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Joya, K.S.; Groot, H.J.M. de

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Electrochemical *in situ* surface enhanced Raman spectroscopic characterization of a trinuclear ruthenium complex, Ru-red

Khurram Saleem Joya^{a,b,c,*} and Huub J. M. de Groot^a



To study the fate of a molecular di- μ -oxo-bridged trinuclear ruthenium complex, $[(\text{NH}_3)_5\text{Ru}-\text{O}-\text{Ru}(\text{NH}_3)_4-\text{O}-\text{Ru}(\text{NH}_3)_5]^{6+}$, also known as Ru-red, during the electro-driven water oxidation reaction, electrochemical *in situ* surface enhanced Raman spectroscopy (SERS) investigations have been conducted on an electrochemically roughened gold surface in acidic condition. It was previously described that on a basal plane pyrolytic graphite electrode in 0.1 M H_2SO_4 aqueous solution, Ru-red undergoes one electron oxidative conversion into a stable higher oxidation state ruthenium complex, Ru-brown, at <1.0 V (vs normal hydrogen electrode (NHE)), and this leads to water oxidation and dioxygen release, but the fate of Ru-red during electrochemistry was not studied in much detail. In this investigation, Ru-red dispersed in acid electrolyte and immobilized on a roughened gold electrode without Ru-red in solution has been subjected to anodic controlled potential experiments, and *in situ* SERS was carried out at various potentials in succession. The electrochemical SERS data obtained for Ru-red are also compared with *in situ* SERS results of an electrodeposited ruthenium oxide thin film on the Au disk. Our study suggests that on a gold electrode in sulfuric acid solution containing Ru-red, one electron oxidative conversion of Ru-red to a higher oxidation state ruthenium compound, Ru-brown, occurs at ca. 0.74 V (vs NHE), as supported by the electrochemical *in situ* SERS experiments. Moreover, at higher potentials and on Au disk, the Ru-red / Ru-brown are not stable and slowly decompose or electro-oxidize leading to deactivation of the tri-ruthenium catalytic system in acidic medium. Copyright © 2013 John Wiley & Sons, Ltd.

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Keywords: Ru-red; surface enhanced Raman spectroscopy; Ru-brown; oxygen evolution; roughened gold surface

Introduction

Water splitting catalysis using biomimetic molecular materials has become one of the most demanding and challenging topics owing to its potential application to produce renewable fuels and environmentally friendly energy carriers.^[1–3] Recently, there has been a strong increase in the scientific literature and research interests related to the field of catalytic water oxidation and molecular bio-inspired oxygen evolving complexes.^[3–5] A significant part of the water oxidation studies has also been focused on understanding the mechanism of oxygen formation, and various spectroscopic techniques have been employed to probe the details of the photosynthetic Mn-cluster for water oxidation reaction.^[6–8] However, *in situ* vibration spectroscopic analyses (Raman, IR) are rarely exploited to gain insight into the catalytic fate of an artificial water oxidation system.^[9,10]

A tri-ruthenium complex, Ru-red (Fig. 1), is one of the early investigated complexes for water oxidation reaction that has shown to be catalytically active for oxygen evolution.^[11] While this system has also been studied in an electrochemical environment, the evolution of various catalytic phases and chemical intermediate species generated from Ru-red during water oxidation was not studied in much detail.^[11–17] It was previously reported that during water splitting by Ru-red in aqueous acids, the tri-ruthenium amine complex undergoes a reversible oxidative conversion into a higher status ruthenium complex, the Ru-brown $[(\text{NH}_3)_5\text{Ru}-\text{O}-\text{Ru}(\text{NH}_3)_4-\text{O}-\text{Ru}(\text{NH}_3)_5]^{7+}$.^[11] On the other hand, this transformation was also described to take place in

electrochemical conditions on a basal plane pyrolytic graphite electrode at +0.96 V (vs normal hydrogen electrode (NHE)).^[16,17] This can ultimately lead to water oxidation and dioxygen formation, as was detected by gas chromatography combined with mass spectrometry.^[11,15]

Combined spectral and electrochemical studies of a solution containing Ru-red did not reveal any decomposition of the complex during the electrochemical process.^[15,17] It has also been reported that the anodic oxidation of Ru-red led to the formation of ruthenium-brown without the formation of oxides of ruthenium.^[11] However, there is only scant direct evidence that Ru-red did not convert into RuO_2 before or during water splitting. This is particularly relevant as RuO_2 is an extremely potent catalyst for oxygen evolution.^[18] *In situ* visible absorption spectroscopy experiments conducted by Ramaraj and Kaneko showed that Ru-brown is unstable when conditions for homogeneous water oxidation are applied, while incorporation in a heterogeneous

* Correspondence to: Khurram Joya, Leiden Institute of Chemistry, Leiden University. E-mail: khurramsj@chem.leidenuniv.nl

a Leiden Institute of Chemistry, Gorlaeus Laboratory, Leiden University, P.O. Box 9502, 2300 RA, Leiden, Netherlands

b Department of Chemistry, University of Engineering and Technology (UET), GT Road, 54890, Lahore, Punjab, Pakistan

c Max Planck Institute for Chemical Energy Conversion (MPI-CEC), Stiftstrasse 34 – 36, D – 45470, Mülheim an der Ruhr, Germany

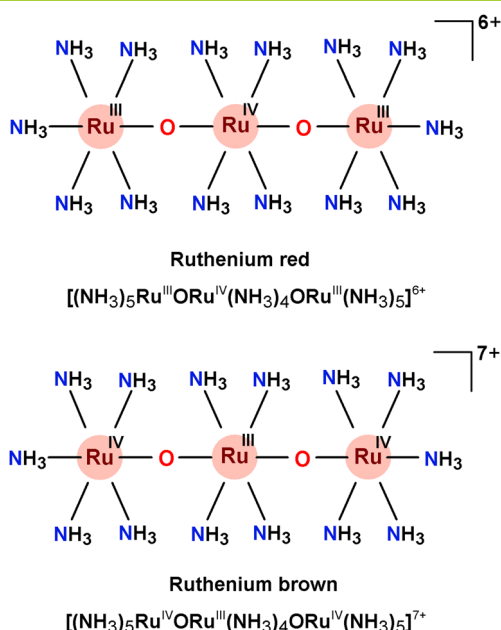


Figure 1. Chemical structural formula of Ru-red and Ru-brown showing ruthenium and oxygen architecture and metal oxidation states. Three Ru nuclei are connected by two oxo-bridges in amine ligands surrounding.

Nafion membrane stabilizes the complex against decomposition and exhibits good catalytic activity for water oxidation.^[15,19]

In this investigation, we follow up on the observation by Kaneko *et al.*^[13] that Ru-red, immobilized on gold and platinum electrodes, undergoes oxidative transformation into metastable ruthenium-brown without the formation of oxides of ruthenium.^[20,21] In order to study the insight of catalytic transitions and to probe the possibility of ruthenium oxide formation, we report here the use of electrochemical *in situ* surface enhanced Raman spectroscopy (SERS) to investigate the Ru-red catalytic fate during the water oxidation reaction on an electrochemically roughened gold surface.^[6–8] Ru-red on a polycrystalline gold disk (Au_{disk}) is one of the simplest examples of a surface modified with a molecular catalyst (Fig. 2), and using gold as a substrate material for Ru-red permits the application of *in situ* electrochemical SERS studies to probe the fate of Ru-red by the vibrational signatures of the catalyst system at the metal–electrolyte interface. Spectroscopic signatures during electrochemical oxidation of

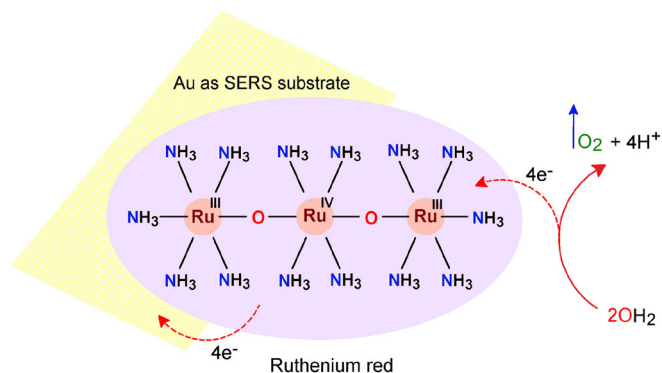


Figure 2. Chemical modification of the roughened gold surface, a SERS substrate, with Ru-red.

Ru-red were determined and investigated for a bare Au_{disk} electrode in contact with a sulfuric acid electrolyte solution containing Ru-red, and for a Ru-red functionalized gold electrode, without Ru-red in the electrolyte solution.^[10] In parallel, we compare the electrochemical properties of Ru-red on gold with those of ruthenium oxide (RuO_x), by using the same experimental conditions as for Ru-red exploiting *in situ* SERS.

Experimental

Materials

$\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ and Ru-red were of reagent grade, obtained from Sigma-Aldrich Co., and used as received. All the solutions were prepared in ultra-pure water (Millipore MilliQ[®] A10 gradient, 18.2 MΩ cm, 2–4 ppb total organic content). All glassware and cells were cleaned by boiling in a 1:1 mixture of concentrated nitric acid and sulfuric acid (for 2 hours and left overnight). Next, the glassware was washed and boiled in ultra-pure water and dried in an oven at 75 °C. The cell was boiled and washed thoroughly with ultra-pure water before each experiment. All solutions were purged with high-purity argon (Linde Gas, 6.0) for 30 min before each measurement to remove the oxygen and an argon atmosphere was maintained both in and above the solution during the electrochemical measurements to make sure that no air/oxygen was entering and intervening with the electrochemical system.

Electrochemical setup

The electrochemical work was conducted in a conventional single-compartment three-electrode glass cell. A three electrode configuration spectro-electrochemical glass cell, having an optical quartz window at the bottom parallel to the gold working electrode (WE), was employed for the electrochemical SERS investigation. A polycrystalline gold disk (diameter $d=5$ mm) were used as WE in voltammetry experiments. The WE in the SERS experiments was a roughened polycrystalline gold disk (diameter $d=5$ mm) embedded in a PTFE shroud. A platinum wire (thickness $\sigma=1$ mm) was used as a counter electrode (CE) and the reference electrode was a mercury–mercury sulfate electrode ($\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$). However, all potentials are referred to the NHE. Cyclic voltammetry, forward potential scans and other electrochemical investigations for *in situ* SERS investigations were performed with a computer-controlled IviumStat (Ivium Technologies, Eindhoven, The Netherlands) and operated by IviumSoft. Prior to the actual experiments, Au_{disk} was polished mechanically with an aqueous slurry of 0.3, 0.1 and 0.05 μm alumina (Buehler Limited) successively, on a Microcloth polishing fabric, until a mirror finish was achieved. After polishing, the electrode was ultrasonically cleaned in Milli-Q (Millipore) water for 15–20 min after each polishing step and rinsed thoroughly with pure water. A spiral platinum CE was flame annealed and washed with pure water before placing into the cell.

SERS characterization

SERS analysis was performed with a HR 800 spectrograph (Jobin Yvon) with a holographic grating of 600 gr mm^{-1} . The confocal hole of the instrument was set at 100 μm. A CCD camera with 1024 × 256 pixels was used as detector. The excitation line source was provided by a 20 mW HeNe laser at 632.8 nm.^[22] However,

the 632.8 nm laser excitation used for SERS spectral measurement falls outside the electronic absorption band of both Ru-red and Ru-brown.^[23] The laser beam was focused through an Olympus 50× microscope objective, which was not immersed in the electrolyte, into a 5 μm spot on the electrode surface. A notch filter was used to filter the SERS signal before reaching the sample. With this configuration, a resolution of 1.2 cm⁻¹ was obtained.^[22a] To make gold surface SERS-active substrate, roughening of the Au disk surface was done by applying 25 potential sweep oxidation–reduction cycles consecutively in 0.1 M KCl (Merck, pro analysis) from 1.25 to –0.25 V *versus* the saturated calomel electrode (SCE: Hg/Hg₂Cl₂/KCl).^[24]

Ru-red immobilization on the gold electrode

Ru-red was immobilized on a freshly roughened Au_{disk} by placing 15 μl of a stock solution of the catalyst (0.05 mM), prepared in a mixture of ultrapure deoxygenated water and MeOH (1:10), and dried for 4–6 h under Ar/N₂. The electrode was subsequently left for at least 32–34 h. After this procedure, it was dipped in ultrapure water to remove the unattached Ru-red molecules and employed directly for electrochemical investigation without any delay.

Electro-deposition of RuO_x

A thin hydrous ruthenium oxide (RuO_x·nH₂O) film was electrochemically deposited on a freshly roughened Au disk from 0.01 M HCl and 0.1 M potassium chloride electrolytes containing 1 mM RuCl₃ in a deoxygenated aqueous solution (pH ≈ 2) by a procedure described in the literature.^[25] In our experimental setup, the electrodeposition of the RuO_x·nH₂O film was realized by scanning the potential of the Au_{disk} electrode from 0.10–1.04 V (vs NHE) for 160–180 cycles in the above chloride electrolyte solution at a scan rate of 50 mV s⁻¹. The ruthenium oxide film thus produced was washed with pure water and employed without any further treatment in SERS and anodic water oxidation experiments using the RRDE setup.

Results and discussion

For electrochemical *in situ* SERS investigations, two types of experiments were conducted for the Ru-red molecular complex. In the first type of experiment, an aliquot of Ru-red solution, prepared in a small quantity of O₂-deaerated deionized water, was dissolved in deoxygenated Ar-saturated aqueous 0.1 M H₂SO₄ solution before the electrochemical characterization experiments. The resulting Ru-red concentration was 0.035 mM. In another set of study, the Ru-red was immobilized on the Au_{disk} as described in the experimental section without containing the tri-ruthenium complex in the electrolyte solution.

Electrochemical SERS investigation on roughened Au_{disk} with Ru-red

The electrochemical *in situ* SERS experiments were conducted in deoxygenated aqueous sulfuric acid with Ru-red in the solution. Figure 3 shows the *in situ* SER spectra of Ru-red on freshly roughened gold at selected potentials. Various Raman shifts were observed for the trinuclear ruthenium-amine catalyst, and peak assignments can be made by comparison with the data reported in the literature. Table 1 gives the Raman shifts (cm⁻¹) for Ru-red

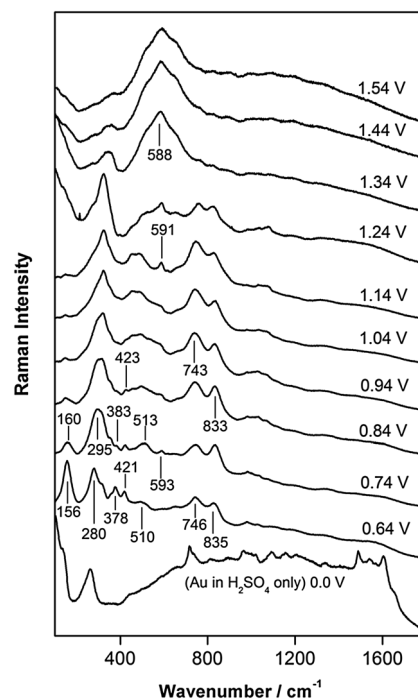


Figure 3. Selected potential-dependent *in situ* electrochemical SER spectra for a freshly roughened Au_{disk} electrode in deoxygenated 0.1 M H₂SO₄ solution containing 0.035 mM Ru-red. The starting potential was 0.6 V, and it was increased to 1.5 V (vs NHE) in successive 0.1 V increments.

Table 1. Raman shifts (wavenumbers cm⁻¹) for Ru-red and Ru-brown as reported previously (Ref. 26–28)

Compound		Raman shifts (wavenumbers cm ⁻¹)	
Ru-red	Ru-brown	Assignment	
157	178	ν ₆	Ru–O
281	294	ν ₅	O–Ru–N
376	390	ν _{2,3,4,8,9}	Ru–N
396			
438	424		
486			
540			
744	778	ν ₁	Ru–O
780			NH ₃
825	840	ν ₇	Ru–O

and Ru-brown in the 100–1000 cm⁻¹ region, which is the finger print region for both species.^[26,27] In the solid state, Ru-red has a nearly linear backbone structure with octahedral surroundings of the metal ions and near C_{4v} symmetry due to packing effects on the molecular skeleton.^[28] Raman data have indicated that Ru-red adopts a near D_{4h} symmetry in solution, with the octahedrons aligned along the backbone, albeit without perfect inversion symmetry, and that Ru-brown has a similar structure.^[27,29–31] For the D_{4h} symmetry, six modes are Raman active, which have been assigned in a series of investigations (Table 1).^[27,31]

The deviation from the D_{4h} is apparent from the observation of a strong antisymmetric mode at 825 nm in Ru-red. Although the principal Raman characteristics of Ru-red and Ru-brown are very

similar, the ν_1 , ν_5 , ν_6 and ν_7 bands for Ru-brown are all shifted to higher wavenumber compared to the corresponding vibrations in Ru-red, by 34, 13, 21 and 15 cm^{-1} , respectively, indicating a stiffening of the backbone when Ru-red is converted into Ru-brown.^[31] Incomplete conversion of Ru-red into Ru-brown was found to produce smaller shifts.^[27,31] However, in particular, the wavenumber of the ν_1 Ru-O symmetric stretch involving the two oxygen adjacent to the central Ru ion is very sensitive to the Ru-red to Ru-brown transition, which is thought to be related to the removal of an electron from an antibonding orbital located on the Ru-O-Ru-O-Ru backbone.^[31] These spectral features allow the detection of the Ru-red to Ru-brown transition, which is one of the aims of our spectro-electrochemical experiment (Fig. 3, Table 1).

In Fig. 3, at low potential (0.64 V vs NHE), the spectrum clearly indicates the presence of Ru-red near or on the electrode surface. The band at 156 cm^{-1} has been attributed to the ν_6 Ru-O stretching mode, which is a characteristic of the presence of Ru-red and is observed previously at 157 cm^{-1} (Table 1). The dominance of 156 cm^{-1} band at 0.64 V is indicative of the Ru-red presence at low potentials in a close proximity of the gold surface. Similarly, the feature at 280 cm^{-1} (at 0.64 V) has been assigned to the O-Ru-N bending vibration, which again ascribed to the existence of Ru-red. However, at higher potential, the Ru-O stretching vibration has shifted to $\sim 175 \text{ cm}^{-1}$ (Fig. 4), which has been observed previously for Ru-brown at 178 cm^{-1} ,^[27] and it is not observed in the spectrum at 0.64 V (Figs. 3, 4). Similarly, the Raman band at 280 cm^{-1} (at 0.64 V) also shifts to higher wavenumbers 294 cm^{-1} at higher electrode potential, which infers to the presence for Ru-brown at electrode potential above 0.64 V (Fig. 4). The smaller features in Fig. 3 at 378, 421 and 510 cm^{-1} could correspond to Raman shifts observed for either

Ru-red or Ru-brown, but the pair of features observed at 746 and 835 cm^{-1} appears characteristic for Ru-red. Both modes are Ru-O stretching modes, reported at 744 and 825 cm^{-1} for Ru-red in solution as shown in Table 1 (the corresponding modes for Ru-brown are at 778 and 840 cm^{-1}). Considering the dominance of the modes at 156, 280, and 746 cm^{-1} at 0.64 V, which are all characteristic of Ru-red (Table 1), we derive that the species most prominently observed at a low potential is Ru-red.

As the electrode potential is stepped positively, some important spectral changes are observed as shown in Fig. 3. In general, changes in intensity and wavenumber may be related to three different effects: a change in identity of the species (e.g. a conversion from Ru-red to a Ru-brown type species) as a result of a change in electrode potential, a change in orientation or structure of the adsorbed Ru-red (or Ru-brown) or an electrochemical Stark tuning effect in which the electric field existing at the interface leads to changes in the vibrational frequencies and the intensity of the SERS lines of the adsorbed species.^[32] As stated earlier, the SER spectra of Ru-red in Fig. 3 show predominantly Ru-red features at the start of the positive potential scan (0.64 V). The band at 280 cm^{-1} shifted to a higher wavenumber ca. 295 cm^{-1} at 0.74 V (vs NHE) indicating the possible formation of Ru-brown or similar species near the Au electrode at this potential, though the 156 and 745 cm^{-1} bands seem to be unaffected. However, the 156 cm^{-1} band decreases in intensity with the positive-rising potential. In spite of the continued dominance of the spectral pair at 740 and 835 cm^{-1} at higher potentials, which we ascribe to Ru-red, the disappearance of the band at 157 cm^{-1} and the shift of the band at 280 to 295 cm^{-1} may indicate the formation of a (small) amount of Ru-brown or a similar species at potentials higher than ca. 0.7 V (vs NHE).

In a previous report by the Kaneko group, the transition of Ru-red to Ru-brown has been observed by *in situ* electrochemical visible absorption spectral studies in a phosphate buffer solution at pH=7.4 on a thin layer ITO electrode during oxidative scans from 0.42 V to 0.75 V (vs NHE).^[15] Although the SER spectra in Fig. 3 contribute to converging evidence for the Ru-red conversion into the Ru-brown at this potential,^[11,15–17] some features attributable to Ru-red remain present. Several studies have indicated that the oxidation may occur at low overpotential with Ru-red, indicating the formation of higher oxidation state Ru species like $\text{Ru}^{\text{V}}\text{-O-Ru}^{\text{V}}\text{-O-Ru}^{\text{V}}$ or similar intermediates and their possible involvement in water oxidation process.^[16,17] However, above this potential in our investigation, the gold oxide species (as indicated by a broad Raman band at 588 cm^{-1}) are observed, and are similar to the response from bare gold in the same electrolyte but without Ru-red in the solution (Fig. S1, Supporting Information).

Figure 4 shows the SER spectra obtained at selected potentials on the Ru-red functionalized freshly roughened Au_{disk} electrode in deoxygenated Ar-saturated 0.1 M aqueous H_2SO_4 (without Ru-red in solution). The starting potential was 0.6 V, and it was increased to 1.5 V (vs NHE) in successive 0.1 V increments. At 1.24 V (vs NHE), the Raman bands at ca. 159 cm^{-1} and 745 cm^{-1} have shifted to ca. 174 cm^{-1} and 770 cm^{-1} , respectively, providing evidence for formation of a Ru-brown type species at this potential. However, no profound changes were observed in the 281 cm^{-1} band. Compared to SER spectra on the gold electrode with Ru-red in the solution (Fig. 3), the SERS analysis of RRA (without Ru-red in the electrolyte solution) shows a delayed appearance of the formation of Ru-brown signals (Fig. 4) suggesting a different catalytic phases of Ru-red for the two systems deposited

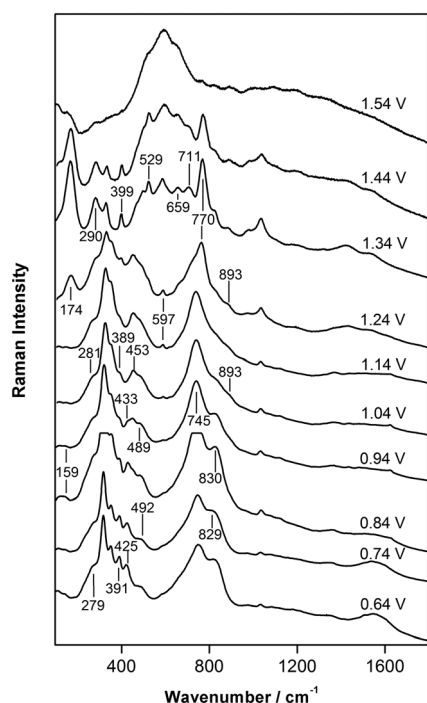


Figure 4. Selected potential-dependent *in situ* electrochemical SER spectra for the Ru-red functionalized freshly roughened Au_{disk} electrode in deoxygenated Ar-saturated 0.1 M aqueous H_2SO_4 (without Ru-red in solution). The starting potential was 0.6 V, and it was increased to 1.5 V (vs NHE) in successive 0.1 V increments.

on the roughened gold electrode, in agreement with the different applied electrode potentials at which the two systems show electrochemical characteristics for their oxidation. With more than 1.34 V applied to the RRA, additional Raman peaks are observed at ca. 529, 659 and 711 cm^{-1} . These modes may be associated with the formation of decomposition products or other monomeric species in the catalyst layer.^[27] Gold oxide vibrations can be discerned in the Raman spectra at potentials above 1.44 V.

Electrochemical SERS Study of electrodeposited ruthenium oxide on roughened Au_{disk}

In order to compare the Ru-red features with the ruthenium oxide during oxidation studies, a thin hydrous film of electrodeposited ruthenium oxide ($\text{RuO}_x \cdot n\text{H}_2\text{O}$) was also investigated by spectro-electrochemical Raman experiments. The SER spectra of a hydrous ruthenium oxide freshly electrodeposited on a roughened gold disk electrode were collected in a 0.1 M H_2SO_4 aqueous electrolyte without Ru-red or free Ru in the solution (Fig. S2, Supporting Information).

Raman shifts observed at wavenumbers 522, 665 and 742 cm^{-1} would be indicative of the presence of ruthenium oxide as it is found to be Raman active in the range of 450–800 cm^{-1} as vibrational modes (Fig. S2, Supporting Information).^[33,34] The intensities of these bands gradually decrease by increasing the potential to more positive values, suggesting the conversion or loss of the ruthenium oxide species on the gold surface. The SER spectra show that the features ascribable to the electrodeposited ruthenium oxide ($\text{RuO}_x \cdot n\text{H}_2\text{O}$) on the gold disk are present until 1.24 V essentially just before the water oxidation sets in (Fig. S2, Supporting Information). For potentials above 1.24 V, the ruthenium oxide features disappear, and a broad band at 597 cm^{-1} due to the formation of gold oxide on the surface dominates the spectrum (Fig. S1, Supporting Information).

Summarizing, the Raman spectra of Ru-red on bare gold with Ru-red in solution, of the Ru-red functionalized gold electrode and of Ru-oxide modified gold electrode, all show different and distinctive features during electrochemical oxidation experiments. For the two systems with Ru-red in contact with gold surface, the Raman data suggest a transition from Ru-red to a Ru-brown type species with increasing potential, and the transition appears to take place at significantly more positive potentials when Ru-red is only on the surface and not in solution. The delay in oxidation behaviour is mirrored by the catalytic activity, which also occurs at significantly more positive potentials for the Ru-red functionalized gold electrode without Ru-red in solution. In particular for the latter system, Raman active modes are observed close to the suggested oxidation potential.^[20,21] These modes show some resemblance to the Raman features observed for ruthenium oxide during electrochemical oxidation. Such features are not clearly observed for the system with Ru-red in solution, while the catalytic activity of the system is somewhat similar to that of the gold electrode modified with Ru oxide.

Conclusions

In this study, spectro-electrochemical investigation of the catalytic phase of Ru-red in acidic media, conducted by *in situ* SERS during application of controlled-potential, is discussed. SERS experiments show that Ru-red undergoes electro-induced oxidative conversion to a higher oxidation state ruthenium compound, probably a form of Ru-brown, at ca. 0.74 V (vs NHE). The Ru-brown type species subsequently loses electrons and, possibly, oxidizes

water to make dioxygen.^[11–15] In another set of experiments on the electrodeposited ruthenium oxide film on the Au_{disk}, the onset of catalytic transitions during electrochemical oxygen is observed at ca. 1.0 V (vs NHE). Thus, a spectro-electrochemical method based on molecular vibrations to study the different catalytic phases using a commercially available trinuclear ruthenium complex is described here. We anticipate that this study will help in establishing spectro-electrochemical characterization of molecular water splitting complexes during catalytic phase.

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Supporting information

Supporting information may be found in the online version of this article.

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