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Enhancement of Electrochemical Hot Electron Injection into Electrolyte Solutions at Oxide-Covered Tantalum Electrodes by Thin Platinum Films

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The previously reported experimental evidence for hot solution-phase electrons generated at Ta_2O_5-covered Ta electrodes in both acetonitrile and aqueous solutions using electrogenerated chemiluminescence (ECL) and electrochemical measurements was extended by observing the effect of thin Pt films. Hot electron injection was monitored by noting the photoemission following reduction of the thianthrene radical cation ($TH^{\bullet+}$), signaling the direct formation of the excited state ($TH^{\bullet+} + e_h^s \rightarrow TH^*$), a process that does not occur at a bulk Pt electrode. We report the enhancement of hot electron injection efficiency by a factor of ~5 by deposition of a thin (<40 nm) Pt film on the Ta/Ta_2O_5 electrode. This enhancement of ECL efficiency at the metal/oxide/Pt/liquid interface is ascribed to the suppression of the Ta_2O_5 surface states by the Pt film. The effect of Pt film thickness was investigated and showed a decrease in emission with increased film thickness, in accord with the expected mean free path of hot electrons in the Pt (e_h^{Pt}). In examining the $Ta/Ta_2O_5/Pt/$ solution system, one can contrast the behavior observed when an electrical connection is made directly to the Pt with that observed when a connection to the Pt is made via the Ta, where e_h^{Pt} species are generated.

Introduction

It seems evident that how contact is made to an inert metal electrode should not affect the electrochemical reactions that occur at the metal/solution interface. However, we show here that by making contact to a thin Pt film via an insulating oxide film, which allows injection of hot electrons into the solution, the electrochemical behavior is different than that found when the film is directly contacted with a metal conductor.

In a previous paper,[1] we discussed the direct production of the excited state of thianthrene (TH) in a MeCN solution at a Ta_2O_5-covered Ta electrode by reaction of the TH radical cation with a hot electron injected into the solution phase from the conduction band edge of Ta_2O_5 (Figure 1A).

$$TH^{\bullet+} + e_h^{\,s} \rightarrow TH^* \qquad (1)$$

This reaction occurs via electron injection into the unoccupied orbital of $TH^{\bullet+}$. Excited state formation does not take place at a Pt electrode, where electron transfer involves injection into the lower occupied $TH^{\bullet+}$ level to form ground-state TH (Figure 1B). Thus, the light emission characteristic of TH* seen at a Ta/Ta_2O_5 electrode but not at Pt provides clear evidence of production of a hot electron into solution (e_h^s) through the oxide film by a thermalized electron in the Ta (e_t^m). However, the efficiency of hot electron injection was small, with a ϕ (photons emitted/injected electron) of about 2×10^{-3}. With a quantum efficiency for TH fluorescence of ~0.036,[2] this yields an injection efficiency of about 0.06. Similar experiments were carried out with a hexamethine cyanine dye (HMC^+), where emission was seen on reduction of $HMC^{\bullet 2+}$ at Ta/Ta_2O_5 but not at Pt ($\phi = 6 \times 10^{-4}$). Comparative electrochemical measurements of a number of one-electron couples suggested that the low efficiency was not caused by significant direct

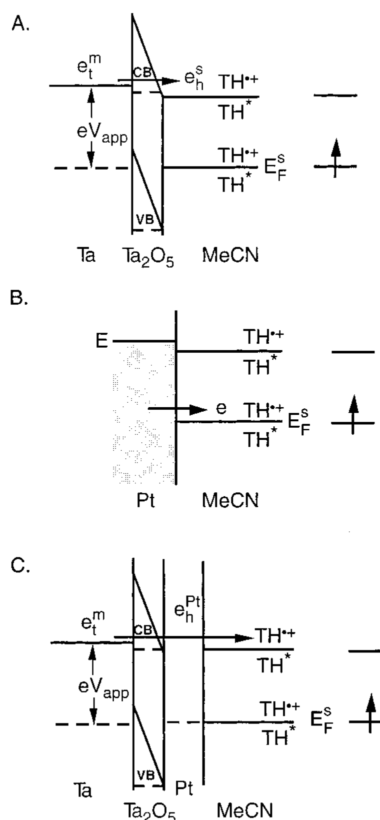

Figure 1. Schematic of electron transfer from electrodes to oxidized $TH^{\bullet+}$ species in solution at (a) Ta/Ta_2O_5, (b) Pt, and (c) $Ta/Ta_2O_5/Pt$ electrodes.

population of the lower state but rather by thermalization of e_h^s or quenching of TH*, probably via surface states with energies located within the gap of the Ta_2O_5. Attempts to remove these states by etching of the Ta_2O_5 with HF or surface modification by silanization did not result in an enhancement of emission.

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We show here that deposition of thin films of Pt on the Ta_2O_5 surface significantly enhanced the emission, as long as the Pt film thickness was below the mean free path of a hot electron in the metal (~50−100 nm for a 3 eV electron) (Figure 1C).[3,4] However, if electrical contact is made directly to the Pt thin film in this structure, no emission results. To our knowledge, this is the first demonstration of the fact that how contact is made to a metal electrode (i.e., directly or via an oxide film) can affect the electrochemistry that occurs in solution at that electrode. The work reported here is related to previous studies of hot electron injection via insulating or semiconductive films covered by thin metal layers.[5−7] For example, Diesing et al.[7] studied the hydrogen evolution reaction in an aqueous medium at an $Al/Al_2O_3/Ag$ electrode structure. In these studies, hot electron injection was identified from the current−potential response[5] or the changes in response when an additional current was passed between the Al and Ag films.[6,7]

Experimental Section

Purification of chemicals and preparation of solutions were the same as described previously.[1] In the aqueous experiment, an excess of PbO_2 (Fisher Scientific) was added to oxidize $Ru(bpy)_3^{2+}$ to the $Ru(bpy)_3^{3+}$ form in a 0.1 M $HClO_4$ solution.

The tantalum foil (Aldrich, 99.999%) electrodes had geometric areas of 0.3−0.5 cm^2. In most cases, ~2.5 nm thick (as determined by XPS) natural oxide films formed in air were used. Thicker oxide films were produced by anodization in a 0.1 M ammonium tartrate (Matheson Coleman & Bell) solution (pH = 6.7). The Pt thin films were prepared by sputtering Pt of different thicknesses on the Ta electrode. Before anodization and Pt film deposition, the electrodes were polished mechanically with 0.5 μm alumina and then cleaned ultrasonically. The Pt film thickness was monitored during deposition with a quartz crystal microbalance. X-ray photoelectron spectroscopy (PHI 5700 ESCA system, Physical-Electronics) was used to measure oxide and Pt thicknesses and surface cleanliness/composition.

XPS yielded spectra with clear Ta peaks (Ta(V) from Ta_2O_5 and Ta(0) from Ta metal) for the Ta/Ta_2O_5 electrode and additional Pt(0) peaks for those with Pt films (Figure 2). The native Ta_2O_5 film on Ta is reported to have a thickness of about 2.5 nm.[8] The oxide thickness was also determined by the XPS relative ratio method.[9]

$$I_{i,o}/I_{j,s} = (c_i/c_j)(T_i/T_j)(\sigma_i/\sigma_j)(\lambda_{i,o}/\lambda_{j,s})[(1 - \exp(-d/\lambda_{i,o}\cos\theta)/\exp(-d/\lambda_{j,s}\cos\theta)]$$

where I is the XPS peak area, T is the transmission function of the spectrometer, σ is the photoionization cross section, λ is the inelastic mean free path, and θ is the angle between the sample normal and the direction of the XPS electron spectrometer. The subscripts o and s indicate the terms are applied to the overlayer and substrate, respectively, and the subscripts i and j indicate the term is applied to a core level of a particular element. For Ta/Ta_2O_5 samples, $T_i = T_j$, $\sigma_i = \sigma_j$, $\lambda_i = \lambda_j = \lambda$ = 8.9 Å, and $\alpha = 90 - \theta$. We used the intensities of Ta^0 peaks (21 and 23 eV) and Ta^{5+} peaks from Ta_2O_5 (26 and 29 eV) at the Ta 4f region with $\alpha = 45°$. The molar fraction ratio, c_i/c_j, was 0.4045 from $\rho_{Ta} = 16.6$ g/cm^3, $\rho_{Ta_2O_5} = 8.2$ g/cm^3, $M_{Ta} = 180.95$, $M_O = 16$, $M_{Ta_2O_5} = 441.89$. Calculations based on these values yielded a thickness, d, of 2.47 nm, in agreement with the literature value.

Thicknesses were also found by determining the XPS sputter depth profile during argon sputtering by monitoring the 71 eV Pt 4f and 23 eV Ta 4f peaks. Sputtering was carried out with a 1 μA Ar^+ beam to yield the profiles shown in Figure 2. The Pt sputtering rate is 2.2 times that of Ta_2O_5, which on calibration yields 1.25 nm/min for Ta_2O_5 and 2.75 nm/min for Pt under our experimental conditions.[10] Thus, a Pt film measured to be 20 nm thick by a quartz crystal monitor during vacuum deposition required about 7 min to remove by Ar^+ sputtering from Ta/Ta_2O_5, yielding 20 nm based on the sputtering rate.

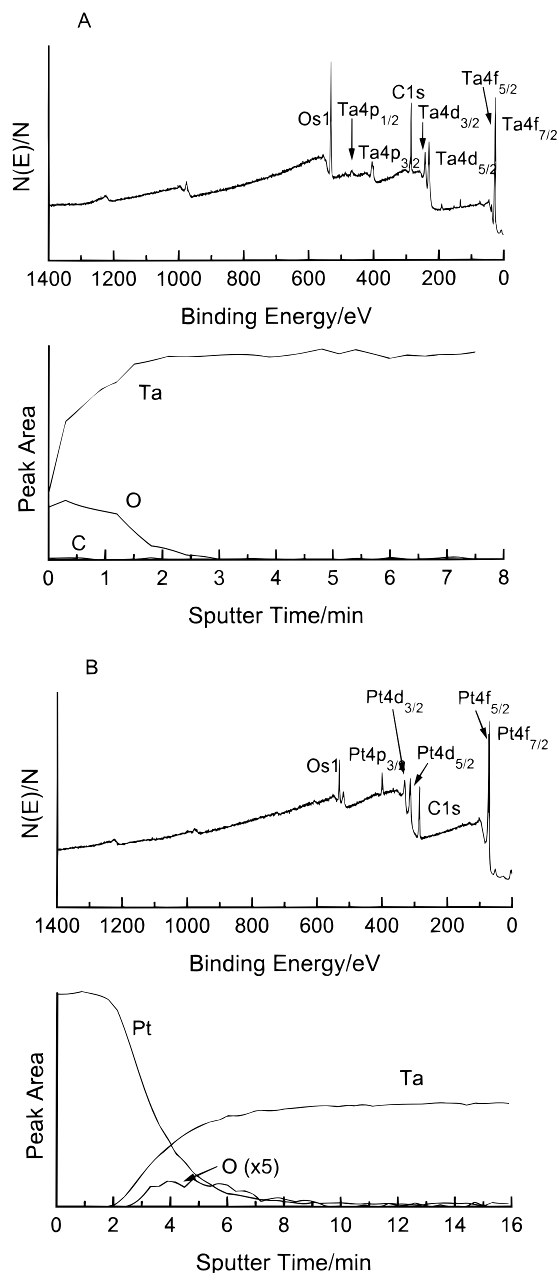

Figure 2. X-ray photoelectron spectra and depth profiles at (a) Ta/Ta_2O_5 and (b) Ta/2.5 nm Ta_2O_5/20 nm Pt electrodes. E_{ion} = 3 keV; i = 1 μA.

The quality of the Pt thin film and the roughness of the surface was studied by atomic force microscopy (AFM) (Nanoscope III, Digital Instruments). A typical AFM image showed a roughness of about 1.8 nm on the native Ta_2O_5 and 18 nm on the 40 nm thick Pt film (Figure 3). The 10 nm film was clearly nonuniform and probably consisted of Pt islands with exposed Ta_2O_5. However, the Pt films thicker than about 40 nm were probably pinhole free. Additional experiments to check the quality of the Pt film were carried out using SEM (JEOL, JSM-35C) and EDX (KEVEX, Analyst 8000).

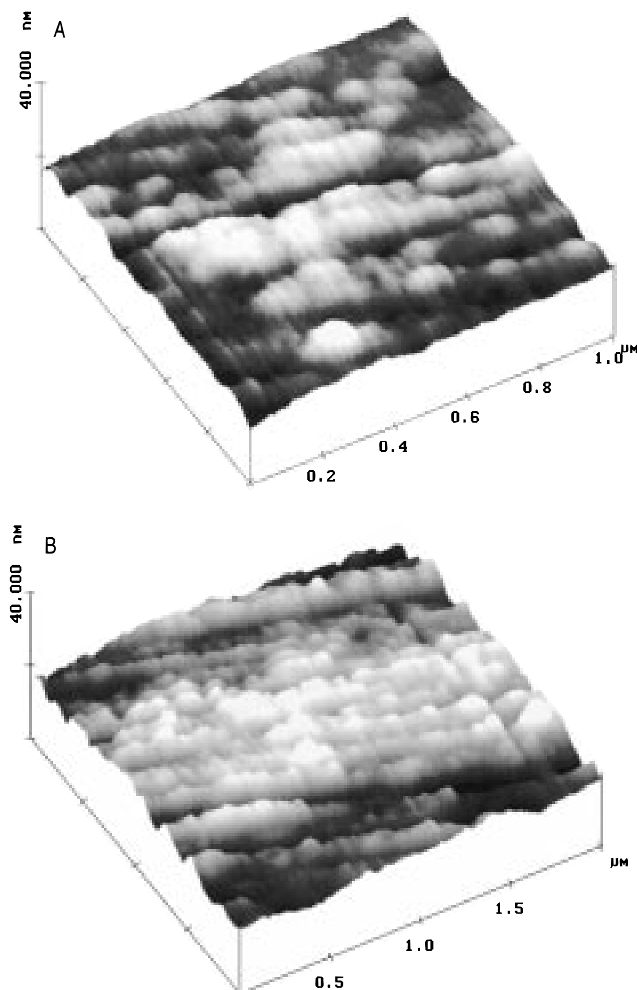

Figure 3. AFM images of (A) Ta/2.5 nm Ta_2O_5 and (B) Ta/2.5 nm Ta_2O_5/40 nm Pt electrodes.

The electrochemical/ECL cell was of conventional design. Bulk electrolysis experiments were performed using a Princeton Applied Research model 173/175 potentiostat/universal programmer. For standard cyclic voltammetric (CV) measurements in MeCN, a silver wire served as a quasireference electrode; its potential was calibrated versus the ferrocene (Fc)/ferrocenium couple by adding Fc and recording its CV at Pt. Potentials in MeCN are reported as V vs aq SCE (taking $E_{1/2}(Fc/Fc^+)$ as +0.3 V vs SCE). Controlled potential ECL and cyclic voltammograms were obtained with a PAR model 175 programmer and model 173/176 potentiostat and a CH Instruments (Memphis, TN) model 660 electrochemical system. ECL measurements were performed as previously reported[1] using a charge-coupled device (CCD) camera (Model CH260, Photometrics, Tucson, AZ) cooled to −130 °C. The spectrometer was calibrated using a Hg−Ar test lamp (Ultra-Violet Products, San Gabriel, CA). ECL experiments were performed in a darkroom, and care was taken to eliminate stray light. The Ta/Ta_2O_5 electrode was sealed with silicone cement to expose only the Pt film side of the electrode to the solution. Ta and Pt wire connections to the electrodes were made by silver epoxy or by spot welding.

Results and Discussion

The Effect of Pt Thin Films. A solution containing the oxidized precursor of TH ($TH^{\bullet+}$) was prepared by bulk electrolysis at 1.4 V vs SCE. The potential of the working electrode was pulsed between 0 and −2.7 V vs SCE at 0.1 s intervals (Figure 4). The ECL at a Ta/Ta_2O_5 electrode is shown in Figure 4 (trace a). The ECL spectrum exhibited a maximum intensity at about 500 nm, identical to the previous literature ECL spectrum of TH;[11] thus, the emitting species is TH in the first excited singlet state by the process shown schematically in Figure 1A. No ECL was detected at a Pt electrode in the same $TH^{\bullet+}$ solution when the potential was pulsed between 0 and −2.7 V (Figure 4, trace b). This is consistent with the direct population of the HOMO from available states in the metal to form the ground state (Figure 1B). However, when a 40 nm thick Pt film was deposited on Ta_2O_5, the emission was 5 times more intense than that of the Ta_2O_5 by itself (Figure 4, trace c). The proposed mechanism is shown schematically in Figure 1C. The Pt film is poised by the $TH/TH^{\bullet+}$ couple in the MeCN solution (at about +1.3−1.4 V vs SCE). However, when the Ta is pulsed to negative potentials, injection of electrons into the Ta_2O_5 does not occur until the electronic level in Ta attains values above the conduction band edge of Ta_2O_5, about −1.1 to −1.4 V vs SCE.[1] The electron in the Ta_2O_5 is injected into the Pt film as a hot electron (e_h^{Pt}). As long as the thickness of the Pt film is smaller than the mean free path of electrons, hot electrons can traverse the Pt film and inject into the solution phase at energies great enough to form the excited state of TH.

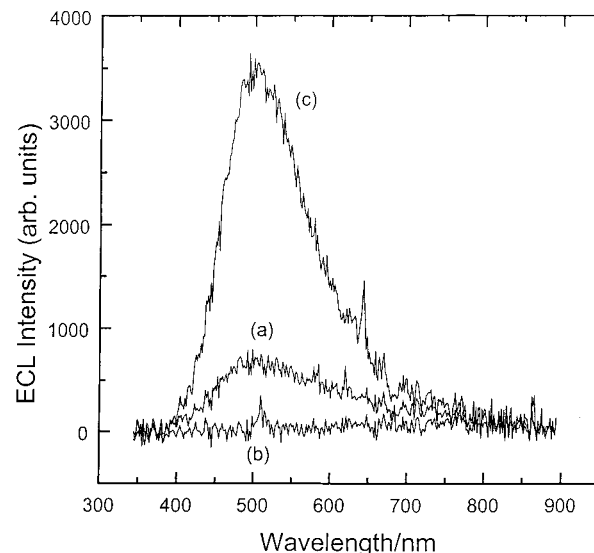

Figure 4. ECL spectra of 7 mM $TH^{\bullet+}$/0.1 M TBAP/MeCN solution at (a) Ta/2.5 nm Ta_2O_5, (b) Pt, and (c) Ta/2.5 nm Ta_2O_5/40 nm Pt electrodes. The exposure time was 5 min. The potential was pulsed between 0 and −2.7 V vs SCE at 0.1 s intervals.

A prerequisite for hot electron injection into solution is that the Pt film thickness be less than the mean free path of a hot electron so that a large fraction can traverse the film without thermalization to the Pt Fermi level. With an increasing Pt film thickness, ballistic electron transport through the film becomes less likely and the electrons lose energy thermally to the Pt. We performed ECL experiments with Pt films of different thickness on the Ta/Ta_2O_5 electrodes, and the ECL signal showed a dependence on Pt film thickness (Figure 5). The emission intensity compared to that of the unmodified Ta_2O_5 layer was 2 times (nonuniform) more intense with a 10 nm Pt film, 5 times with 40 nm, $^1/_2$ with 100 nm, and no emission was detected with a Pt film thickness of 500 nm. In fact, no emission was detected with a Pt thickness greater than 100 nm. At a 100 nm thickness, the emission was seen only at the edges

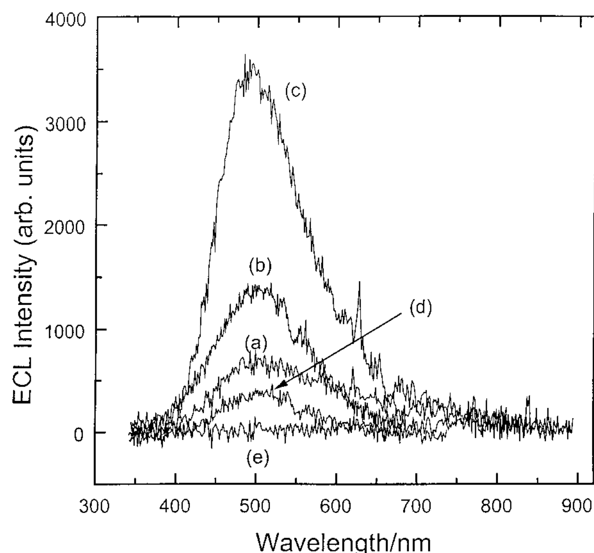

Figure 5. ECL spectra of 7 mM $TH^{\bullet+}$/0.1 M TBAP/MeCN solution at a Ta/2.5 nm Ta_2O_5 electrode with Pt film thicknesses of (a) 0, (b) 10, (c) 40, (d) 100, and (e) 500 nm. The exposure time was 5 min. The potential was pulsed between 0 and −2.7 V vs SCE at 0.1 s intervals.

of the electrode, which probably represents thinner layers of Pt at these locations. The brightest emission was obtained when the Pt thickness was in the range of 10−40 nm. The thicker Pt film electrodes behaved like a bulk Pt electrode. The effect of the Pt thin-film structures is in general agreement with that expected for Pt thickness and hot electron mean free path values deduced from theory and experiment.[3−5] Hot electron mean free paths in metals with energies from several tenths of a volt to a few volts above the Fermi level have been measured by photoemission or tunnel-emission techniques.[3] The results showed a path of about 40−100 nm at 1−2 eV above the Fermi level for Au and Ag, similar to the optimum thickness range for Pt. The XPS, SEM, and AFM results show that above about 40 nm thickness a complete Pt film is produced.

Effect of Mode of Electrical Contact to the Pt. The proposed mechanism suggests that the observed emission should be different if the Pt film is contacted directly rather than through the Ta_2O_5 film. To study this effect, the Ta/Ta_2O_5/Pt electrode was equipped with two wire contacts, a Ta wire to the Ta plate and a Pt wire to the Pt thin film (Figure 6). The same ECL experiments were carried out by applying potential pulses via the two different electrical paths from the potentiostat to either the Ta wire (Ta−Ta_2O_5−Pt film−solution path) or the Pt wire (Pt film−solution path) at the same working electrode with a native oxide film. We would expect that hot electron injection would occur only when the Ta contact was used. However, as shown in Figure 6, essentially the same light emission was found with the Pt and Ta contact, with ECL emission enhanced via both paths. These results suggest that the resistance of the Pt film is sufficiently high that a large fraction of the electrons from the Pt contact proceed through a few shorts in the 2.5 nm Ta_2O_5 film to the Ta, become hot, inject back into the Pt film and then the solution rather than flow, and thermalize in the Pt film itself; that is, the 2.5 nm oxide film does not effectively prevent contact between the Pt and Ta.

To prevent back current flow through the oxide film, experiments with thicker (70 nm) oxide films were carried out. This film is sufficiently resistive that current flow through the oxide film from Pt becomes less likely and contact to the Pt should lead to direct electron exchange with the solution. By applying a pulse of 0 to −7 V (a higher electric field was needed with the thicker oxide) at Ta/70 nm Ta_2O_5/Pt we could distinguish the hot-electron process via the Ta path and the normal electron-transport process at the metal electrode via the Pt path (Figure 7), because no emission was observed with a −7 V pulse directly to the Pt.

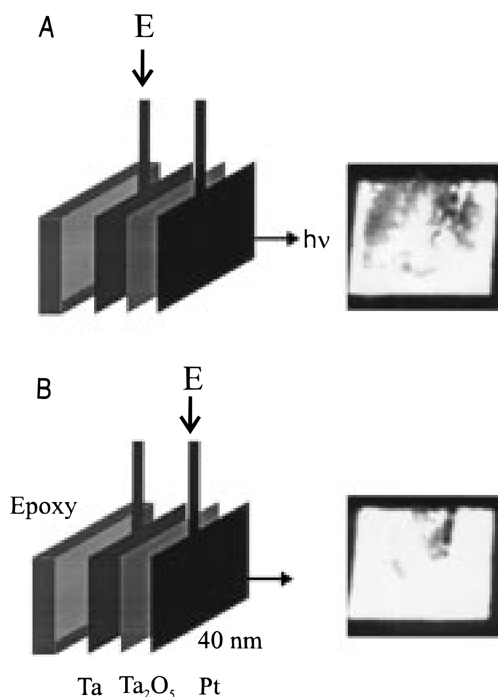

Figure 6. ECL of $TH^{\bullet+}$ at a Ta/2.5 nm Ta_2O_5/40 nm Pt electrode with the potential applied via (A) the Ta wire (Ta/Ta_2O_5/Pt/solution path) and (B) the Pt wire (Pt solution path). The exposure time was 5 min. The potential was pulsed between 0 and −2.7 V.

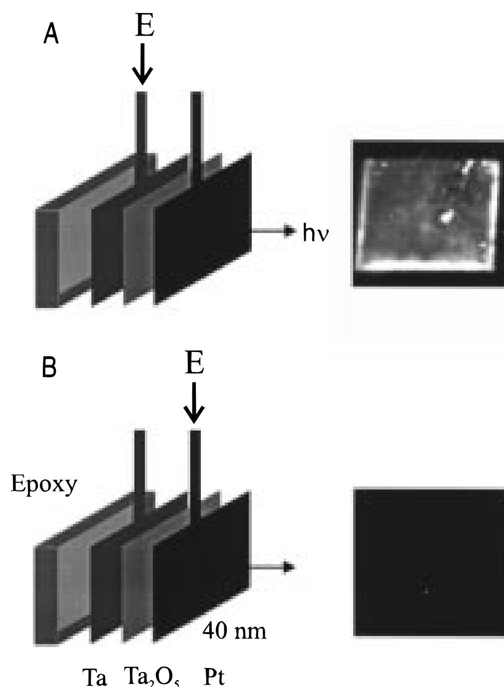

Figure 7. ECL of $TH^{\bullet+}$ at a Ta/70 nm Ta_2O_5/40 nm Pt electrode with the potential applied via (A) the Ta wire (Ta path) and (B) the Pt wire (Pt path). The exposure time was 5 min. The potential was pulsed between 0 and −7 V.

This was further tested with a $Ru(bpy)_3^{3+}$ aqueous solution. Again to prohibit back current flow from Pt to Ta, we applied a 0.1 s −7 V pulse through a 70 nm oxide film. In this experiment, ECL was observed from hot electron reduction of

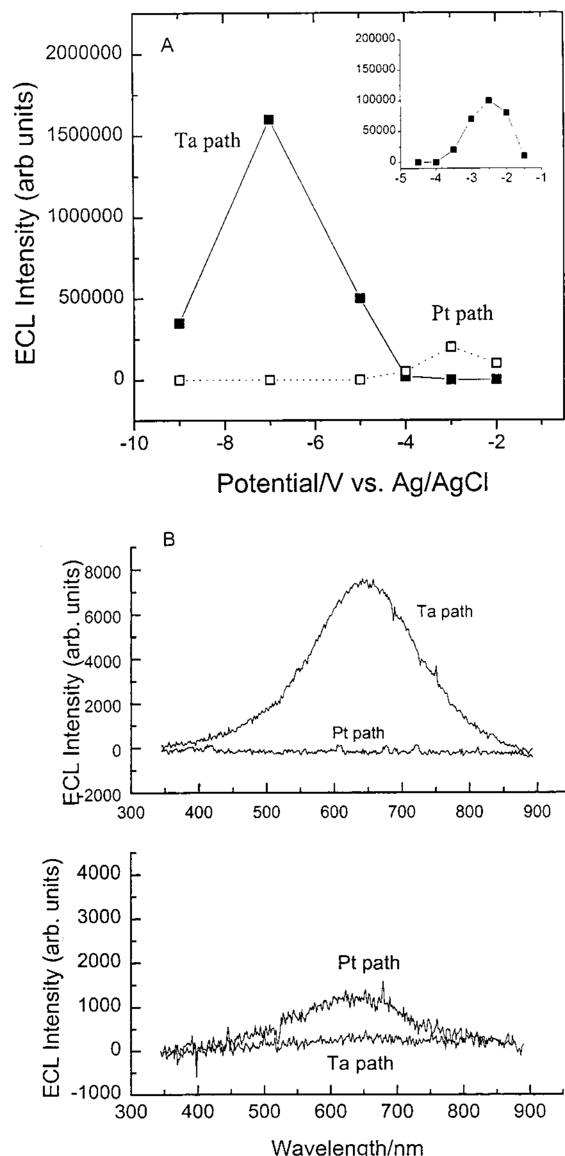

Figure 8. (A) ECL intensities of an aqueous 0.5 mM $Ru(bpy)_3^{3+}$/0.1 M $HClO_4$ solution at a Ta/70 nm Ta_2O_5/40 nm Pt electrode via the two different electrical contact paths, with 0.1 s cycling between 0 V and the negative potential shown. Inset shows emission at a 40 nm Pt disk in glass electrode. (B) ECL spectra at −7 V (top) and −3 V (bottom) under the same conditions as in (A).

$Ru(bpy)_3^{3+}$ to $Ru(bpy)_3^{+}$ via the Ta path, but no ECL was observed via the Pt path (Figure 8). These results are, however, somewhat compromised by the large amount of H_2 evolved at the Pt during the reductive pulse. Indeed, some emission is seen with a direct contact to the Pt at smaller potential pulses (Figure 8A) and at a separate 40 nm Pt disk in glass electrode (Figure 8A, inset). A possible explanation is that the low potential emission seen with the Pt contact results from generation of $Ru(bpy)_3^{+}$ along with H_2 evolution and emission occurs because of the annihilation reaction, well-known in nonaqueous solvents,[12] of this species with $Ru(bpy)_3^{3+}$. The more intense emission with the Ta contact at more negative potential pulses might then be ascribed to a hot-electron process directly into $Ru(bpy)_3^{3+}$.

These measurements are interesting in that they demonstrate different electrochemical behavior in contacting the Pt via an oxide, where hot electrons are produced, and directly where only thermal electrons are possible. This general behavior was also suggested by the experiments of Diesing et al.[6,7]

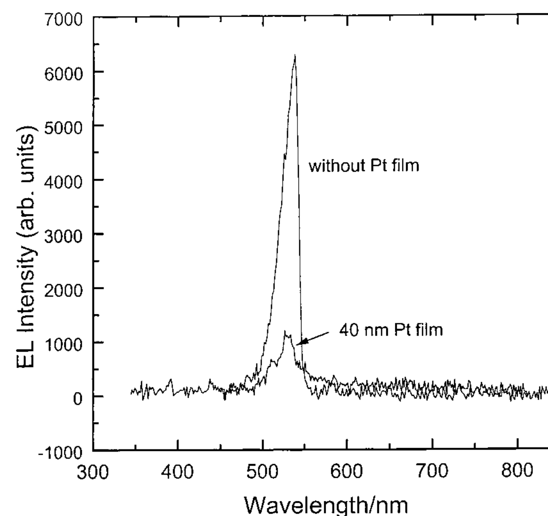

Figure 9. Electroluminescence in an aqueous 0.1 M potassium oxalate solution at Ta/2.5 nm Ta_2O_5 and Ta/2.5 nm Ta_2O_5/40 nm Pt electrodes. The exposure time was 1 min. The potential was pulsed between 0 and −5.0 V at 0.1 s intervals.

Mechanism of Pt Film Enhancement. In our earlier paper,[1] we ascribed the low efficiency of excited-state production at the Ta/Ta_2O_5 structure to thermalization of hot electrons via states, e.g., surface states, in the Ta_2O_5 band gap. Such states are important in the electroluminescent (EL) emission seen at Ta/Ta_2O_5.[13] These states would represent dangling bonds as well as defect and impurity sites at the surface and are known to be important in the behavior of semiconductor electrodes.[14] If this is the case, then the Pt acts to suppress or block these states. There have been many previous studies of the interaction of metals and metal ions with semiconductor surfaces where the surface states are affected, e.g., metals with Ge[15] or silver with p-InP.[16] Indeed, much of the behavior of semiconductor electrodes is dominated by surface state processes. From the location of the band edges of Ta_2O_5 and the work function of Pt, the Pt energy level should lie near the middle of the band gap and hence should be capable of blocking states in the gap. The cathodic subband-gap EL emission of a Ta/Ta_2O_5 electrode observed in a 0.1 M aqueous oxalate solution[17] is greatly decreased by a 40 nm thick Pt film (Figure 9). However, the thick films of Pt would also be expected to be very effective in thermalizing hot electrons as well as quenching excited states produced at the surface, so the strong effect of Pt on enhancing the emission intensity is indeed unexpected.

Conclusions

The process of electrochemical hot electron injection into electrolyte solutions at a Ta/Ta_2O_5 electrode is inefficient. However, the efficiency can be improved by the deposition of a thin Pt film on the Ta/Ta_2O_5 electrode. The thickness of the Pt film must be below the mean free path of a hot electron in the metal. We have demonstrated that how electrical contact is made to an underlying metal electrode, either directly to the Pt film or via the Ta_2O_5 film, does affect the electrochemistry that occurs in solution at the electrode.

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