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# Electrochemical Preparation of Bilayer p-n Junction of n-CdS / p-P3HT

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Organic-inorganic p-n junction composed of electrically conducting poly(3-hexylthiophene) (P3HT) and cadmium sulphide (CdS) was prepared by electrodeposition of P3HT on ITO prior to CdS on P3HT by using the same method. This approach provides a low cost route for production of improved charge transfer photovoltaic cells. The optical properties of resulting hybrid films were analyzed by UV-visible spectrophotometry, the combined bandgap energy is between that of P3HT films (1.81 eV) and CdS (2.42 eV). The hybrid CdS/P3HT film presents a higher photocurrent response than that of pure P3HT and absorbs radiation in wider region.

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**Keywords:** Bilayer, electrodeposition, cadmium sulphide, poly (3 – hexylthiophene ), photoelectrochemical properties

## 1. INTRODUCTION

Solution processible conducting polymers especially poly(3-hexylthiophene) (P3HT) have been studied extensively because of its interesting optical, electrical properties and chemical stability. It can be used as organic solar cells, polymer light emitting diodes, sensors, and variety of other applications with these properties [1]. However one of the crucial drawbacks in conducting polymer based devices is their low electron mobility. The poor ability of conducting polymer in transporting photogenerated carriers to the charge accepting electrodes leads to charge recombination. Insertion of an inorganic high electron affinity layer such as CdS in the device helps delays electron hole recombination after photoexcitation [2]. Also, Li et al reported that by inserting a layer of CdS between active polymer layer and Al electrode, the power conversion efficiency of the solar cell was enhanced [3]. Among intensively studied metal chalcogenide semiconductors, cadmium sulphide (CdS) is an interesting II-VI semiconductor due to its intrinsic properties of medium band gap which can absorb visible light, good chemical stability and ready preparation [4]. Thin films of CdS are widely used in solar cells due to its n-type behaviour which can form heterojunctions with p-type semiconductors. Since p-type CdS is very difficult to be fabricated because of strong self-compensation effect due to the sulfur vacancies and the depth of acceptor level in CdS (~1 eV) [5], some researchers worked on p-type Cu doped CdS [6, 7]. However, the concentration of Cu in CdS was difficult to be controlled [8]. For replacement, readily p-type conducting polymer films with high hole mobility are good candidates to be combined with n-type CdS.

Vacuum evaporation is a commonly used physical method for thin film preparation in the production of organic/inorganic hybrid electronic devices. But polymers usually have too large molar mass for evaporation and they decompose if excessive heat provided [9]. Therefore, in this study, we report the deposition of both organic and inorganic layers using electrodeposition at room temperature. Electrodeposition of thin films on conductive substrates is a widely used electrochemical method for its inexpensive instrumentation, easy control of growth parameters through applied potential, current, pH and temperature of the bath [10]. Electrodeposition of CdS on P3HT can be achieved because of chemical stability of P3HT and its solubility in only organic solvent.

## 2. EXPERIMENTAL

*Preparation of P3HT thin films on ITO.*-- Thin films of P3HT were deposited on ITO-coated glass substrates by using electrodeposition. A two-electrode cell system was used to deposit P3HT thin films with platinum wire (99.9%) as the counter electrode. Deposition bath consisted of 0.05 M 3-hexylthiophene monomer and 0.10 M tetrabutylammonium tetrafluoroborate (TBATFB) in acetonitrile was aged at room temperature for 5 days. Potential of 5 V was applied for the electrodeposition.

*Preparation of CdS thin films on P3HT.*-- A three-electrode cell was used for the electrodeposition with Ag/AgCl as reference electrode, previously electrodeposited P3HT on ITO as working electrode and a platinum wire (99.9%) as counter electrode. The composition of the bath is based on Fatas et al [11], it is consisted of a mixture of solution A (0.01 M $CdSO_4$, 0.17 M $(NH_4)_2SO_4$ and 0.01 M glycerol) and solution B (0.35 M $Na_2S_2O_3$ and 0.75 M NaCl) at ratio of A:B=1:3, pH was adjusted to 3.1 using 0.1 M sulphuric acid. Pulse electrodeposition of CdS on P3HT was carried out at $E_{on}$ -0.90 V and $E_{off}$ 0 V at room temperature for 1 hour.

*Characterization of P3HT thin films and CdS/P3HT hybrid films.*-- For the characterization of as-deposited P3HT thin films and hybrid CdS/P3HT films, UV-visible absorption spectras were measured with Perkin Elmer UV/VIS spectrometer Lambda 20. Photoelectrochemical behaviour of P3HT films was performed using a linear sweep voltammetry.

## 3. RESULTS AND DISCUSSION

*Cyclic voltammetry.--* The electrodeposition potential of CdS films on P3HT was predetermined by using cyclic voltammograms. The voltammograms obtained in solution containing only supporting electrolyte and in solution containing $CdSO_4$ and $Na_2S_2O_3$ are shown in Fig. 1. Potential was swept between 1.0 V and -1.0 V vs. Ag/AgCl electrode and starting from 1.0 V towards cathodic direction.

For solution containing only supporting electrolytes (without cadmium or sulfur source) (dotted line), there was no oxidation or reduction peak observed in both cathodic and anodic sweep. Only current rise observed above -0.7 V which is corresponded to hydrogen evolution indicates the stability of P3HT films in aqueous solution in potential range for the cathodic electrodeposition of CdS on them. In order to determine the electrodeposition potential, voltammogram of P3HT electrode in solution containing 0.01 M $CdSO_4$ and 0.35 M $Na_2S_2O_3$ at pH 3.1 was also recorded (smooth line), it shows flowing of cathodic current at potentials more negative than -0.5 V which is attributed to the formation of CdS on P3HT and light yellow film forms on the electrode. A wide oxidation peak appears in the anodic sweep at -0.15 V corresponding to the redissolution of initially formed cadmium metal on the electrode to $Cd^{2+}$ ions into the solution. A deposition potential of -0.90 V was chosen because of higher deposition current produced.

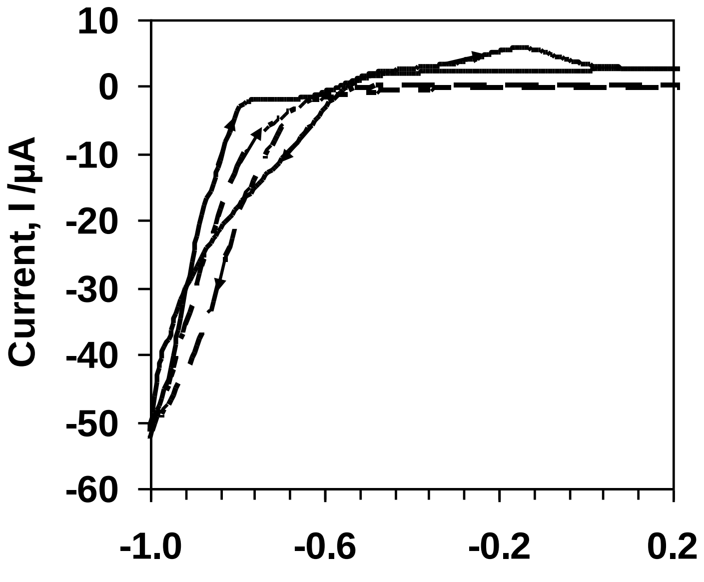

**Figure 1.** Cyclic voltammogram of P3HT in supporting electrolyte (dotted line) and in solution containing 0.01 M $CdSO_4$ and 0.35 M $Na_2S_2O_3$ at pH 3.1 (smooth line).

*Optical properties.--* Optical absorption spectrum of P3HT/ITO and CdS/P3HT/ITO films are shown in Fig. 2. The absorption edges were found to be at around 685.5 nm and 600 nm relatively for P3HT and CdS/P3HT.

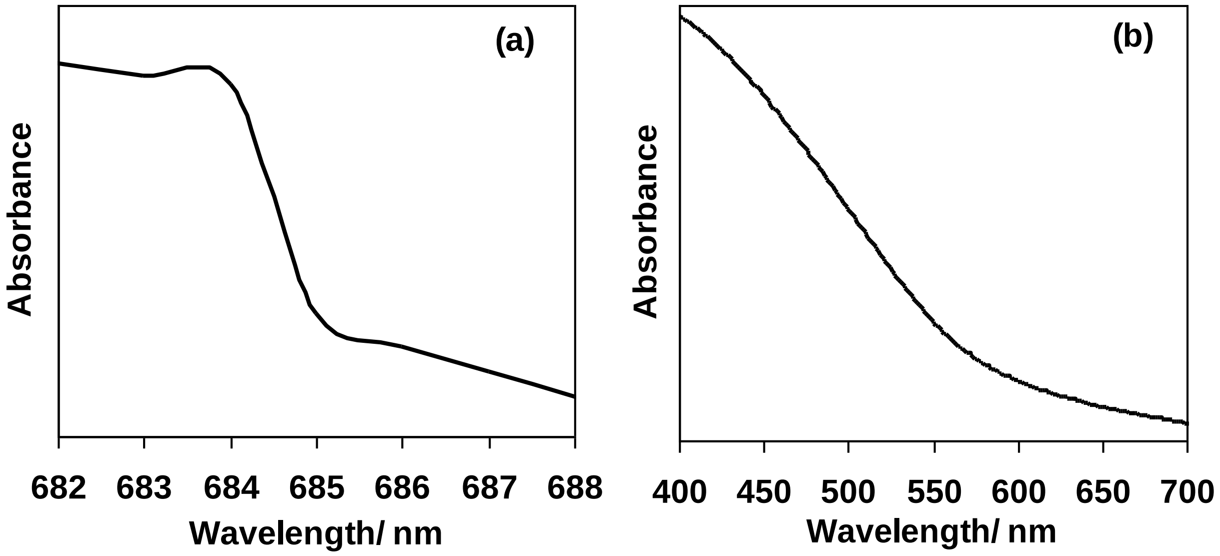

**Figure 2.** UV-vis absorption spectra of (a) pure P3HT film and (b) CdS/P3HT hybrid film.

The absorbance data was treated with Stern [12] equation to determine the band gap energy ($E_g$) and transition type of the semiconductor by plotting the $(Ah\nu)^{2/n}$ versus ($h\nu$) where n=4 for indirect transition and n=1 for direct transition.

The band gap, $E_g$ was determined by extrapolating the straight-line portion of the plot of $(Ah\nu)^2$ versus ($h\nu$) to the energy axis at A=0 (Fig. 3) since better linearity was obtained in the $(Ah\nu)^2$ versus ($h\nu$) plots. The band gap value of the P3HT/ITO was 1.81 eV [13] and after the electrodeposition of second layer CdS the hybrid CdS/P3HT/ITO films have band gap value of 2.07 eV, both with direct transition. The combined bandgap energy is between that of P3HT films and CdS (literature value 2.40 eV [14]).

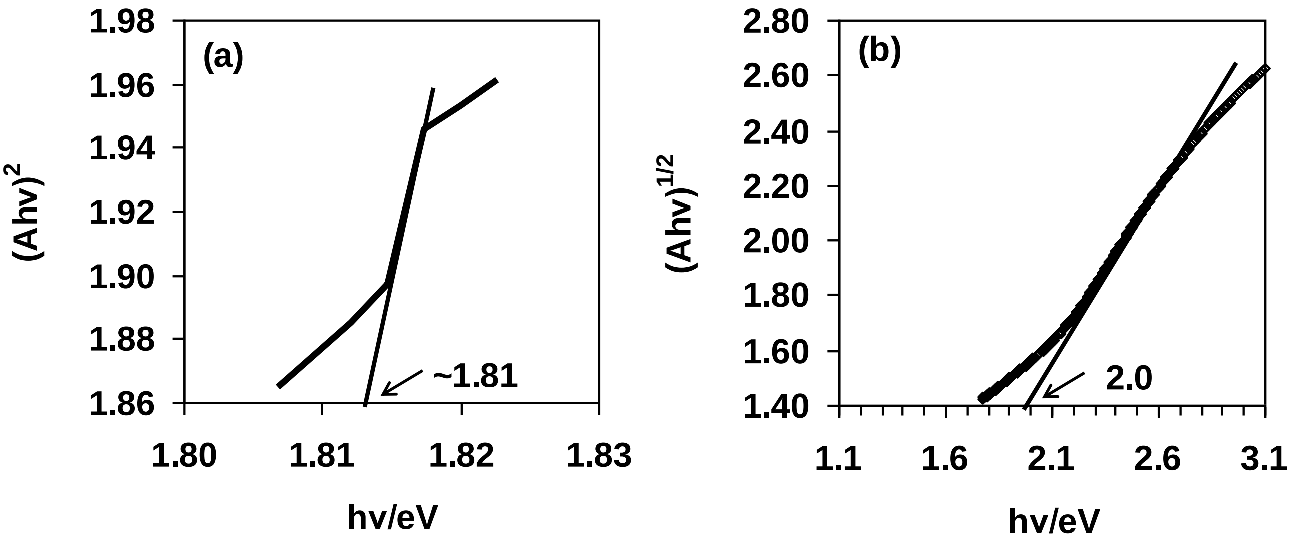

**Figure 3.** Plot of (a) $(Ah\nu)^2$ vs. $h\nu$ for pure P3HT film and (b) $(Ah\nu)^{1/2}$ vs. $h\nu$ for CdS/P3HT hybrid film.

*Photoelectrochemical properties.*-- Photoelectrochemical behaviour of P3HT/CdS hybrid films was measured using a three-electrode cell immersed in 0.01 M $Na_2S_2O_3$ electrolyte and illuminated with white light (300 W). The light was manually chopped to better delineate dark and photocurrent. The formation of an electron-hole pair resulted when semiconductor absorbs light. Photocurrent will be produced when the resulting charges are transferred to an acceptor. The current density-voltage curves are shown in Figure 4.

The photocurrent of P3HT was apparent on the anodic direction (Fig. 4(b)) thus the deposit is an p-type substance with holes as the majority carriers [15]. However, CdS/P3HT presents a higher photocurrent response than that of pure P3HT and absorbs radiation in a wider region by showing photoactivity at both the anodic and cathodic direction, photocurrent was more obvious at the cathodic sweep which is belongs to the n-type CdS deposited on the surface of P3HT (Fig. 4(a)). When combined with conjugated polymers, inorganic layer of CdS will act as electron acceptors because it has relatively higher electron affinity than conducting polymers [16]. The majority charge carriers in the P3HT are holes and in CdS are electrons. Upon illumination of light, the charge separation induced by photoexcitation drives the holes through the P3HT and the electrons through the CdS, consequently photocurrent is generated.

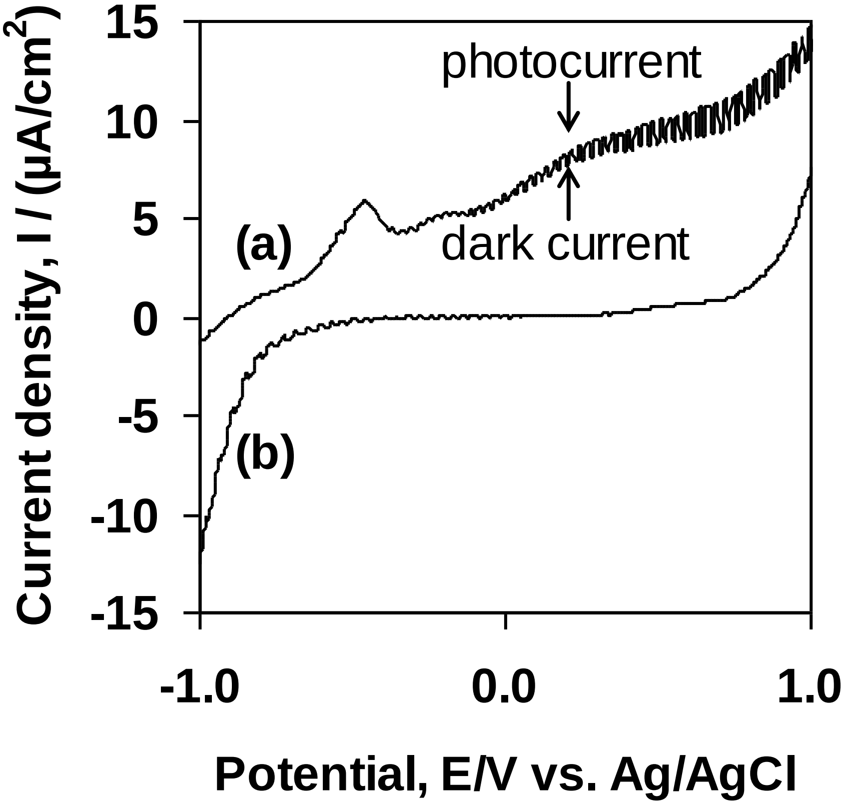

**Figure 4.** Current density-voltage curves of (a) CdS/P3HT hybrid film and (b) pure P3HT film.

The inorganic CdS acts as both the dissociation centers and generation centers by preventing or delaying electron-hole recombination, simultaneously producing excitons. The electrons from the n-type CdS occupy the holes in the p-type semiconductor in the p-n junction region [2]. Under applied electric field, the electrons are pushed to the n-type region while the holes are pushed to the p-type region. Light absorption in hybrid films is therefore enhanced by the different charge carrier transport paths [17].

## 4. CONCLUSION

In conclusion, we fabricated organic-inorganic hybrid p-n junction films based on P3HT and CdS by using electrochemical deposition method. Cyclic voltammetry of P3HT in bath containing supporting electrolytes showed that P3HT is stable in aqueous solution under applied potential and suitable to be used as base layer for cathodic electrodeposition of CdS. The optical properties of resulting hybrid films were analyzed by UV-visible spectrophotometer, the combined bandgap energy is 2.07 eV between that of P3HT films (1.81 eV) and CdS (2.42 eV). The photoelectrochemical properties were recorded in the form of current density-voltage curves showed CdS/P3HT presents a higher photocurrent response than that of pure P3HT and absorbs radiation in a wider region. Photoelectrochemical property of pure P3HT was enhanced after the deposition of a layer of n-type CdS on it.

## ACKNOWLEDGEMENT

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