

Research of Gerischer model in transferring electrons between energy states of CdS thin film and ferro-ferric redox system

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ABSTRACT

In this study, we describe interfacial electron transfer by semi classical theory described by Marcus and then developed by Gerischer, in which heterogeneous electron transfer is used for semiconductor/electrolyte interface. In this research, CdS thin film was electrodeposited on the indium tin oxide (ITO) and selected as an electrode for experiments. The kinetic constant rate and reorientation energy were measured in the solution with different concentrations of redox system: Fe^{3+}/Fe^{2+} . Increase of Fe^{3+} resulted in the increase of cathodic current. This increase is concern with the vicinity of redox potential to the valence band (VB) edge of CdS. The I-V curve and electrochemical impedance spectroscopy admitted reduction of Fe^{+3} on the VB of CdS.

Keywords: Fe³⁺/Fe²⁺ redox, cadmium sulfide, Gerischer model, indium tin oxide.

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INTRODUCTION

Cadmium sulfide (CdS) is one of the most important groups of II to VI semiconductors with suitable band gap of 2.4 eV (Memming, 2001). It is a particularly interesting choice due to its relatively high absorption coefficients, special optical properties and ease of fabrication (Jia et al., 2006). CdS solar cells as a promising candidate for photovoltaic device are usually fabricated on indium tin oxide (ITO) (Yoshida, 1995).

The researchers have studied the nanostructured semiconductor electrodes (Chiba et al., 2006), but few have investigated the effect of redox electrolytes to improve the performance of the solar cells. The most

common electrolyte is the triiodide/iodide (I_3^-/I^-) redox couple (Nazeeruddin et al., 2001). Although, this redox couple works efficiently, it has disadvantages (Wang et al., 2010). Therefore, it is important to study another redox couple.

In 1960 Gerischer developed a model in which the charge transfer occurred in terms of electronic energies in the solid and of energy levels in solution, the latter

being associated with ions. This model was a suitable approach for semiconductor electrodes, because of electrons transfer via the conduction or valence band (Gerischer, 1990).

This paper highlights recent progresses about effect of redox electrolytes in aqueous solvents on the photoelectrochemical behavior of CdS solar cells. We describe interfacial electron transfer reactions by semi classical theory of electron transfer which was originally developed by Marcus for donor-acceptor system in homogenous medium (Gerischer, 1990).

THEORY

Considering a simple redox reaction, the Nernst equation can be written in terms of electrochemical potentials:

$$\mu_{e,redox} = \mu_{e,redox}^{\circ} + kT \ln\left(\frac{C_{ox}}{C_{red}}\right)$$
(1)

Where $\mu_{e,redox}$, C_{ox} and C_{red} are the electrochemical potential of electrons in the redox system and the concentrations of the Ox and Red species, respectively. The electrochemical potential $\mu_{e,redox}$ is equivalent to a Fermi level of a redox system, $E_{F,redox}$, that the same reference level is used for the solid electrode and the redox system (Equation 2):

$$\mu_{e,redox} = E_{F,redox} \tag{2}$$

Usually the corresponding redox potential is given on a conventional scale using the Ag/AgCl as a reference electrode. In the Gerischer model, an electron transfer occurs from an occupied state in the metal or the semiconductor to an empty state in the redox system (Gerischer, 1990).

In this approach, the rate of electron transfer depends on the density of energy states on both sides of the interface. For instance, in the case of an electron transfer from the valence band of a semiconductor to the redox system the rate is given by:

$$\mathbf{j}_{\nu}^{-} = \mathbf{e} \, \mathbf{k}_{\nu}^{-} \mathbf{N}_{\nu} \, \mathbf{C}_{ox} \tag{3}$$

Where k_{ν}^{-} and N_{ν} are the rate constant and density of states in the valence band, respectively. The negative sign means cathodic current. So if we consider that N_{ν} is approximately constant and related to inherent characteristics of CdS semiconductor, then the ratio of $j_{\nu}^{-} / C_{\alpha x}$ in Equation 4 is a criterion of change in the value of k_{ν}^{-} :

$$\mathbf{j}_{v}^{-} / C_{ox} = \mathbf{e} \, \mathbf{k}_{v}^{-} \mathbf{N}_{v} \tag{4}$$

According to Equation 5, the value of k_{ν}^{-} is dependent on an exponential expression of redox Fermi ($E_{F,redox}^{\circ}$), edge of the valence band at the semiconductor-electrolyte junction (E_{ν}^{s}) and reorientation energy of redox (λ) respectively. The k is Boltzmann constant and T is absolute temperature.

$$k_{\nu}^{-} = k_{0} - \exp\left(\frac{\left(E_{\nu}^{s} + \lambda - E_{F,redox}^{\circ}\right)^{2}}{4kT\lambda}\right)$$
(5)

The accurate rate constant k_v^- as defined by Equation 5

can only be calculated if the λ is known besides the energy difference $E_v^s - E_{F,redox}^\circ$. If $E_v^s + \lambda = E_{F,redox}^\circ$ then k_v^- equals to maximum value of constant rate, k_0 . To estimate the value of k_v^- , it can be approximately substituted by j_v^- / C_{ox} . Equation 5 could be converted to Equation 6 which is a natural logarithm and summarized to Equation 7, while *a* is corresponding to Equation 8. By plotting $\ln k_v^-$ versus $E_{F,redox}^\circ^2$ (according to Equation 7) the value of λ can be calculated from slope of this line which is $\frac{1}{4kT\lambda}$.

$$\ln k_{\nu}^{-} = \ln k_{0} - \frac{\left(E_{\nu}^{s} + \lambda - E_{F,redox}^{\circ}\right)^{2}}{4kT\lambda}$$
(6)

$$\ln k_{\nu}^{-} = -\frac{E_{F,redox}^{\circ}^{2}}{4kT\lambda} + a$$
(7)

$$a = \ln k_0 - \frac{(E_v^s + \lambda)^2 - 2(E_v^s + \lambda)E_{F,redox}^\circ}{4kT\lambda}$$
(8)

The value of $4kT\lambda$ is about 0.1 eV so λ should be obtained in order of 1 eV (Memming, 2001; Memming, 2008; Nozik and Memming, 1996).

EXPERIMENTAL

Materials and solutions

ITO was used as a substrate, and materials, $Cd(NO_3)_2$, thiourea, NaOH, $K_3Fe(CN)_6/K_4Fe(CN)_6$ all with analytical grade (Merck) were used. Different concentrations of $K_3Fe(CN)_6/K_4Fe(CN)_6$ solutions as concentrations of Ox/Red were prepared with different values of 0.02/0.02, 0.02/0.2, 0.2/0.2 and 2/0.02.

Instruments and techniques

All electrochemical measurements were carried out in a conventional three-electrode cell powered by a μ -Autolabpotentiostat/galvanostat and a frequency response analyzer (Metrohm, model 12/30/302, The Netherlands). The frequency range 100 kHz to 10 MHz and modulation amplitude 5 mV were employed for Electrochemical Impedance spectroscopy (EIS) Studies. The impedance studies were carried out in open circuit potential and fitted by Zview3.1 software. The ITO set as

a working electrode, graphite as a counter and Ag/AgCl electrode as a reference electrode and 100 W tungsten lamp as light source.

Electro-deposition of CdS thin film

The ITO sheet with area of 1 cm² was used and cleaned with distilled water, acetone, and ethanol and then was ultra-sonicated in the isopropanol. Chronoamperometry technique was used to electrodeposit the cadmium and sulfur for 1 min separately. At the first the Cd was reduced on the ITO in solution of 0.1 M Cd(NO₃)₂. Then sulfide ion, S²⁻, was oxidized in the alkaline solution (pH > 10) containing 0.2 M thiourea. After electrodepositing of each layer, the surface of electrode was rinsed with distilled water to remove unabsorbed ions. The resulting electrode is denoted as ITO/CdS. The underpotential deposition (UPD) procedures mentioned above was repeated 10 times to achieve 10 layers of CdS.

RESULTS AND DISCUSSION

Figure 1 shows the cyclic voltammetry (CV) of the ITO/CdS in the redox electrolyte with different concentrations of Fe³⁺/Fe²⁺ that is reported in Table 1. Within range from +0.5 to -0.7 V/Ag/AgCl are observed oxidation and reduction peaks related to the redox system of Fe³⁺/Fe²⁺. The relation of Fe³⁺/Fe²⁺ redox system clearly effects on the reduction peak current of Fe^{3+} , I_p , in the range from +0.5 to -0.5 V/Ag/AgCl so that accordance to third column in Table 1, the highest reduction peak current is related to the redox electrolyte of Fe^{3+}/Fe^{2+} with 2/0.02 ratio which results in $E_{F redax}$ to be more positive in accordance with Equation 1. As a result $E_{F, redox}$ approximates to the valence band edge of CdS. In addition, simultaneous increase of Fe³⁺ concentration and $E_{F,redox}$ effectively increases the value of I_p. As can be seen another cathodic current initiate at -0.7 V/Ag/AgCl and continues up to the more negative potentials, which is related to the reduction of H_2O and Fe^{3+} . It seems that reduction of Fe^{3+} is simultaneously accompanied with the reduction of H₂O in this region because reduction current increases as Fe³⁺ concentration increases. The reduction on the CdS surface would be relevant to the CdS band structure and potential of Fe^{3+}/Fe^{2+} . So the position of the energy bands at the surface of CdS in aqueous solutions must be considered (Memming, 2001).

According to the references, the valence and conduction band position of CdS in the dark are placed at +0.7 and - 1.7 V/Ag/AgCl, respectively (Memming, 2001). The electrochemical standard potential of Fe^{3+}/Fe^{2+} is 0.58 V/Ag/AgCl.

According to Figure 1 and Table 1, reduction of Fe^{3+} ions initiates at +0.5V/Ag/AgCl. With accordance to the valence band position of CdS which is at +0.7V/Ag/AgCl, the reduction current of Fe³⁺ should occur in the valence band of CdS due to vicinity of energy levels. It can be observed that by increasing of oxidized species (Fe³⁺) from 0.02 to 2 M the value of $E_{F redox}$ changes from 0.58 to 0.74 V/Ag/AgCI. This change leads to redox Fermi level of Fe³⁺/Fe²⁺ approximate to the energy level of CdS valence band and consequently reduction current in this region is increased. In addition similar procedure is seen in the more cathodic region in which Fe³⁺ and H₂O reduces. Increasing of oxidized species (Fe^{3+}) from 0.02 to 2 M, results in change in the value of $E_{F, redox}$ from 0.58 to 0.74 V/Ag/AgCl according to Equation 1. It causes reduction in current from -0.013 to -0.026A at -1.8 V/Ag/AgCl. The change of the j_ from -0.013 to -0.026A results in change of k_{v}^{-} from 0.65 to 0.013 according to Equation 4; this means the rate constant has decreased 50 orders. So when concentration of oxidized species and consequently $E_{F,redox}^{\circ}^{2}$ increases, the kinetic constant rate decreases inversely. This is in good agreement with Equation 7, that increase of $E_{\textit{F.redox}}^{\circ}{}^2$ causes decrease of the $ln k_{\nu}^{-}$ because of negativity of $E_{\it F.redox}^{\,\circ}\,\,^2/\,4kT\lambda$. The reorientation energy of redox (λ) from slope of this line is obtained 0.7eV that this value is logical and accordance to Gerischer model.

The open circuit potential (OCP) of the ITO/CdS electrode in the redox electrolyte of Fe³⁺/Fe²⁺ with different concentrations is about +0.4 V/Ag/Ag/Cl. The current-voltage (I-V) diagram of this electrode in the different redox concentrations is plotted from OCP to 0.0 V/Ag/Ag/Cl in the dark and light condition (Figure 2). Theoretically, current difference at applied potential in the dark and light conditions is concerned with the light induced processes (Memming, 2001). Under applied overvoltage and in the dark, cathodic current follows Equation 9 where j_0 is exchange current.

$$j_{v}^{-} = -j_{0}[\exp(-\frac{e\eta}{kT}) - 1]$$
 (9)

The value of j_v^- in the dark condition is only dependent on applied overvoltage, η .

According to Figure 2, the value of j_v^- at 0.0V/Ag/AgCl in the dark and light conditions for two experiments with high ratio of ox/red (2/0.02 and 0.2/0.02) shows that light induced current is effectively higher than experiments with other ratios. This phenomenon clearly admits



Figure 1. CV diagram of ITO/CdS in the redox electrolyte with different concentrations of Fe²⁺/Fe³⁺.

Table 1. Kinetic constant rate from approximated relation by substituting j_{ν}^- / C_{ax} instead of k_{ν}^- .

| Ox / R ed(M) | $E_{F, redox}$ (V) | $I_p(A) \times 10^4$ | $E_{F, redox}^{\circ 2}$ | ^a j_{ν}^{-} (A) | a j_v^- / C_{ox} | ^a ln k_v^- |
|--------------|--------------------|----------------------|---------------------------|--------------------------------|--------------------|-------------------------|
| 0.02/0.02 | +0.58 | 6.93 | 0.49 | -0.013 | 0.65 | -0.43 |
| 0.02/0.2 | +0.52 | 23.5 | 0.59 | -0.012 | 0.6 | -0.51 |
| 0.2/0.02 | +0.64 | 7.7 | 0.68 | -0.017 | 0.085 | -2.46 |
| 0.2/0.2 | +0.58 | 20 | 0.49 | -0.021 | 0.105 | -2.25 |
| 2/0.02 | +0.74 | 50 | 0.77 | -0.026 | 0.013 | -4.34 |
| | | | | | | |

 $^{\rm a}$ related to reduction of H_2O at -1.8 V/Ag/AgCl.



Figure 2. LSV of the ITO/CdS in the redox electrolyte with different concentrations of ${\rm Fe}^{3+}\!/{\rm Fe}^{2+}.$



Figure 3 The Nyquist plots of CdS in different concentrations of redox electrolyte in the dark and under illumination condition at the OCP.



Figure 4. (a) The Bode-phase and (b) the Bode plots of ITO/CdS in different concentrations of redox electrolyte in the dark and under illumination condition at the OCP.

relationship between Fermi redox energy and band energy position in CdS.

Figure 3 is related to the Nyquist spectra of CdS thin film at the OCP in the dark and under light conditions for the two concentrations of redox electrolyte (2/0.02 and 0.2/0.02) with the highest values of j_v^- . These spectra were fitted to Randles equivalent circuit. In the high frequency, the value of R_s is related to the resistance of the CdS thin film in different concentrations of redox electrolyte. In addition, the diameter of semicircle (R_{ct}) is concerned with resistance of charge carriers in semiconductor. The decrease of R_{ct} at light condition is due to the increase of the charge carriers (such as electron in n-type semiconductors).

The difference of the current density is comparable to the transfer of the charge carrier for redox electrolyte 2/0.02 with respect to 0.2/0.02. Consequently, the difference of R_{ct} values are confirmed I-V plots. On the other hand, the value of the charge transfer resistance is related to the current density j_{ν}^- reversely. The value of R_{ct} in the redox electrolyte 2/0.02 is near to its value in the redox electrolyte 0.2/0.02 when the CdS thin film is in the darkness. However, the values of R_{ct} differ remarkably under illumination in two media of redox electrolyte. This result is observed in Bode plots (Figure 4b) clearly. Also, Figure 4a shows the Bode phase plot related to the Nyquist plot in Figure 3.

CONCLUSION

| Chronoamperometry | technique | was | used | to |
|-------------------|-----------|-----|------|----|
|-------------------|-----------|-----|------|----|

electrodeposit the cadmium and sulfur for 1 min separately on the ITO (ITO/CdS). The CV of the ITO/CdS in the redox electrolyte with different concentrations of Fe³⁺/Fe²⁺, show the highest reduction current is related to the redox electrolyte of Fe³⁺/Fe²⁺ with 2/0.02 ration and $E_{F,redox} = 0.74$ eV. In accordance with the valence band

position of CdS, reduction current of Fe³⁺ should occur in the valence band. Experiments show that when concentration of oxidized species and consequently

 $E_{F.redox}^{\circ}^{2}$ increases, the kinetic constant rate decreases

inversely. The light induced current at 0.0V/Ag/ is high when ratio of ox/red (2/0.02 and 0.2/0.02) is high. The EIS studies for these two ratios show difference of the current density is comparable to the transfer of the charge carrier for redox electrolyte 2/0.02 with respect to 0.2/0.02. The value of R_{ct} in the redox electrolyte 2/0.02 is near its value in the redox electrolyte 0.2/0.02 when the CdS thin film is in the darkness.

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