Supporting Information for

A Kinetic Model of the Photocatalytic Effect of a Photosystem I Monolayer on a Planar Electrode Surface

By Peter N. Ciesielski, David E. Cliffel, and G. Kane Jennings

Additional Optical Characterization of the Photoelectrochemical System

The visible absorbance spectrum of the PSI suspension (shown in green in Figure S1) exhibits maxima in the blue region, due to the Soret band of chlorophyll $a$, and in the red region due the $Q_y$ transition of chlorophyll $a$. The electrochemical mediators $K_3$Fe(CN)$_6$ and $K_4$Fe(CN)$_6$ display strong absorbance in the blue region, and absorption of photons from this region of the visible spectrum can initiate electronic transitions that cause photochemical reactions to occur.$^1$ In order to minimize any contributions to the measured photocurrent due to these photochemical reactions of the electrochemical mediator, the system was irradiated with a light source equipped with a red filter (emission spectrum shown in red in Figure S1) to avoid photoexcitation of the $K_3$Fe(CN)$_6$/K$_4$Fe(CN)$_6$ redox couple in the electrolyte. The intensity of filtered light at the electrode surface was measured to be 27.5 mW/cm$^2$, and the emission spectrum exhibited a maximum at 648 nm; thus, the photonic flux $N_\lambda$ incident the electrode was calculated from the intensity at the electrode surface by the expression

$$N_\lambda = \frac{P\lambda}{hcN_A}$$

where $P$ is the intensity of the light reaching the electrode in units of W·cm$^{-2}$, $h$ is Plank’s constant, $c$ is the velocity of light, $N_A$ is Avogadro’s constant, and $\lambda$ was assumed to be 648 nm for all photons to yield an approximate photonic flux of $1.5 \times 10^{-7}$ mol·cm$^{-2}$·s$^{-1}$. The fraction of
Although both PSI and the electrochemical mediator absorb strongly in the blue region of the visible spectrum, irradiation of the electrode using a lamp equipped with a red filter excites only chlorophyll pigments bound in the antenna complexes of PSI. This eliminates contributions to photocurrent produced by photoexcitation of the electrochemical mediator. The absorption spectra of PSI and the electrochemical mediators were collected from solutions of $1.6 \times 10^{-6}$ M PSI in pH 7 PBS and 100 µM K$_3$Fe(CN)/100 µM K$_4$Fe(CN)$_6$, respectively, using a Varian Cary 5000 UV-VIS-NIR spectrophotometer. The emission spectrum of the red-filtered, Gebrauch KL 2500 LCD lamp was collected using an Ocean Optics USB 2000 fiber optic spectrometer. The absorbance and emission spectra were normalized to their maxima and minima.

Photons of wavelength $\lambda$ absorbed by the PSI monolayer, $\theta_\lambda$, is related to the absorbance of the film at $\lambda$ by the expression

$$\theta_\lambda = 1 - \frac{I(\lambda)}{I_0(\lambda)} = 1 - 10^{-A(\lambda)}$$

where $I_0(\lambda)$ is the intensity of light of wavelength $\lambda$ before passing through the PSI film, $I(\lambda)$ is the intensity after passing through the film, and $A(\lambda)$ is the absorbance of the PSI film at wavelength $\lambda$, which is defined as

**Figure S1. Emission Spectrum of Light Source and Absorption Spectra of PSI and Electrochemical Mediator.** Although both PSI and the electrochemical mediator absorb strongly in the blue region of the visible spectrum, irradiation of the electrode using a lamp equipped with a red filter excites only chlorophyll pigments bound in the antenna complexes of PSI. This eliminates contributions to photocurrent produced by photoexcitation of the electrochemical mediator. The absorption spectra of PSI and the electrochemical mediators were collected from solutions of $1.6 \times 10^{-6}$ M PSI in pH 7 PBS and 100 µM K$_3$Fe(CN)/100 µM K$_4$Fe(CN)$_6$, respectively, using a Varian Cary 5000 UV-VIS-NIR spectrophotometer. The emission spectrum of the red-filtered, Gebrauch KL 2500 LCD lamp was collected using an Ocean Optics USB 2000 fiber optic spectrometer. The absorbance and emission spectra were normalized to their maxima and minima.
The absorbance of a PSI monolayer in the visible region was below the detection limit of the spectrometer and thus, could not be measured; however, the absorbance in the region of the lamp emission spectrum was estimated to an order of magnitude using the Beer-Lambert law, \( I = b \varepsilon c \), with the previously published extinction coefficient of 57,000 M\(^{-1}\)·cm\(^{-1}\) for the red peak of chlorophyll \( a \) bound within PSI complexes\(^2\) using a corresponding volumetric concentration estimated by assuming a film thickness of 7 nm.\(^3\) These assumptions correspond to a volumetric concentration of 3 mM for the PSI film, which yields an absorbance of \( \sim 10^{-4} \), and leads to an approximate absorbance fraction, \( \theta \), of \( 2 \times 10^{-4} \) in the red region from Beer-Lambert law.

**Modeling Transport and Heterogeneous Reactions of Electrochemical Mediators**

In order to completely specify the system of differential equations that comprise conservation statements for the surface concentrations of the oxidation states of the reaction centers of PSI (developed in the main text), similar conservation statements must be developed for the concentrations of the reduced and oxidized form of the electrochemical mediator, and the diffusional transport of this mobile redox couple must be accounted for. Considering the electrode an infinite planar surface with \( x \) was designated as the direction parallel to the surface normal such that \( x = 0 \) at the electrode/electrolyte interface, and assuming that no homogeneous reactions occur within the system, the 1-dimensional continuity equation for oxidized and reduced mediators, respectively, is given by

\[
\frac{\partial C_o}{\partial t} = -D_o \frac{\partial^2 C_o}{\partial x^2}
\] (4)
and

\[ \frac{\partial C_R}{\partial t} = -D_R \frac{\partial^2 C_R}{\partial x^2} \]  

(5)

where the \( x \) is the dimension normal to the electrode surface, and \( D_O \) and \( D_R \) are the diffusion coefficients of the oxidized and reduced forms of the electrochemical mediator, respectively.

Before any reactions take place, the concentrations of the reduced and oxidized forms of the electrochemical mediators are assumed equal to their initial bulk concentrations \( C_O^* \) and \( C_R^* \) everywhere within the electrolyte, which yields the initial conditions

\[ C_O|_{t=0} = C_O^* \]  

(6)

and

\[ C_R|_{t=0} = C_R^* \]  

(7)

The assumption that the concentrations of the electrochemical mediators very far away from the electrode surface remain unaffected by the heterogeneous reactions occurring at \( x = 0 \) yields the boundary conditions

\[ C_O|_{x=\infty} = C_O^* \]  

(8)

and

\[ C_R|_{x=\infty} = C_R^* \]  

(9)

The reactions of the electrochemical mediators with the electrode surface directly can be described by the chemical equation

\[ O \xleftarrow{k_{\text{electrode}}} R \]  

(10)

with the corresponding rate equations

\[ r_s = k_M^0 \exp\left[-\alpha_M f\left(E - E_M^0\right)\right] C_{O,(x=0)} \]  

(11)
and

\[
r_g = k_M^0 \exp\left[\left(1 - \alpha_M^0\right) f \left(E - E_M^0\right)\right]C_{R,(x=0)}
\]

(12)

where \(k_M^0\), \(\alpha_M\), and \(E_M^0\), are the standard rate constant, transfer coefficient, and formal potential of the electrochemical mediator, respectively. In dark conditions, the boundary conditions for equations (4) and (5) at the electrode surface are specified by equating the flux of the electrochemical mediator at the electrode surface to the rates of the reactions described in equations (11) and (12); however, irradiation of the electrode initiates charge separation within PSI complexes at the electrode surface, which prompts the redox reactions to occur between PSI’s reaction centers and the electrochemical mediators (these rate expressions are developed in the main text). During periods of irradiation, the boundary conditions for equations (4) and (5) at the electrode surface are described by equating the rate expressions that describe the PSI/mediator interactions, as well as rate expressions that describe the mediator/electrode interactions (given by equations (11) and (12)), to the flux of the redox couple at the electrode surface to obtain:

\[
-D_O \frac{\partial C_O}{\partial x} \bigg|_{x=0} = k_M^0 \exp\left[\left(1 - \alpha_M^0\right) f \left(E - E_M^0\right)\right]C_{R,(x=0)} + k_3 \Gamma_{F_0} C_{R,(x=0)}
\]

(13)

\[
-k_M^0 \exp\left[-\alpha_M^0 f \left(E - E_M^0\right)\right]C_{O,(x=0)} - k_2 \Gamma_{F_0} C_{O,(x=0)}
\]

\[
-D_R \frac{\partial C_R}{\partial x} \bigg|_{x=0} = k_M^0 \exp\left[-\alpha_M^0 f \left(E - E_M^0\right)\right]C_{O,(x=0)} + k_2 \Gamma_{F_0} C_{O,(x=0)}
\]

(14)

\[
-k_M^0 \exp\left[\left(1 - \alpha_M^0\right) f \left(E - E_M^0\right)\right]C_{R,(x=0)} - k_3 \Gamma_{F_0} C_{R,(x=0)}
\]

The solutions to these equations are surfaces that correspond to the concentrations of the reduced and oxidized forms of the electrochemical mediator throughout space and time. A representative solution for equation (5) is shown in Figure S2.
Figure S2. Representative Solution to the PDE System. The surface plot shows the solution to the PDE system for the reduced form of the electrochemical mediator during the simulation of a chronoamperometric experiment of 120 s at a potential of 0.34 V vs Ag/AgCl. Far from the electrode surface, the concentration remains equal to the bulk concentration. At the electrode surface, the concentration decreases due to the heterogeneous consumption of the reactant as current is generated. A faster decay in concentration is observed at $x = 0$ when the electrode is irradiated ($t = 50 – 70$ s) due to consumption of the reactant by PSI. This simulation was performed with $C^*_R = 1 \times 10^{-9}$ mol/cm$^3$ to highlight the effect of photocurrent generation on the concentration of the electrochemical mediator.

Previous studies of the transfer coefficient of the $K_3Fe(CN)_6/K_4Fe(CN)_6$ redox couple in similar systems have reported an overpotential dependence of this parameter, and have developed linear empirical relationships for $\alpha_M$ and the overpotential, $\eta$, of the form

$$\alpha_M = a\eta + b$$

with $a$ and $b$ values ranging from $0.72 – 1.16$ V$^{-1}$ and $0.44 – 0.5$ respectively.$^{4-6}$
Empirically determined values of the transfer coefficient displayed an approximately linear dependence on overpotential at small values of $\eta$ with asymptotic behavior at larger overpotentials. A logistic function was used to represent these trends.

Empirically determined values for $\alpha_M$ obtained from the experiments in this work also exhibited an approximately linear dependence on overpotential at small values of $\eta$; however, asymptotic behavior was observed at larger overpotentials. To account for this departure from linearity at larger overpotentials, the empirically determined transfer coefficients were fit to a logistic function of the form

$$\alpha_M = \frac{a}{1 + \exp\left[-(b + c\eta)\right]} + d$$

and the best fit parameters obtained were $a = 0.67$, $b = 1.4$, $c = 45$, and $d = 0.14$. The empirically determined values of $\alpha_M$ are plotted with the logistic model in Figure S3. The low
standard rate constant and strong overpotential dependence of the transfer coefficient observed in this system compared to previously reported values for these parameters for this redox couple at unmodified gold electrodes could be due to electrochemical impedance imparted to the present system by the adsorbed SAM/protein film.

References


