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LETTERS

EQCM Investigations of Dye-Functionalized Nanocrystalline Titanium Dioxide Electrode/ Solution Interfaces: Does Luminescence Report Directly on Interfacial Electron Transfer Kinetics?

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Electrochemical quartz crystal microbalance (EQCM) experiments have been performed on dye-functionalized nanocrystalline titanium dioxide electrode/solution interfaces. The experiments show that reversible, potential-induced dye desorption occurs in both aqueous and nonaqueous environments at potentials close to the conduction band edge. Previous experiments have reported that potentiostatic filling of empty conduction band or near-band-edge surface states has dramatic effects on the corresponding photophysical and photochemical behavior of surface-bound dyes. Most notably, apparent *decreases* in the efficiencies of charge injection and *increases* in dye luminescence yield were found to accompany potential changes. Detailed analyses have emphasized the role of surface-state filling in decreasing the driving force for injection processes and thus, increasing the luminescence quantum yield. The electrochemically stimulated dye detachment phenomenon reported here provides a compelling alternative or additional mechanistic explanation for the profound potential dependence of the interfacial luminescence responses.

Introduction

Light-induced charge transfer at wide band gap semiconductor/solution interfaces is a starting point for a number of technologically interesting catalytic processes including environmental contaminant degradation,¹ chemical fuel production,² and electrical power generation.³ For electricity generation, the most efficient devices rely upon (1) nanocrystalline semiconductor electrode surface functionalization via visible-lightabsorbing molecule ("dye") attachment, (2) photoexcitation of the attached dye, and (3) an ensuing cascade of redox processes, beginning with dye-to-semiconductor electron injection. The crucial electron injection process has been examined via photocapacitance techniques,⁴ transient absorbance methods,⁵ time-resolved and steady-state luminescence methods,⁶ photocurrent yield measurements,⁷ and other experimental methods. Among the more compelling general findings are correlations and inverse correlations between photocurrent yield, luminescence intensity, injection yield, and externally applied electrode potential. Most notably, when a dye-functionalized semiconductor electrode is increasingly negatively biased, the molecular (dye) luminescence intensity systematically increases while both the photocurrent yield and the injection yield systematically decrease.^{6b,7} The variations are most pronounced at potentials near the electrode's conduction band edge (E_{cb}).

Advantage has been taken of these observations and related time-resolved luminescence measurements to infer rates for electron injection.^{7a} The rates display a remarkable potential dependence, decreasing by orders of magnitude as $E_{\rm cb}$ is approached from more positive potentials.^{7a} Typically, the potential dependence has been interpreted in terms of potentiostatic electron addition to the electrode. The addition evidently leads to near-band-edge surface-state filling, negative shifts in

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the electrode's Fermi level, and a systematic diminution of the thermodynamic driving force for electron injection.^{7a} From conventional electron transfer theory, exponential decreases in injection rate are expected to accompany decreases in driving force, provided that injection occurs in the Marcus normal region. Finally, the decrease in injection rate apparently permits excited state deactivation via an internal radiative pathway to become kinetically competitive.

We report here on an electrochemical quartz crystal microgravimetry (EOCM) study of dye-functionalized metal-oxide semiconductor/solution interfaces under conditions of negative bias (potentiostatic electron addition). The study was motivated by recent EQCM and photochemical QCM studies of naked TiO₂, SnO₂, and ZnO electrodes in aqueous and nonaqueous environments.8 Those studies showed that electron addition (surface reduction) is accompanied by mass increases corresponding to charge-compensating proton intercalation (aqueous environments), alkali metal ion intercalation (nonaqueous environments), or alkylammonium cation adsorption (nonaqueous environments). We reasoned that an analogous investigation of dye-functionalized electrodes might provide complementary information. As shown below, we find that negative biasing of functionalized electrodes stimulates electrode mass decreases that are interpretable in terms of dye detachment. Notably, the detachment phenomenon provides an alternative mechanism for luminescence generation and suggests an alternative or additional interpretation for the profound biasing effects upon luminescence responses reported previously.

Experimental Section

Nanocrystalline titanium dioxide films were prepared as previously reported.^{8a,b,d} Briefly, 22 g/L TiO₂ colloids were prepared by the acidic hydrolysis of titanium(IV) isopropoxide (Aldrich, 97%). The resultant sols were dialyzed against distilled water until their pHs were approximately 2. Sols were then concentrated by rotary evaporation to yield slightly viscous sols of 50–100 g/L TiO₂. Triton X-100 (Aldrich, 1 drop/mL sol) was added to the sols to facilitate film formation; films were formed by spin-coating the sols (2000 rpm, 1 min, 5–10 coats) onto masked gold-coated quartz crystal resonators (ICM, Oklahoma City, OK). Sintered, nanocrystalline films were formed by firing the electrodes in air at 450 °C for ca. 1.5 h. The sensitizing dye, Ru(dcb)₃^{4–} (dcb = 2,2'-bipyridine-4,4'-dicarboxylic acid), was introduced to the film by soaking in a buffered (pH 3) solution of dye overnight.⁹

EQCM measurements were performed as previously described on an apparatus previously described.⁸ Electrolyte solutions consisted of 0.1 M LiClO₄ in pH 3 buffer (Fisher) or acetonitrile (distilled from CaH₂) and were deoxygenated by bubbling with nitrogen prior to each experiment. Electrochemical measurements were made in a one-compartment cell using a platinum wire counter electrode and an ssce, Ag/AgCl, or silver wire pseudoreference. Potentials are reported versus ssce.

Results

EQCM experiments were performed on dye-coated, nanocrystalline films of TiO₂. Figure 1a shows the current versus potential plot from an aqueous EQCM scan. As the TiO₂ film is scanned to potentials negative of the conduction band edge, cathodic current arises from reduction of the TiO₂ film. The voltammetric response is similar to that reported previously for naked (underivatized) electrodes, implying that the response is electrode based rather than dye based. Monitoring the fundamental frequency of the quartz crystal substrate versus potential



Figure 1. Plots of (a) current versus potential, and (b) QCM crystal frequency versus potential for a $\text{Ru}(\text{dcb})_3^{4-}$ -functionalized, nanocrystalline TiO₂ electrode/water interface. Scan rate: 50 mV/s.



Figure 2. Plot of QCM crystal frequency versus time for a $\text{Ru}(\text{dcb})_3^{4-}$ -functionalized, nanocrystalline TiO₂ electrode/water interface. Scan conditions: -50 to -750 mV vs SSCE; 50 mV/s; 5 scans.

(Figure 1b) reveals a positive frequency shift, indicating a loss of mass from the functionalized electrode. At 50 mV/s (and faster), the mass loss appears irreversible. This phenomenon takes place in both aqueous (water/buffer/electrolyte, Figure 1) and nonaqueous (acetonitrile/electrolyte) solutions. Furthermore, the onset potential for the frequency increase is, in both environments, slightly positive of the apparent conduction-bandedge energy. Repeated cyclings result in cumulative dye desorption, the magnitude decreasing slightly with each successive scan (Figure 2). Unlike previous experiments on SnO₂ and ZnO, the TiO₂ electrodes proved stable to repeated cyclings, displaying unchanging electrochemistry after many cycles.

Discussion

The mass loss in Figures 1 and 2 is notable in that it (1) coincides with the potentials measured for induced fluorescence noted in previous studies, (2) is reversible or irreversible, depending upon the scan rate, similar to the luminescence responses reported earlier, and (3) occurs only with dye-coated

SCHEME 1



semiconductor electrodes. *Naked* films of TiO₂, SnO₂ and ZnO display only mass uptake due to charge-compensating cation intercalation.⁸ We conclude that the mass decrease is associated with dye desorption.¹⁰

The observation of dye desorption has interesting implications in the context of "interfacial" luminescence behavior. If TiO_2 surface-site reduction results in dye desorption, dye luminescence can arise from desorbed $Ru(dcb)_3^{4-}$ as shown in Scheme 1.

Dye readsorption appears to be a relatively slow process: fast surface reduction and reoxidation (cyclic voltammetry performed at 50 mV/s and faster) of the TiO₂ films evidently releases dye molecules that do not re-adsorb within the time frame of the electrochemical scan. Slower electrochemical scanning (≤ 10 mV/s) allows the dye time to re-adsorb within the measurement window. This compares favorably with the known potentialdependent luminescence behavior of Ru(dcb)34- on related SnO₂^{7a} and TiO₂^{7b} electrodes. We speculate that in both types of experiments (EQCM and luminescence) eventual dye reattachment is facilitated by the mesoporous nature of the electrode material. Thus, dye molecules can likely be desorbed from the electrode surface without escaping from the porous metal-oxide network and entering the surrounding electrolyte solution. Such an interpretation, if correct, might account for the previously observed potentiostatic dependence of the $Ru(dcb)_3^{4-}$ (or the related sensitizer, $Ru(dcb)(bpy)_2$) excitedstate lifetime.⁷ A desorbed dye molecule would still be subject to energy- or electron-transfer quenching by any remaining proximal bound dye molecules. Time-resolved luminescence measurements would thus report on the rates of these processes rather than the direct electron injection process.

Finally, it is important to note that Scheme 1 does not account directly for the potential-induced loss of photocurrent and the decrease in injection yield encountered in functioning photoelectrochemical cells;^{7a,7b} too small a fraction of the chromophoric material is desorbed to accommodate either observation. For example, the +80 Hz frequency shift recorded in Figure 2 corresponds to a mass loss of \sim 300 ng or 1.4 μ g per cm^2 (geometric electrode area). This, in turn, corresponds to only $\sim 3 \times 10^{-10}$ moles of dye (13 ± 5 monolayers of dye on a hypothetical flat surface) or approximately 7% of the dye initially present in our experiments. We suggest, however, that Scheme 1 does likely account for the potential-induced dye luminescence effect. Absolute luminescence intensity information is lacking in the various literature reports, thereby precluding a quantitative comparison to the EOCM experiments. Nevertheless, we find that dissolution (in water) of a quantity of dye equal to that desorbed in a typical EQCM experiment yields a readily observable luminescence response, i.e., a response that is orders of magnitude above the detection limit for a standard spectrofluorimeter such as a Spex Fluorolog 3.¹¹

Conclusions

EQCM measurements involving dye-functionalized nanocrystalline TiO₂ electrode/solution interfaces show that potentialinduced dye desorption occurs in both aqueous and nonaqueous environments. The desorption effects are reversible under slow scan conditions and are most prominent in the vicinity of the conduction band edge. As such, they provide a compelling alternative or additional explanation for the observation of reversible, potential-induced photoluminescence^{6,7} from such interfaces. We hope to investigate the effect of substituting phosphonate (PO₃²⁻) anchors for the carboxylates; presumably stronger surface binding will inhibit dye desorption and alter the luminescence behavior.

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(9) TiO₂ films were also sensitized with Ru(dcb)₂(SCN)₂ (purchased from Solaronix SA) by overnight immersion in 0.5 mM ethanol solution. EQCM measurements performed on these films produced results similar to those obtained from the Ru(dcb)₃^{4–}-sensitized films.

(10) It should be noted that irreversible dye desorption at substantially more negative potentials (with respect to the conduction band edge) has been reported previously. See: Zaban, A.; Meier, A.; Gregg, B. A. *J. Phys. Chem. B.* **1997**, *101*, 7985, and ref 7a.

(11) Implicit in an exclusive Scheme 1 interpretation of potential-induced luminescence effects is that surface-attached dye molecules, i.e., the majority of the available dye molecules, remain spectrofluorimetrically silent (even at applied potentials negative of E_{CB} , where electron injection is known to be inefficient or absent). Obviously, if bound dyes did remain nonluminescent at these potentials, then quenching mechanisms other than electron injection would need to exist. While a search for alternative quenching mechanisms is beyond the scope of the present study, at least two candidate schemes can be suggested: (1) energy transfer from RuL_3^{2+*} to filled trap sites (sites displaying an absorbance overlap with the dye emission spectrum), or (2) reductive quenching by filled trap sites ($Ti^{III} + RuL_3^{2+3}$) \rightarrow Ti^{IV} + RuL₃¹⁺; $\Delta G \approx -35$ kcal/mol, assuming that the putative trap sites are energetically close to the apparent conduction band edge). Note that both schemes would become operative only at potentials close to E_{CB} or negative of E_{CB} , consistent with the very high injection yields typically encountered at more positive potentials.