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Intervalence transfer of ferrocene moieties adsorbed on electrode surfaces by a conjugated linkage

Wei Chen, Lauren E. Brown, Joseph P. Konopelski, Shaowei Chen *

Department of Chemistry and Biochemistry, University of California, 1156 High Street, Santa Cruz, CA 95064, United States

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ABSTRACT

Effective intervalence transfer occurred between the metal centers of ferrocene moieties that were adsorbed onto a ruthenium thin film surface by ruthenium–carbene π bonds, a direct verification of Hush's four-decade-old prediction. Electrochemical measurements showed two pairs of voltammetric peaks where the separation of the formal potentials suggested a Class II behavior. Additionally, the potential spacing increased with increasing ferrocene surface coverage, most probably as a consequence of the enhanced contribution from through-space electronic interactions between the metal centers. In contrast, the incorporation of a sp^3 carbon spacer into the ferrocene–ruthenium linkage led to the diminishment of interfacial electronic communication.

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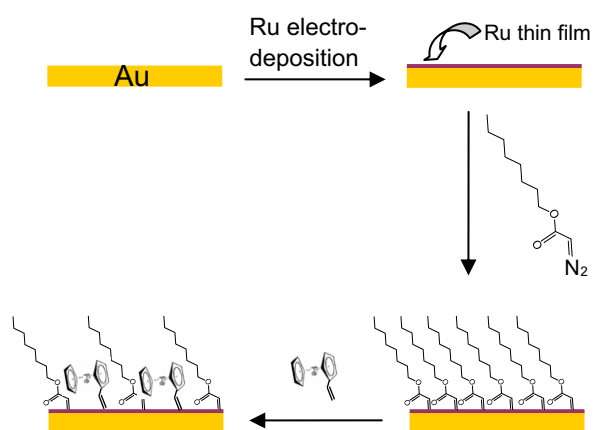
Intervalence charge transfer (IVCT) is an important process in both chemical and biological systems and has been studied extensively in the past few decades [1–5]. This phenomenon is typically observed with organometallic complexes in which at least two redox centers are linked with a conjugated spacer to allow extensive intramolecular charge delocalization, leading to the emergence of new optical and electronic characteristics. Quantum mechanically, the extent of such intramolecular electronic communication is mainly determined by two factors: (i) through-space interactions that entail direct overlap of the orbitals of the metal centers and electrostatic interactions between the metal centers; and (ii) through-bond interactions that arise from metal–ligand–metal overlap and may involve σ or π metal–ligand bonds. Both of these factors may be readily manipulated by the chemical structure of the bridging ligands. Forty years ago, Hush [6] predicted that effective electronic communication might also occur between metal centers at the electrode/electrolyte interface when they were bound onto the electrode surface by conjugated chemical linkers. Yet, there has been little experimental verification of this hypothesis until recently when we demonstrated that when ferrocene moieties were bound onto ruthenium nanoparticle surface by ruthenium–carbene π bonds, intervalence transfer was observed in both electrochemical and near-infrared spectroscopic measurements, which was further confirmed by density functional theory calculations [7]. This suggests that effective intraparticle charge delocalization indeed occurred and the particles behaved as a Class II compound [8]. In this Letter, we expand the study to two-dimensional metal films by carrying out electrochemical studies of ferrocene moieties that are bound onto a ruthenium thin film surface.

The results strongly suggest that with a conjugated chemical linker, intervalence transfer indeed occurs between the ferrocene functional groups, whereas with a saturated alkyl spacer, the ferrocene moieties behave independently. Such an electrochemical system provides a more direct verification of Hush's hypothesis and we believe that this is the first of its kind.

The experimental procedure is outlined in Scheme 1. First, a thin film of ruthenium was electrodeposited onto a gold disk electrode surface. Here a polycrystalline gold disk electrode (sealed in a glass tubing) was firstly polished with alumina slurries (0.05 μm) and then cleansed by sonication in 0.1 M HNO_3 , H_2SO_4 , and Nanopure water (18 $\text{M}\Omega\text{ cm}$) for 10 min successively. The gold electrode was then electrochemically polished in 0.1 M H_2SO_4 by rapid potential sweeps within the potential range of +0.90 V and –0.5 V (vs Fc^+/Fc). The clean gold electrode was then immersed into a RuCl_3 solution (0.2 mM with 0.1 M H_2SO_4), and a Ru thin film was formed by electrodeposition at –0.75 V (vs Fc^+/Fc) for 5 min (longer deposition time did not result in drastic difference in the eventual electrochemical measurements). Based on the charge accumulated during the electrodeposition process, the average thickness of the Ru thin film was evaluated to be 10 to 20 monolayers [9]. The resulting electrode was denoted as Au/Ru. The freshly prepared Ru film was then immediately immersed into a dichloromethane solution containing 10 mM octyl diazoacetate (ODA, the synthesis of which has been detailed previously [10]) for 12 h where the strong affinity of the diazo moiety to ruthenium surfaces led to the formation of $\text{Ru}=\text{C}$ π bonds (and the concurrent release of nitrogen) and hence the formation of a carbene self-assembled monolayer on the ruthenium surface (denoted as Au/Ru=C8) [7,10,11]. The electrode was then incubated into a solution of either vinylferrocene or allylferrocene in dichloromethane typically for 2 days where olefin metathesis reactions [7,10,11] were

* Corresponding author.

E-mail address: schen@chemistry.ucsc.edu (S. Chen).



Scheme 1. Schematic of electrode surface functionalization.

exploited for the incorporation of the respective ferrocene moiety into the surface monolayer, with the electrode referred to as Au/Ru=CH-Fc and Au/Ru=CH-CH₂-Fc, respectively. The resulting electrode was then rinsed with a copious amount of dichloromethane and dried with a gentle stream of nitrogen before being subject to electrochemical characterizations.

The formation of an ODA monolayer on the Ru surface was first examined. Similar to the well-known alkanethiol self-assembled monolayers that effectively suppress interfacial faradaic reactions, the ODA monolayer is anticipated to exhibit significant hindrance to charge transfer of solution redox couples to the electrode surface. We used potassium ferricyanide K₃[Fe(CN)₆] as the probe molecule. Fig. 1 shows the cyclic voltammograms of the Au/Ru and Au/Ru=C8 electrodes in 10 mM K₃[Fe(CN)₆] at a potential sweep rate of 0.1 V/s. It can be seen that at the Au/Ru electrode (black curve), a pair of very well-defined voltammetric peaks can be seen with a formal potential ($E^{\circ'}$) of -0.144 V (vs Fc⁺/Fc) and peak splitting (ΔE_p) of 72 mV. These are ascribed to the electron-transfer reaction of the ferricyanide/ferrocyanide couple, $\text{Fe}(\text{CN})_6^{3-} + e \leftrightarrow \text{Fe}(\text{CN})_6^{4-}$. At the Au/Ru=C8 electrode (red curve), similar voltammetric features were observed with $E^{\circ'} = -0.133$ V and $\Delta E_p = 87$ mV, yet the peak currents were drastically suppressed by about 50%, suggesting the successful formation of an ODA monolayer on the Ru surface. Note that surface derivatization by ODA was exclusive to ruthenium and none occurred on the gold surface [11]. The fact that the ferricyanide/ferrocyanide voltam-

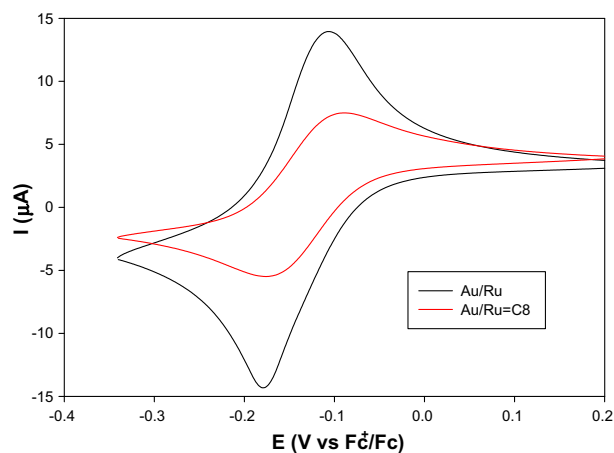


Fig. 1. Cyclic voltammograms (CV) of the Au/Ru and Au/Ru=C8 electrodes in an aqueous solution containing 10 mM potassium ferricyanide and 0.1 M KCl. Potential sweep rate 0.1 V/s. Gold electrode surface area 0.72 mm².

metric peaks remained quite well-defined at the Au/Ru=C8 electrode suggests that the ODA monolayer was not sufficiently compact and/or the gold electrode was not fully coated by the ruthenium film. Previously, we found that carbene-passivated ruthenium nanoparticles were stable enough to survive repetitive drying and dispersion, indicative of the formation of a compact carbene protecting layer [7,10]. Thus, it is likely that the electrodeposited ruthenium did not cover the entire gold electrode surface and the surface defects gave rise to the apparent voltammetric features of the ferricyanide/ferrocyanide couple. Such 'porous' surface structures were anticipated to allow ready access of vinyl-terminated derivatives such as vinylferrocene and allylferrocene to the ruthenium film surface for olefin metathesis reactions. Their voltammetric characteristics were then examined and compared.

Fig. 2 shows the cyclic voltammograms (CVs) of the Au/Ru=CH-Fc and Au/Ru=CH-CH₂-Fc electrodes in dichloromethane with 0.1 M tetrabutylammonium perchlorate (TBAP). It can be seen that their voltammetric profiles are drastically different. Specifically, two pairs of voltammetric peaks can be clearly seen with the Au/Ru=CH-Fc electrode with the formal potentials ($E^{\circ'}$) of -0.105 V and $+0.155$ V (vs Fc⁺/Fc) and a potential spacing ($\Delta E^{\circ'}$) of 260 mV. Additionally, the peak currents increase linearly with potential sweep rates, in agreement with surface-confined systems (not shown). These may be ascribed to the redox reaction of the ferrocene moieties, $\text{Fc}^+ + e \leftrightarrow \text{Fc}$. The appearance of two instead of one pair of voltammetric peaks strongly suggests that interfacial intervalence charge transfer occurred between the surface-adsorbed ferrocene metal centers, and the potential spacing ($\Delta E^{\circ'}$) of 260 mV was highly comparable to those observed with biferrocene derivatives [12–14], suggestive of Class II behaviors as defined by Robin and Day [8]. Note that this potential spacing is somewhat larger than that found when the ferrocene moieties are bound onto ruthenium nanoparticle surface through a similar Ru=C conjugated linkage (~ 200 mV). This may be accounted for, at least in part, by two contributing factors. First, intervalence charge transfer is better facilitated by a ruthenium thin film than by a nanometer-sized ruthenium particle, probably because the former behaves as a better sink for charge delocalization [7]. Second, the close proximity of the surface-confined ferrocene moieties on ruthenium thin film surfaces is anticipated to lead to enhanced through-space electronic interactions between the metal centers. It should be noted that direct orbital overlap decays exponentially with

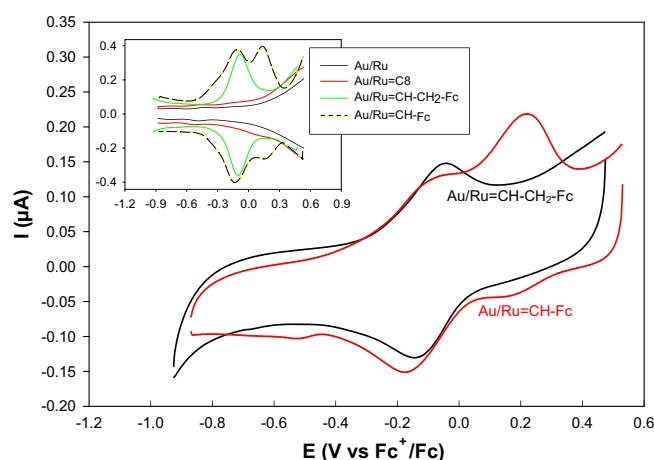


Fig. 2. Cyclic voltammograms (CV) and square wave voltammograms (SWV, inset) of Au/Ru=CH-Fc and Au/Ru=CH-CH₂-Fc electrodes in dichloromethane containing 0.1 M tetrabutylammonium perchlorate (TBAP). The SWV profiles for the Au/Ru and Au/Ru=C8 electrodes were also included in the figure inset. In CV, potential sweep rate 0.1 V/s. In SWV, increment of potential 4 mV, amplitude 25 mV and frequency 15 Hz.

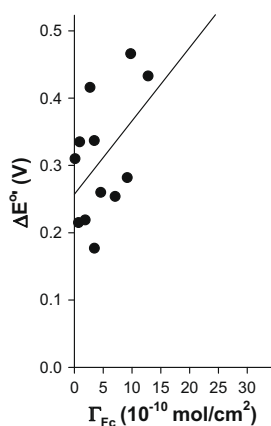


Fig. 3. Variation of the separation of the formal potentials (ΔE°) of the Au/Ru=CH–Fc electrode with ferrocene surface coverage. Symbols are experimental data obtained from voltammetric measurements as exemplified in Fig. 2 and line is linear regression.

distance and thus is prominent only at short range, whereas electrostatic interactions decrease inversely with distance and represent a long-range contributing factor. In fact, the potential spacing has been found to enlarge with increasing surface coverage of ferrocene moieties (estimated from the voltammetric peak areas), as manifested in Fig. 3. For instance, one can see that when the ferrocene surface coverage increases from 4.6×10^{-10} mol/cm² to 1.3×10^{-9} mol/cm², ΔE° increases from 260 mV to 430 mV (note that the surface coverages were most likely to be overestimated as they were normalized to the geometrical area of the electrode; and the scattering of the data points probably arose from the variation of the structure and quality of the ruthenium films which were deposited onto a polycrystalline gold surface).

Extrapolation to zero surface coverage by linear regression shows a ΔE° of ca. 250 ± 50 mV, which most probably reflects the through-bond interactions between the metal centers. Interestingly, in previous studies [15,16] with two-dimensional self-assembled monolayers of ω -ferrocenyl alkanethiols on a gold surface, a potential splitting of ca. 100 mV was sometimes observed, which might serve as a first-order approximation of the through-space contributions, in reasonable agreement with the present observations. The through-space effect was much less prominent when the ferrocene moieties were bound onto nanoparticle surfaces possibly because of the three-dimensional curvatures of the nanocrystalline cores [7].

In contrast, at the Au/Ru=CH–CH₂–Fc electrode, only a single pair of voltammetric peaks can be seen (formal potential -0.090 V), very similar to that of ferrocene monomers. This suggests that the intervalence transfer is effectively impeded because of the sp³ carbon spacer, in accord with previous studies of biferrocene derivatives linked by an ethylene spacer ($-\text{CH}_2-\text{CH}_2-$)

[14,17] and allylferrocene-functionalized ruthenium nanoparticles [7].

The variation of the voltammetric features can also be manifested in square wave voltammetric (SWV) measurements (inset). Again, two pairs of voltammetric peaks are very well-defined with the Au/Ru=CH–Fc electrode, whereas only a single pair of peaks are observed with the Au/Ru=CH–CH₂–Fc electrode. Furthermore, the Au/Ru and Au/Ru=C8 only exhibited featureless voltammetric profiles within the same potential range.

In summary, olefin metathesis reactions were exploited to incorporate redox-active ferrocene moieties onto carbene-functionalized ruthenium thin film surfaces. When the ferrocene groups were directly bound onto the electrode surface by a conjugated linkage, effective intervalence transfer occurred, as manifested by the appearance of two pairs of voltammetric peaks and the potential spacing suggested Class II characteristics. In contrast, with the insertion of a sp³ carbon spacer, the ferrocene moieties were found to behave independently and only one pair of voltammetric peaks were observed. In essence, these studies provide a first direct verification of Hush's hypothesis [6] made four decades ago that effective electronic communication might take place when redox-active moieties were anchored onto an electrode surface by a conjugated linker.

Acknowledgment

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