using a 50 W halogen spot lamp. Illumination intensity of 0.008 W/$cm^2$ at the CdS surface was measured with a lux meter. The temperature was kept constant at 20 °C throughout all PEC measurements. Current density was calculated by dividing measured current values by the CdS electrode area immersed inside the redox couple solution.

Electrode stability was investigated as described earlier [5,20–22], in a different glass walled PEC cell, using a polarographic analyzer (Pol 150) equipped with an MDE 150 Polarographic stand. The CdS film was used as a working electrode, a platinum sheet as a counter electrode and an Ag/AgCl as a reference electrode. Short-circuit current ($I_{SC}$) values were measured with time while keeping the electrode under 0.0086 W/$cm^2$ illumination intensity and 0.00 V applied bias (vs. Ag/AgCl) at 20 °C. Short-circuit density ($J_{SC}$) plots were obtained from values of short circuit current values divided by CdS electrode area immersed inside the redox couple solution.

## 3. Results

### 3.1. ECD/CBD-CdS film characterization

The ECD/CBD-CdS film was characterized by electronic absorption spectra, photoluminescence (PL) spectra, XRD and AFM. Film crystallinity and uniformity were studied in comparison with other ECD-films and CBD-CdS films reported earlier [2–4,23–27].

The electronic absorption spectra are shown in Fig. 1. The ECD/CBD-CdS film showed an absorption band edge at 530 nm, which resembled that for CBD-CdS reported earlier [1–4]. This corresponds to an energy band gap ($E_{bg}$) value of ~2.3 eV. Annealing the ECD/CBD-CdS film caused no shifting in value of band gap, which indicates no complete sintering or particle growth in the film. That is to say that the smaller particles did not combine to form larger particles during annealing, but interparticle connections occurred. PL spectra showed an emission band at 535 nm, Fig. 2, which resembled the electronic absorption spectral data. Annealing the film caused no shifting in emission peak. The results are justified as annealing was conducted at a relatively low temperature (250 °C) not high enough to cause complete sintering of nanoparticles.

XRD patterns are shown in Fig. 3. The films involved fcc (Zinc Blende) lattices, as reported earlier [5,16,23,24,27] for the separately prepared ECD- and CBD-CdS films. The XRD data showed that the ECD/CBD-CdS particles are slightly larger (~22 nm) than the reported ECD particles (18 nm) or CBD particles (17 nm) prepared separately [5]. Again, annealing the ECD/CBD film caused no change in crystal type or nano-particle sizes, as calculated by