Scanning Electrochemical Microscopy. 42. Studies of the Kinetics and Photoelectrochemistry of Thin Film CdS/Electrolyte Interfaces

Santosh K. Haram† **and Allen J. Bard***

Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712

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We report here the novel use of scanning electrochemical microscopy (SECM) to study photoelectron transfer (PET) kinetics at the semiconductor/electrolyte interface. The model system chosen consisted of a polycrystalline cadmium sulfide thin film in contact with methyl viologen ($MV^{2+/+}$) and triethanolamine (TEOA) as redox mediator and hole scavenger, respectively. In the absence of illumination, SECM approach curves to CdS films deposited on glass showed negative feedback, consistent with an insulating substrate. Upon film illumination, positive feedback was obtained due to photoelectron reduction of MV^{2+} at the interface. The dependence of the pseudo-first-order rate constants (k_{eff}) on light intensity and scavenger and mediator concentrations was estimated and the quantum efficiency as a function of light intensity was determined.

Introduction

In this study, scanning electrochemical microscopy (SECM) was used to study the kinetics of photoelectron transfer (PET) reactions at the semiconductor/electrolyte interface (SEI). SECM has been demonstrated to be an effective means of determining electron transfer (ET) kinetics at polymer/liquid,[1,3] immobilized enzyme,[4,7] and liquid/liquid[8,12] interfaces, as well as in corrosion studies.[13,16] However, previous SECM studies of the SEI have concentrated on imaging active sites on TiO_2[17,18] Ta_2O_5[19,20] and obtaining topographic information. Only two reports consider the use of SECM to investigate ET at SEI. Horrocks et al.[21] probed dark ET kinetics at the WSe_2 and Si/electrolyte interfaces, while Kemp et al.[22] described the use of transient techniques to investigate chlorophenol decomposition kinetics on illuminated TiO_2 particulate films. Here we report the use of SECM steady-state measurements to obtain ET kinetic information about processes at an illuminated SEI. This work aims to understand PET using SECM feedback mode. The model system chosen in this case was a CdS thin film in contact with aqueous methyl viologen. This choice was dictated by the simplicity of this system. Moreover, while the kinetics of the dispersed CdS colloid/MV system has been well-studied by such methods as time-resolved spectroscopy,[23] rotating ring disk electrode voltammetry,[24,26] and impedance spectroscopy,[27] similar studies of PET at the CdS thin film/MV interface have not appeared.

The substrate in this case, the solution containing MV^+ and TEOA, and the CdS thin film was at the open circuit. The SECM response at a Pt tip showed negative feedback in the dark as the substrate cannot reduce tip-generated MV^{2+}, i.e., the film behaved as an insulator. However, upon illumination, MV^{2+} can be reduced to MV^+ at the film/solution interface and the tip current increased in the vicinity of the SEI, giving positive feedback. The amount of the feedback was a measure of the rate of generation of MV^+. By fitting experimental approach curves to theory, apparent pseudo-first-order rate constants (k_{eff}) for the PET reaction could be estimated. The dependence of k_{eff} on light intensity and the concentration of MV and triethanolamine (TEOA) was determined and the quantum efficiency of the reaction as a function of light intensity was estimated.

Experimental Section

Chemicals. All chemicals were of the highest available purity and were used without further purification. Solutions were prepared in Milli-Q water (18 MΩ). Cadmium acetate, thiourea, ammonium hydroxide (30%), methyl viologen, triethanolamine, zinc granules (30mesh), mercuric chloride, and potassium chloride were purchased from Aldrich.

Deposition CdS Films. CdS films (ca. 10*μ*m thick) were deposited on glass substrates by the method[28,31] previously reported for electroless deposition (or chemical bath), with slight modifications. Typically, 10 mL of 0.1 M cadmium acetate, followed by 10 mL of 0.2 M thiourea, was added to 150 mL of 0.2 M TEOA in a 250 mL stoppered flask under constant stirring. Then 1 mL of 30% NH_4OH was subsequently added. After vigorous stirring, the contents were transferred to a cylindrical cell containing 18 precleaned (piranha solution) glass slides (2.3 cm × 2.3 cm) thermostated at 60 °C. Hydrolysis of thiourea leads to the formation of S^{2-} ions that, in turn, react with cadmium acetate to form bright orange CdS films on the substrates. After a stipulated time, the films were removed and rinsed with copious amounts of Milli-Q water. To obtain thicker films, this procedure was repeated. After the final deposition, the films were again rinsed with water and then dried under a stream of Ar gas. All such prepared films were stored in a desiccator prior to use.

PET−SECM Measurements. *Setup*. A schematic of the experimental setup is given in Figure 1. Cyclic voltammmograms and approach curves were obtained using a CHI 900 SECM instrument (CH instruments, Austin, TX). The SECM platform was replaced by a custom-designed one so that measurements could be conducted in an inert atmosphere with provision for illumination of the films from below. The light source for film illumination consisted of a 300 W tungsten halogen lamp with an 8 cm IR filter (0.05 M $CuSO_4$). The

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† Present address: Department of Chemistry, University of Mumbai, Vidyanagari, Mumbai 400 098, India.

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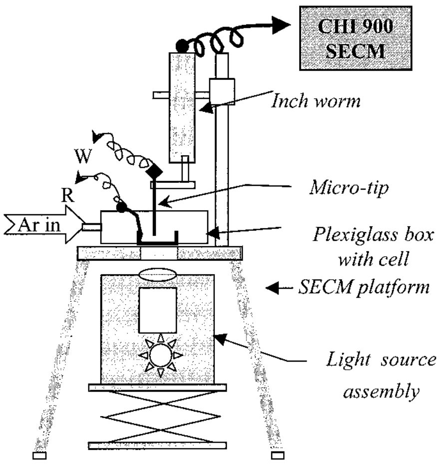

Figure 1. The setup used for PET−SECM measurements. The CdS film was back-illuminated, as it was technically difficult to illuminate from the top due to inch-worm assembly. The cell was enclosed in the plexiglass box. The positive pressure of Ar was always maintained in the box through out the experiment in order to avoid air oxidation of MV^+.

intensity of the source was controlled by a rheostat and measured by an optical power meter (Newport Model 1815C).

Microelectrodes (ME) Preparation. SECM tips were prepared by heat-sealing Pt wires (25 μm diameter Goodfellow, UK) in borosilicate glass capillaries under vacuum, followed by polishing and sharpening as previously described.[32] The viability of the resulting tip was determined by slow sweep cyclic voltammetry (CV) in a 2 mM ferrocyanide, 0.1 M KCl solution. Tips were characterized by an RG ($=r_g/a$, where r_g is the tip radius and a the radius of the Pt wire) between 3 and 5. The tip was polished with 0.05 μm alumina (Buehler, Lake Bluff, IL), rinsed with water and ethanol, and dried prior to each measurement.

Preparation of Redox Mediator Solution. The chosen redox mediator MV^{2+}/MV^+ undergoes photoreduction at the substrate upon illumination. Thus, to study this reaction in feedback mode requires that MV^{2+} is generated at the SECM tip, i.e., MV^+ is the initial redox species in solution. Freshly prepared Zn amalgam was used to reduce a solution of aqueous MV^{2+} to MV^+, and the resulting violet solution was immediately transferred to the SECM cell using a syringe that was degassed with Ar. Approach curves were obtained by plotting tip current (i_T) for MV^+ oxidation as a function of distance (d) from the film/solution interface at various light intensities. Fresh solution was used for each measurement to maintain the same concentration of MV^+ throughout.

Experimental Procedures and Data Analysis

Illumination of the CdS/electrolyte interface leads to the following of series of photochemical reactions:

$$\mathrm{CdS} \xrightarrow{h\nu} \mathrm{CdS}(e_{\mathbf{CB}} + h_{\mathbf{VB}}) \tag{1}$$

$$\mathrm{CdS}(e_{CB} + h_{VB}) \xrightarrow{k_r} \mathrm{CdS} + \Delta \tag{2}$$

$$h_{VB} + \mathrm{TEOA} \xrightarrow{k_{ht}} \mathrm{TEOA}^+ \tag{3}$$

$$e_{CB} + MV^{2+} \xrightarrow{k_{et}} MV^+ \tag{4}$$

where k_r, k_{ht}, and k_{et} are the rate constants for recombination, oxidation, and reduction, respectively. As CdS is an n-type semiconductor, oxidation occurs by the capture of holes by TEOA at the CdS surface and reduction by transfer of electrons. In the presence of excess TEOA, the overall kinetics of reactions 1−4 are governed by k_r and $k_{et.}$ However, at moderate light intensities, k_r is negligible and reaction 4 is the rate-determining step.[33] Thus, experimental rate constants can be correlated with k_{et}.

To study PET at the SIE using SECM, a CV was first recorded for the $MV^{2+/+}$ redox couple. Subsequently, the tip was biased at a potential in the diffusion-limited region (−0.72 V vs Ag/AgCl). Approach curves, where tip current is monitored as a function of distance d, were obtained by moving the tip toward the SEI. The tip current was normalized by the diffusion limiting current, $i_\infty = nFDCa$, where D is the diffusion coefficient; C, the bulk concentration of MV^+; a, the electrode radius; and F, Faraday's constant. In the absence of illumination, tip-generated MV^{2+} is not reduced at the semiconductor solution interface; thus, as the tip approaches the film, diffusion of MV^+ to the tip is hindered and tip current decreases (so-called negative feedback). Such approach curves fit to the following approximate analytical equation for feedback to an insulator:

$$I_T^{\mathrm{ins}}(L) = \frac{1}{0.292 + 1.5151/L + 0.6553\exp(-2.4035/L)} \tag{5}$$

where, $L = d/a$.

From such fits, the exact tip distance from the film could be calculated. The tip was then withdrawn to a distance far from the substrate and the approach curve was repeated under film illumination. The photoreduction of tip-generated MV^{2+} to MV^+ at the SEI leads to an increase in tip current close to the interface (positive feedback). At high intensities, feedback reaches a limiting value and fits the equation for feedback to a conductor:

$$I_T^{C}(L) = \frac{0.78377}{L} + 0.3315\exp\left(-\frac{1.0672}{L}\right) + 0.68 \tag{6}$$

Under these conditions, the rate of reaction is mass transfer limited and PET kinetic parameters cannot be estimated.

Depending on experimental conditions (light intensity, film thickness, and redox concentration) chosen, feedback in the intermediate region between conducting and insulating extremes can be obtained. In this region, tip current is governed by the PET rate at the SEI and the feedback response can be fitted to the following equation, enabling estimation of the pseudo-rate constant (**k_{eff}**):

$$I_T^{k}(L) = I_S\left(1 - \frac{I_T^{\mathrm{ins}}}{I_T^{C}}\right) + I_T^{\mathrm{ins}} \tag{7}$$

$$I_S = \frac{0.78377}{L\left(1 + \frac{1}{\Lambda}\right)} + \left[\frac{0.68 + 0.3315\exp\left(-\frac{1.0672}{L}\right)}{1 + F(L,\Lambda)}\right] \tag{8}$$

where I_T^{ins} and I_T^{C} are given in the eqs 5 and 6, respectively. I_S is the kinetically controlled substrate current; $\Lambda = (k_{\mathrm{eff}}d/D)$, k_{eff} is equal to the apparent heterogeneous rate constant (cm s^{-1}), and

$$F(L, \Lambda) = \frac{(^{11}/_{\Lambda} + 7.3)}{110 - 40L} \tag{9}$$

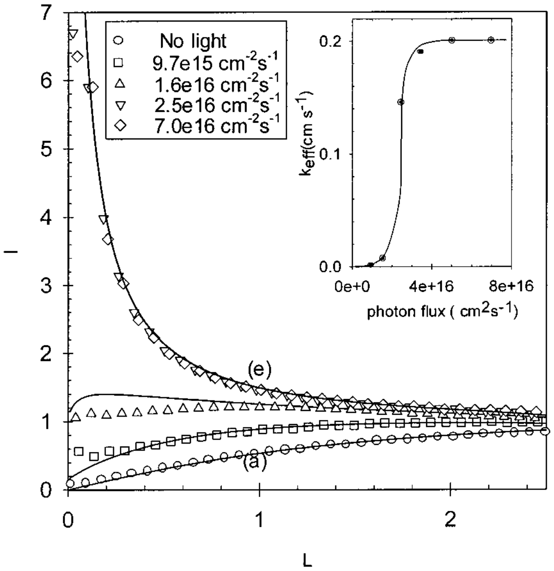

Figure 2. Approach curves recorded at various light intensities on CdS film in 0.1 mM MV^{+} as a redox, 50 mM TEOA as a hole scavenger, and 0.1 M KCl supporting electrolyte in the inert atmosphere. (a) in the dark and (e) high intensity of illumination. The solid lines are fits of eq 7 at various values of k_{eff}. The inset depicts a plot of k_{eff} vs photon flux. The hyperbolic nature of the curve was attributed the mass-transfer limit reached at high photon flux. The actual k_{eff} could be higher than 0.2 cm s^{-1} at higher illumination at those intensities.

This procedure allows us to probe the localized kinetics at a small portion of the macroscopic substrate at open circuit.

Results and Discussion

Effect of Light Intensity. Figure 2a (hollow circle) depicts a typical dark approach curve to the CdS film at a low MV^{+} concentration (0.1 mM) in the presence of excess (50 mM) hole scavenger. As expected, this fit very well to the theoretical approach curve to an insulator given by eq 5; thus the film is insulating. In the same figure, the approach curve (e) obtained under high illumination intensity ($<5 \times 10^{16}$ photons cm^{-2} s^{-1}, integrated between 400 and 550 nm) is given, where positive feedback is due to photogeneration of MV^{+} at the CdS/solution interface. As can be seen, this fit well to the theoretical curve for a conductor given by eq 6 and the reaction is under mass-transfer control. To determine k_{eff}, approach curves were recorded at various light intensities, and the corresponding plots are given in the same figure. Fitting these curves to eq 7 allowed determination of k_{eff} at each light intensity, and this dependence is plotted in Figure 1 (inset). At low to moderate intensities, the rate increases with intensity, while at very high intensities (ca. 5×10^{16} photons cm^{-2} s^{-1}) it saturates (i.e., a hyperbolic relation). This dependence did not fit a relation proportional to the square root of the light intensity, as typically expected for recombination-limited rates.[33] Thus, the observed saturation can probably be attributed to mass-transport limitations.

Determination of Quantum Efficiency. To determine the quantum efficiency (ϕ), knowledge of the photocurrent generated at the substrate (I^{k}_{sub}) and the photon flux are required. While the photon flux can be experimentally determined, we do not have direct knowledge of the generated photocurrent, as the CdS film was on insulating substrate (glass). From eq 8, however, the substrate current (I^{k}_{sub}) as a function of tip distance can be estimated for various values of k_{eff}. Thus, values of I^{k}_{sub} obtained from fitting the approach curves with the tip at close proximity to the film ($L = 0.2$) were used to estimate the substrate current and ϕ. The dependence of ϕ on photon flux is given in Figure 3. The low magnitude of ϕ was attributed the back-illumination configuration in which a large part of the light was absorbed by the film before it reached to the SIE. The decrease in ϕ at higher intensities is due to mass-transport limitations rather than the dominance of the recombination rate at these photon fluxes.

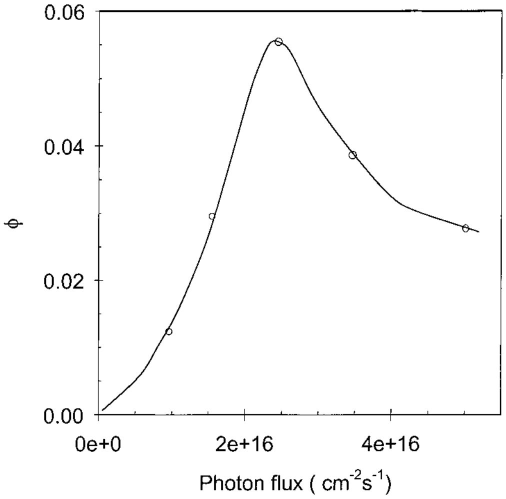

Figure 3. Change in quantum efficiency as a function of photon flux. Deviation at higher intensity was attributed to approaching the kinetics at the mass-transport limit of the SECM.

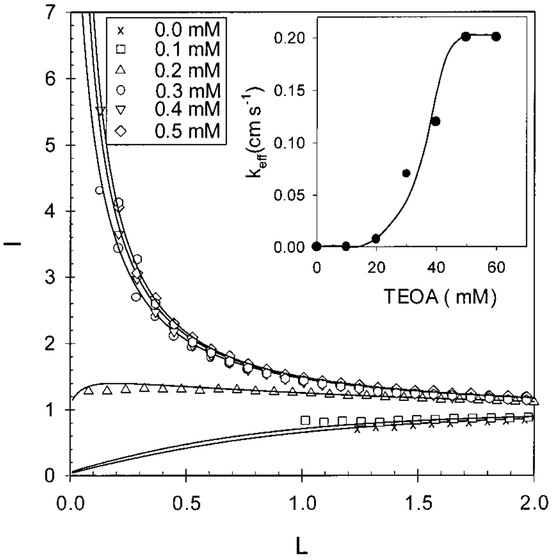

Figure 4. Approach curves recorded at various TEOA concentrations. The $[MV^{+}] = 0.1$ mM in 0.1 M KCl. The solid lines are fits of eq 7 at various values of k_{eff}. The inset depicts a plot of k_{eff} vs [TEOA].

Effect of TEOA Concentration. To consider the effect of the hole scavenger concentration on PEC, approach curves were obtained at mass-transport-limit illumination, and the TEOA concentration was varied from 0 to 1.0 mM. Typical approach curves obtained in the absence of added TEOA are depicted in Figure 4. In this case, the rate of hole transfer, and thus electron transfer, is negligible and the film behaves as an insulator. As the concentration of added TEOA increases, there is a concomitant increase in the rate of electron transfer and this results in an increase in feedback measured at the SECM tip. Values for k_{eff} were obtained by fitting approach curves obtained at each TEOA concentration, and the resulting dependence of k_{eff} on TEOA concentration is given in Figure 4 (inset). The plot is sigmoidal, indicating that the rate saturates to the mass-transport limit at [TEOA] > 5 mM. At concentrations below this, reaction kinetics are dictated by k_h rather than by k_{et}.

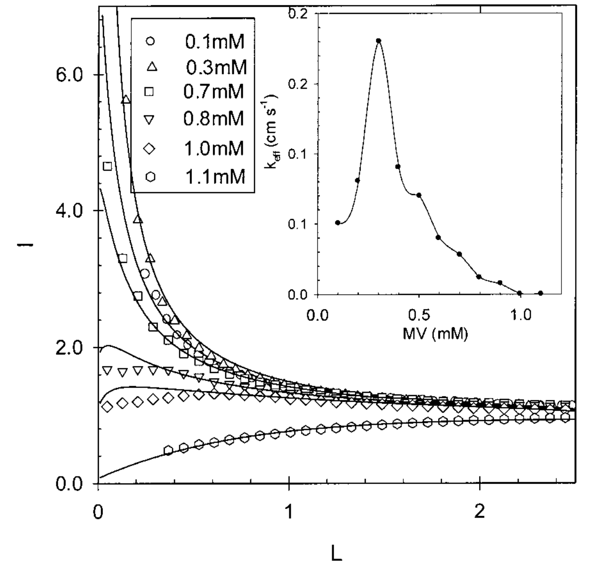

Figure 5. Approach curves recorded at various MV^+ concentrations. The [TEOA] = 50 mM in 0.1 M KCl. The solid lines are fits of eq 8 at various values of k_{eff}. The inset depicts a plot of k_{eff} vs $[MV^+]$. The peak in the plot indicates the balancing of turn over of MV^+ oxidation at tip with turn over of MV^{2+} photochemical reduction at CdS.

Effect of MV^+ Concentration. MV^+ concentration was also varied systematically from 0.1 to 1.2 mM in the presence of excess TEOA and at the mass-transport-limited light intensity. Resulting approach curves are given in Figure 5. As above, these were fit to theory (Equation 7) to obtain a value for k_{eff} at each concentration, and the dependence of rate on MV^+ concentration is also given in Figure 5 (inset). k_{eff} should increase with increasing MV^+ concentration. However, as seen in the plot, it reaches a maximum value and then begins to decrease. For $[MV^+] \geq 1.2$ mM, the film approaches insulator behavior and fit well to the theory for insulator (eq 5). This phenomenon is due to incomplete turnover of tip-generated MV^{2+} at the SEI, where the rate is now limited by the available electrons generated in the film. The positive feedback current under these conditions only makes a small contribution to the total tip current. For $[MV^+] = 0.3$ mM, the ratio of tip to substrate turnover was equal to unity. In the preceding theoretical treatment, heterogeneous PET is treated as a pseudo-first-order reaction, where it is assumed that the concentration of electrons in the film is much greater than that of solution electron acceptors, and thus does not change significantly during the SECM measurement (constant composition approximation). At low concentrations of MV^+, this approximation is valid; however, at high concentrations the reaction is second order and the rate is determined by both the flux of film and solution species. Unwin and co-workers[34] have demonstrated that lifting the above constant composition approximation, i.e., taking diffusion of both reacting species into account, is advantageous, as it raises the upper limit for the accessible experimental rate constant. In this case, this would require precise control of the film thickness and a means of quantifying the flux of photogenerated electrons in the film.

Conclusion

From these studies, we have demonstrated that SECM can be used to probe the kinetics of PET at semiconductor/solution interfaces. Effective pseudo-first-order rate constants were determined as a function of light intensity and MV^{2+} and TEOA concentrations. It was not possible to obtain the actual bimolecular rate constant due to difficulties in quantifying the steady-state concentration of photogenerated electrons in the CdS film. However, at high light intensities and low MV^+ concentration in the presence of excess TEOA, PET is mass-transport-limited. Thus, the reaction under investigation can be assumed to be fast.

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