

# Photo-electrochemistry at polymer/semiconductor interface

## Characterization of surface modified CdS based photovoltaic cells

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The photoelectrochemical (photovoltaic and photocatalytic) properties of single crystal CdS electrodes modified with polymeric films of  $\{\text{Ru}(\text{v-bpy})_3\}^{2+}$  (v-bpy is 4-vinyl-4-methyl-2,2-bipyridine) are presented. Such modified electrodes exhibit longer lifetimes than their native counterparts when operated in a photovoltaic cell with the free and immobilized ferro/ferri cyanide redox system. The photocatalytic behavior with  $\text{I}_3^-/\text{I}^-$  with and without sulfite solution has also been investigated. © 1999 Kluwer Academic Publishers

### 1. Introduction

Photoelectrochemical studies of semiconductor/electrolyte interfaces have been the subject of much research in recent times, in order to improve the solar energy conversion efficiencies of these devices [1–12]. A wide range of materials has been investigated both as single crystals and as amorphous thin films. Although fundamental studies are often done on the single crystal model, large scale conversion of solar energy will necessarily rely on the amorphous and polycrystalline forms.

One of the most critical problems confronting the use of semiconductor electrodes in a liquid junction photovoltaic cells is the propensity of many of these materials to undergo photo corrosion. This is especially true for nonoxide-type semiconductors, such as Si, CdS, CdSe and GaAs. Many approaches have been advanced for the stabilization of these semiconductors under operation [13–22]. These include the modification of the surface with fast outer-sphere redox couples such as ferrocene [13], various viologens [15–17] and others [18–20], as well as the use of conducting polymers such as polypyrrol [21]. The formation of a different surface layer that will be less susceptible to decomposition has also been employed [22]. A particularly good example was given by Bard and co-workers on the formation of platinum selenides for the protection of Si photo anodes [23]. The effects of the electrolytic medium have also been explored. Wrighton and co-workers [24] employed a very concentrated (15 M) aqueous solution of LiCl in order to lower the activity of water, thereby suppressing decomposition. In addition, in the case of the cadmium chalcogenides (sulfide and selenide) the presence of a polysulfide electrolyte [25–27] greatly enhances the stability of the semiconductor

under operation. Surface modification of semiconductor electrodes has been employed for electrocatalytic application, such as the photo-assisted evolution of hydrogen [15–16], chloride oxidation [28, 29] and  $\text{CO}_2$  reduction [30] to name but a few.

This paper is a presentation of the study of the photoelectrochemical properties of both native and surface modified CdS electrodes. Films of poly  $[\text{Ru}(\text{v-bpy})_3]^{2+}$  were used as a surface modifier. The photovoltaic properties have been investigated in aqueous ferro/ferri cyanide solution, while the  $\text{I}_3^-/\text{I}^-$  couple in the presence of aqueous  $\text{SO}_3^{2-}$  was used to study the photo-catalytic properties.

### 2. Experimental

#### 2.1. Materials

Single crystals of n-CdS, obtained from Cleveland Crystals Inc. were polished to smoothness with (3  $\mu\text{m}$ ) diamond paste. Ga-In eutectic was rubbed onto the back of the crystal as an ohmic contact. A copper wire was attached to the crystal with conducting silver paint (ACME). The wire was inserted into 6 mm glass tubing and the electrode was masked with torr-seal (Varian) or chemigrip (Chemplast), except for the surface under investigation (typically 0.041  $\text{cm}^2$ ). Prior to use, the electrodes were etched in conc. HCl for 2 min and rinsed with deionized water.

#### 2.2. Chemicals

Acetonitrile (Burdick and Jackson distilled in glass) was dried over 4P molecular sieves. Tetra n-butyl ammonium perchlorate (TBAP) (G. F. Smith) was twice recrystallized from ethyl acetate and dried in vacuo at

70 °C for 72 h.  $[\text{Ru}(\text{v-bpy})_3]^{2+}$  (where v-bpy is vinyl bipyridine) was prepared according to a previously reported procedure [31, 32]. All other reagents were of at least reagent grade quality and were used without further purification.

### 2.3. Electrochemistry

Electrochemical experiments were performed with a PAR. model 179 Potentiostat, 179 Digital coulometer and 175 Universal Programmer or with a BAS 100 B Electrochemical Analyzer. Data were recorded on either Soltec or Hewlett-Packard X-Y recorders or on a Nicolet digital oscilloscope. Conventional three-compartment electrochemical cells, separated by medium porous frits and provided with a flat Pyrex window were employed.

Modification of CdS electrodes with poly $[\text{Ru}(\text{v-bpy})_3]^{2+}$  films was performed in acetonitrile solution containing 2.0 mM  $[\text{Ru}(\text{v-bpy})_3]^{2+}$ , and 0.10 M TBAP as supporting electrolyte. Reductive electropolymerization was used by successive scanning of the potential between  $-0.9$  V and  $-1.8$  V vs. SSCE. Photoelectrochemical studies were performed in either an aqueous solution of (50 mM/5mM) or 10/1 ratio of  $[\text{Fe}(\text{CN})_6]^{-4/-3}$  in 0.1 M KCl or aqueous  $\text{SO}_3^{2-}$  solutions in the absence or presence of iodide ions with 0.1 M KCl. All potentials are referenced to a sodium saturated calomel electrode (SSCE) to minimize the liquid junction potential. Experiments were conducted at room temperature. Capacitance measurements were carried out by using a Princeton Applied Research Model 5204 Lock-in analyzer in conjunction with a Hewlett-Packard Model 200 CDR Oscillator which provided a sinusoidal signal of 10 mV (peak to peak amplitude). All measurements were reported at 1 KHz frequency.

### 2.4. Irradiation sources

Irradiation of the electrodes was performed with an Oriel Model 6130 100 W quartz-halogen lamp. For photo current spectral measurements, a Laser Precision Model CTX 534 Light Chopper, and an Oriel Model 7240 monochromator and an EG & G Electro-optics Model 450-1 radiometer/photometer were used. White IR free light of 10 mW was used for illumination of the electrodes. Absorption spectra were performed on a Hewlett-Packard Model 8451 Diode Array spectrophotometer.

## 3. Results and discussion

### 3.1. Modification of CdS

Successive scanning of CdS single crystal electrodes' potentials from  $-0.9$  V to  $-1.8$  V vs. SSCE. in 2.0 mM  $[\text{Ru}(\text{v-bpy})_3]^{2+}$ , and 0.10 M TBAP as supporting electrolyte was controlled to give  $\approx 5 \times 10^{-9}$  mol/cm<sup>2</sup> of poly  $[\text{Ru}(\text{v-bpy})_3]^{2+}$  films. Such surface coverage corresponds to  $\approx 80$  nm or 60 mono layers. The density of countered Ru<sup>2+</sup> centers on the CdS surface is approximately  $3 \times 10^{21}$  atom/cm<sup>-3</sup> which represents  $10^4$

times the hole density of the native electrode under illumination. The overlapping of the potential window of both CdS and poly  $[\text{Ru}(\text{v-bpy})_3]^{2+}$  substantiate the interest in such modification. The polymeric film permeability plays an important role in the modified CdS electrodes' outcome. Studies show that more than 30% of the positive centers in poly  $[\text{Ru}(\text{v-bpy})_3]^{2+}$  films [33] can be paired with anionic redox active centers such as  $[\text{Fe}(\text{CN})_6]^{-4/-3}$ . This creates a different environment, where the redox system (that interacts within the photo activated CdS window) consists of free and immobilized ions. The measured diffusion coefficients,  $D$ , of the immobilized redox anions were  $\approx 10^{-3}$   $D$  of their free state.

### 3.2. Photoelectrochemical behavior

Cyclic voltammograms of native and surface modified CdS in aqueous iron hexacyano complex couples as well as in non-aqueous ferrocene couples of similar concentration and ratio, with and without illumination are shown in Fig. 1. From this figure the following comments can be deduced.

- (1) The photocurrent begins to appear at a more negative potential in the aqueous iron hexacyano complex couple, than in the non-aqueous ferrocene solution. Although SSCE was used as a reference electrode to minimize the liquid junction, however the large difference in the flat band potential in aqueous and the non aqueous cannot be interpreted as un-eliminate liquid junction. This can be attributed to a less negative flat band potential in non-aqueous solution. Furthermore, iron hexacyano complex enhances the kinetics due to the formation of the surface active  $\text{K}_2\text{CdFe}(\text{CN})_6$  compound.
- (2) The photocurrent was always higher in aqueous than in non-aqueous electrolytes, and also higher for the native electrode than for the modified one.
- (3) The CV in ferrocene solution shows an irreversible cathodic peak at  $-0.55$  V vs. SSCE, due to the reduction of photo generated  $\text{Cd}^{2+}$  in the first scan.
- (4) The CV of CdS electrodes in the dark does not show any irreversible peak, negating any  $\text{O}_2$  or  $\text{Cd}^{2+}$

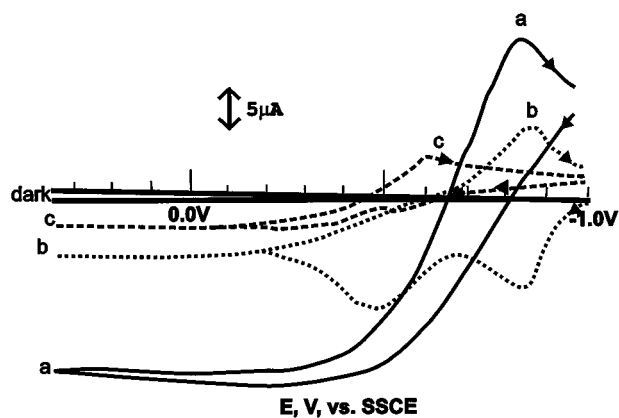
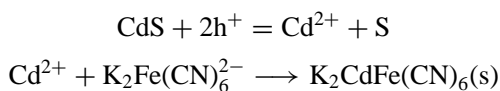


Figure 1 Cyclic voltammograms of CdS electrodes in (10:1) Ferro/Ferri cyanide (a, b) and Ferrocene (c) under illumination. (a) Native CdS (b) CdS modified poly  $[\text{Ru}(\text{v-bpy})_3]^{2+}$  (c) Native CdS in Ferrocene.

reduction. Considering that the following reactions took place during the photo corrosion of CdS in  $\text{K}_2\text{Fe}(\text{CN})_6^{2-}$  solution:



consequently, the semiconductor surface is modified by the insoluble  $\text{K}_2\text{CdFe}(\text{CN})_6$  layers after the first anodic scan. However, the fact that the reverse scan results in an irreversible cathodic peak at  $-0.8$  V vs. SSCE which is correspondent to the reduction of  $\text{Cd}^{2+}$  (Fig. 1a), suggest that the above reactions concurrently took place. On the other hand, the modified electrodes exhibit a reversible wave at  $-0.9$  V vs. SSCE (Fig. 1b), as well as an irreversible anodic peak at  $-0.5$  V. Such behavior is related to the very complex interface which consists of free and immobilized  $[\text{Fe}(\text{CN})_6]^{-4}$  as well as an over layer of insoluble  $\text{K}_2\text{CdFe}(\text{CN})_6$ .

(5) The solvent is an important factor on the photoelectrochemical behavior of the CdS electrode, because the photocurrent produced in the aqueous iron hexacyano complex couple is higher than that in the non-aqueous ferrocene solution (Fig. 1a and c).

### 3.3. Photo current spectra

The photo current spectra of native and surface modified CdS electrodes in the presence of  $[\text{Fe}(\text{CN})_6]^{-4/-3}$  and thianthrene redox couple are shown in Fig. 2. The sharp raise in the photo current at about 488 nm corre-

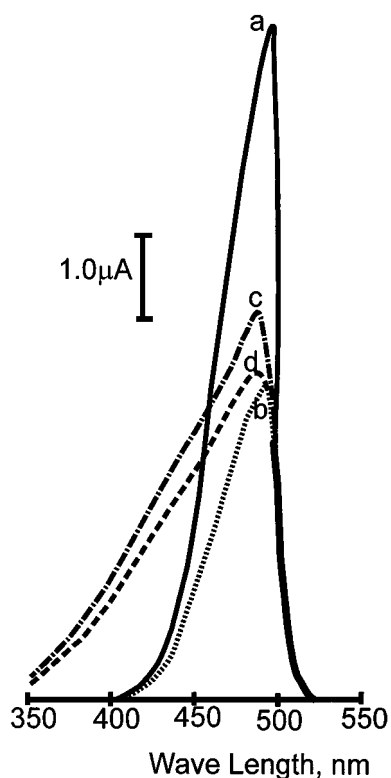


Figure 2 Photocurrent spectra in (10 : 1) Ferro/Ferricyanide for (a) Native CdS (b) CdS modified poly  $[\text{Ru}(\text{v-bpy})_3]^{2+}$  and in (10 : 1) Thianthrene redox couple for (c) Native CdS (d) CdS modified poly  $[\text{Ru}(\text{v-bpy})_3]^{2+}$ .

sponds to a band gap of about 2.4 eV. A sharpness at this wavelength also indicates that the absorption characters are dominated by the bulk properties of CdS. It is worth noting that for the modified electrode, the polymeric film of poly  $[\text{Ru}(\text{v-bpy})_3]^{2+}$  had a clear filtering effect; thus, the observed currents were smaller than the corresponding ones for the unmodified electrode. In non aqueous (7.5 mM/0.75 mM) thianthrene redox couple, both native and modified CdS electrodes show less photo current than in the aqueous  $[\text{Fe}(\text{CN})_6]^{-4/-3}$  solutions; however, the filtering effect was higher in aqueous solution than in non aqueous solution. The aqueous  $[\text{Fe}(\text{CN})_6]^{-4/-3}$  is immobilized by either ion exchange with the counter ions of  $\text{Ru}^{2+}$  centers (ion pairing) or by forming insoluble  $\text{K}_2\text{CdFe}(\text{CN})_6$ , causing this decrease in the photo current. The fact that thianthrene does not undergo ion pairing or insoluble salt formation is a confirmation of this statement. The percentage of the photocurrent loss in aqueous  $[\text{Fe}(\text{CN})_6]^{-4/-3}$  solution upon modifying the native electrode is more than 50%, compared to 15% in non aqueous thianthrene solution (Fig. 2c, d). Aqueous  $[\text{Fe}(\text{CN})_6]^{-4/-3}$  solution is chosen to be the redox solution in this study, because the photo current generated from it was almost twice that generated from the non aqueous thianthrene.

### 3.4. Photovoltaic cells

Regenerative liquid junction photovoltaic cells with ferro/ferricyanide (10 : 1) as the redox couple in 0.1 M KCl were constructed with both native and surface modified CdS. The power curves for these cells are presented in Fig. 3a and b, respectively. It is obvious that the native CdS electrode exhibits a significantly larger short circuit current than the modified electrode and we ascribe this to the following effect of the electropolymerized film of  $[\text{Ru}(\text{v-bpy})_3]^{2+}$ . It is known that  $[\text{Ru}(\text{v-bpy})_3]^{2+}$  can absorb light and produce  $([\text{Ru}(\text{v-bpy})_3]^{2+})^*$ , an excited state [34] that is considered to be an active reducing agent. In the presence of  $\text{Fe}^{3+}$ ,

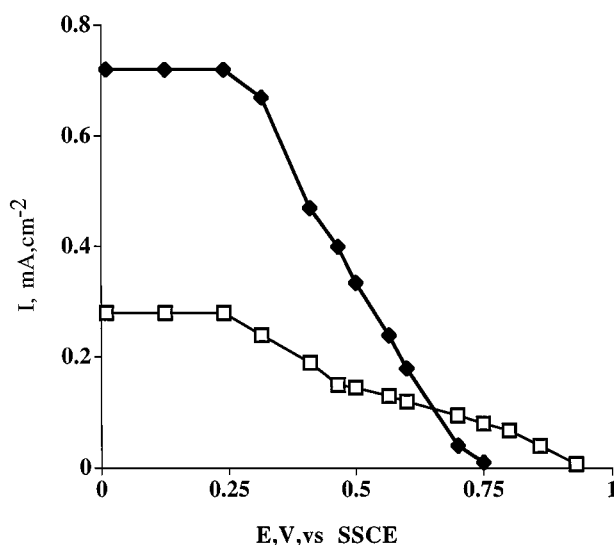
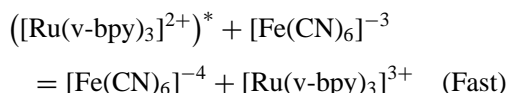
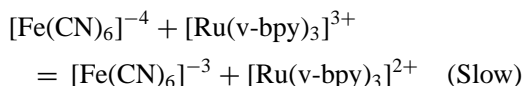


Figure 3 Power Curve of photovoltaic cells based CdS electrodes in (10 : 1) Ferro/Ferricyanide (1) Native CdS (2) CdS modified poly  $[\text{Ru}(\text{v-bpy})_3]^{2+}$ .

the following may occur:



$\text{Fe}^{2+}$  and  $[\text{Ru}(\text{v-bpy})_3]^{3+}$  react back according to the following equation:



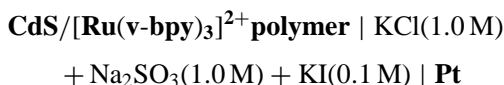
The slow rate of the second reaction ( $3.16 \times 10^{-4}$  cm/s) quenches the possible enhancement made by the excited complex ( $[\text{Ru}(\text{v-bpy})_3]^{2+})^*$ , which leads to thermalizing the light energy and consequently, a lower photocurrent. The modified electrode appears to have a higher open circuit voltage. The value of the fill factors was 0.4 for the native CdS electrode as compared to a value of 0.3 for the modified one.

### 3.5. Photocatalytic cell

The following notation represents a photocatalytic cell based on CdS:



and



The photo catalytic effect is used to carry out the following reaction:



where KCl is used as a supporting electrolyte, and  $\text{Na}_2\text{SO}_3$  is used for the reduction of the photo liberated iodine in order to avoid absorption of light.

Understanding the photoelectrochemical behavior of CdS in the aforementioned cell electrolyte requires studying the behavior of CdS (native and modified) in KCl solution and in the presence of sulfite ions. Fig. 4

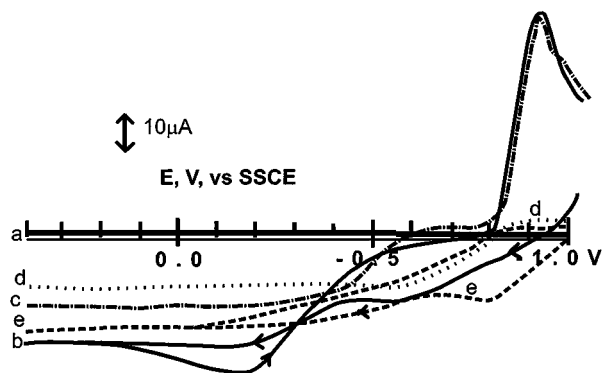


Figure 4 Cyclic voltammograms of illuminated CdS in (a) (b, c, d, e) in darkness (b) 0.1 M KCl (c) 0.1 M KF (d) 0.1 M KCl + 1.0 M  $\text{Na}_2\text{SO}_3$  (e) 0.1 M KCl + 1.0 M  $\text{Na}_2\text{SO}_3$  + 0.05 M KI Scan rate 100 mV/sec.

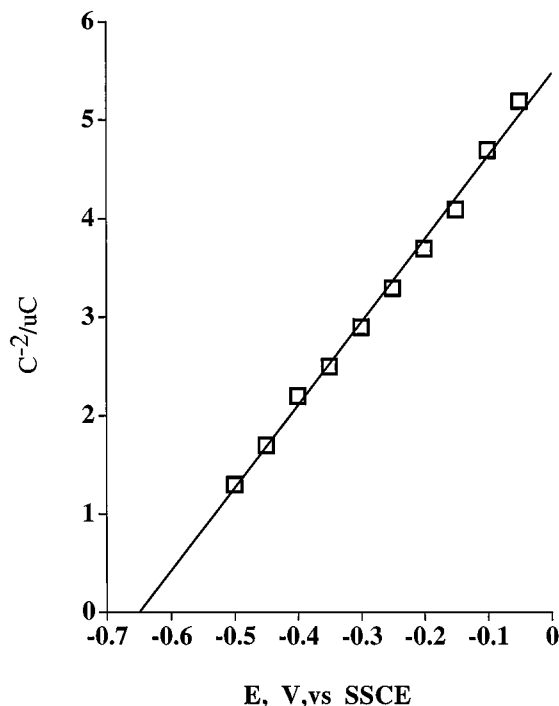


Figure 5 Mott-Schottky plot of CdS in 1.0 M  $\text{Na}_2\text{SO}_3$  + 0.1 M KCl.

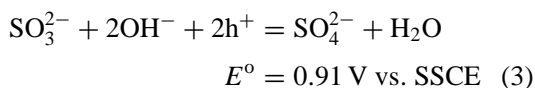
illustrates the cyclic voltammograms with and without illumination of CdS in 0.1 M KCl solution. The produced photo current can be attributed to photo corrosion of CdS as well as possible oxidation of  $\text{Cl}^-$  through the following reaction:



The fact that the photo current in KCl solution is higher than that in the presence of KF solution (Fig. 4b, c) is evidence for such a statement. This result is expected, because the redox potential of  $\text{F}/\text{F}^-$  is 2.6 V, while that of  $\text{Cl}/\text{Cl}^-$  is 1.35 V. The calculated valance band edge from Fig. 5, is 1.75 V, which indicates that the oxidation of  $\text{F}^-$  on illuminated CdS is impossible. Quantitative treatment of the photoelectrochemical behavior of CdS indicates that the amount of  $\text{Cd}^{2+}$  produced during the photo corrosion is estimated to be  $1.3 \times 10^{-8}$  mol/cm<sup>2</sup> ( $1.73 \times 10^{-3}$  mol/cm<sup>3</sup>). Furthermore, comparing the total charge due to the photo current in KCl and in KF solutions indicates that 25% of the resultant photo current is due to oxidation of  $\text{Cl}^-$ . The forward scan has less photo current than the reverse one. This behavior suggests that the product of the forward scan enhances the electrode's photo response. It is possible that  $\text{Cl}_2$ , as one of the products, caused an etching of the electrode surfaces, and reactivated the interface [35].

Upon the addition of 1 M  $\text{SO}_3^{2-}$  to 0.1 M KCl (pH 8.5), the photo current had decreased (Fig. 4d), while the peak of  $\text{Cd}^{2+}$  reduction had disappeared. Such results suggest that  $\text{SO}_3^{2-}$  either inhibits the photo corrosion of CdS or forms an overlayer of insoluble  $\text{CdSO}_3$ . However, the behavior of CdS in sulfite solution has been discussed earlier [36], as the oxidation of  $\text{SO}_3^{2-}$  to  $\text{SO}_4^{2-}$  or  $\text{S}_2\text{O}_6^{2-}$  can take place according to the

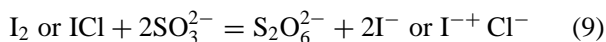
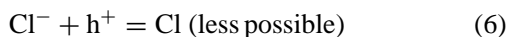
following equations:



In the presence of  $\text{Cl}^-$  such reactions are less likely for the following reasons. First, it needs a  $2 \text{h}^+$  step which is kinetically unlikely to occur. Second, reaction 4 requires a higher S-S bond energy (425 kJ/mol) in order to have the formation of  $\text{S}_2\text{O}_6^{2-}$  ( $^{-2}\text{O}_3\text{S}-\text{SO}_3^{2-}$ ) in comparison to that of Cl-Cl bond which needs less energy (243 kJ/mol) [27].

Addition of  $\text{I}^-$  to the  $\text{Cl}^-/\text{SO}_3^{2-}$  electrolyte again increases the photo current to about 30% compared to that in the  $\text{Cl}^-/\text{SO}_3^{2-}$  electrolyte (Fig. 4e). This is evidence that the photo oxidation of  $\text{I}^-$  through reaction 1 took place. Because this reaction is a one electron transfer, it is kinetically possible. On the other hand, the energy for I-I or I-Cl bond formation is very low, making these bonds thermodynamically possible.

On the basis of these facts, the mechanism of the photo catalytic reactions at CdS in  $\text{Cl}^-/\text{SO}_3^{2-}/\text{I}^-$  electrolyte can be written as follows:



When the  $\text{SO}_3^{2-}$  is consumed through reaction 9, no further reduction of  $\text{I}_2$  will take place.

Similar behavior has been reported for the modified CdS electrode, except that lower photo currents than that shown in Fig. 4 have been observed. Such behavior can be explained by the fact that the photo catalytic oxidation of  $\text{I}^-$  requires that the latter has to diffuse through the poly  $[\text{Ru}(\text{v-bpy})_3]^{2+}$  film. However, the possible partial ion pairing between  $\text{I}^-$  and  $\text{Ru}^{2+}$  centers may delay the diffusion process. Fig. 6 indicates that the photo current of the modified electrode almost reaches the photo current of the native electrode after two hours. Furthermore, formation of entrapped particles of  $\text{CdSO}_3$  within the polymer network decreases the intensity of the illuminations.

#### 4. Electrode stability

##### 4.1. A-In aqueous $[\text{Fe}(\text{CN})_6]^{-4/-3}$

The stability of native and modified CdS in electrodes was studied by monitoring the photo current versus time in the ferri/ferro redox system. The results presented in Fig. 6 show that the native CdS electrode exhibits a sharp decrease in photocurrent (Fig. 6a) initially and then the output stabilizes. The constant output after  $\approx 60$  min, indicates an inhibition of the corrosion process due to the formation of a stable over-layer of

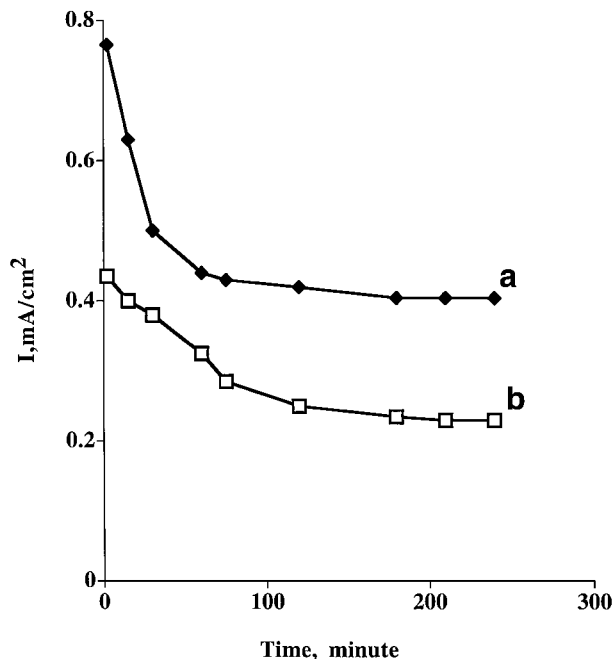


Figure 6 Stability curve in (10:1) Ferro/Ferri cyanide solution for (a) Native CdS (b) CdS modified poly  $[\text{Ru}(\text{v-bpy})_3]^{2+}$ .

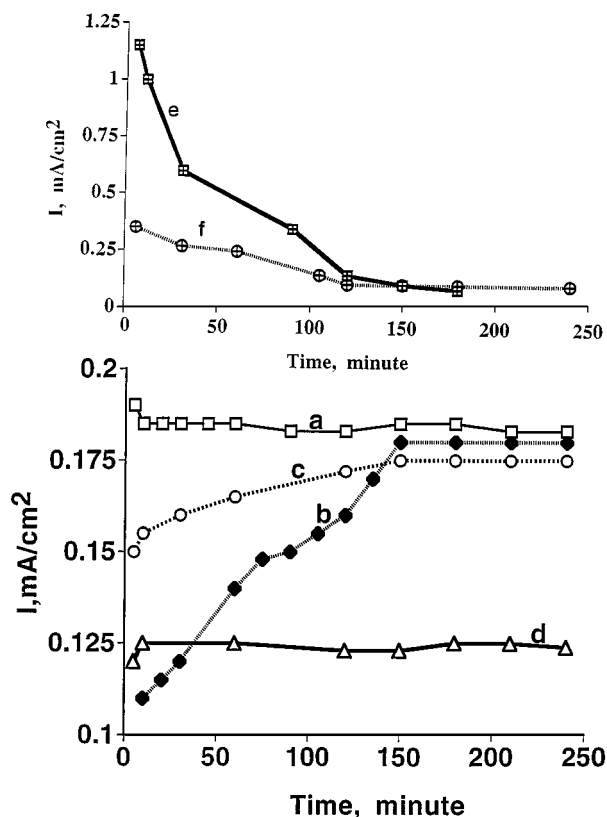


Figure 7 Stability curve of (a) Native CdS in 0.1 M KCl + 1.0 M  $\text{Na}_2\text{SO}_3$  + 0.05 M KI (b) CdS modified poly  $[\text{Ru}(\text{v-bpy})_3]^{2+}$  in electrolyte a (c) Native CdS in 0.1 M KCl + 1.0 M  $\text{Na}_2\text{SO}_3$  (d) CdS modified poly  $[\text{Ru}(\text{v-bpy})_3]^{2+}$  in electrolyte c (e) Native CdS in 0.1 M KCl (inset) (f) CdS modified poly  $[\text{Ru}(\text{v-bpy})_3]^{2+}$  in 0.1 M KCl (inset).

$\text{K}_2\text{CdFe}(\text{CN})_6$ . For the modified electrode, the initial decrease is significantly slower and in addition, the output remains invariant after about two hours (Fig. 6b). Such behavior of the modified electrode is due to formation of  $\text{K}_2\text{CdFe}(\text{CN})_6$  on the surface as well as

the partial immobilization of  $[\text{Fe}(\text{CN})_6]^{-4/-3}$  anions through the ion exchange process.

#### 4.2. B-In aqueous $\text{I}_3^-/\text{I}^-$

Fig. 7 illustrates the variation of the maximum photocurrent with time for native and modified CdS in (a) native CdS in 0.1 M KCl + 1.0 M  $\text{Na}_2\text{SO}_3$  + 0.05 M KI, (b) modified CdS in electrolyte a, (c) native CdS in 0.1 M KCl + 1.0 M  $\text{Na}_2\text{SO}_3$ , (d) modified CdS in electrolyte c, (e) native in 0.1 M KCl and (f) modified in 0.1 M KCl. It can be noticed that (1) electrolyte (c) exhibited the best stability, (2) the increase of photocurrent with time for the modified electrode in the electrolyte c, is due to the possible diffusion of  $\text{I}^-$  through poly  $[\text{Ru}(\text{v-bpy})_3]^{2+}$  matrix and (3) addition of electrolyte b improved the photocurrent, which is consistent with the previous results obtained by Hodes *et al.* [37].

#### 5. Conclusions

Photovoltaic and photocatalytic properties at the modified CdS single crystal electrodes have been investigated. Although the modified electrode shows a lower photocurrent, it produces a larger open circuit potential than the native electrode in the designed photovoltaic cell. The kinetics of the charge transfer between the immobilized redox system and fixed  $\text{Ru}^{2+}$  centers in the polymer film can contribute to and explain the filtering effect of the modifier. The formation of an over-layer of  $\text{K}_2\text{CdFe}(\text{CN})_6$  insoluble complex and/or the polymer film on the electrode's surface offer a greater inhibition of the photocorrosion process. On the other hand, while the polymeric film offers more corrosion protection, it does not reduce the photo catalytic current in (KCl/ $\text{Na}_2\text{SO}_3$ /KI solutions) to as great an extent. The full output of the photocurrent can be reached after complete diffusion of the  $\text{I}^-$  takes place. No enhancement to the photo conversion efficiency for the modified electrode with poly  $[\text{Ru}(\text{v-bpy})_3]^{2+}$  has been reported; however, the modification of semiconductor electrodes represent a forward step towards developing a photoelectrochemical cell with immobilized or solid redox reagents.

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