

In-situ Surface Enhanced Electrochemical Chemiluminescence and Raman Scattering with Screen-printed Gold- and Silver-Electrodes

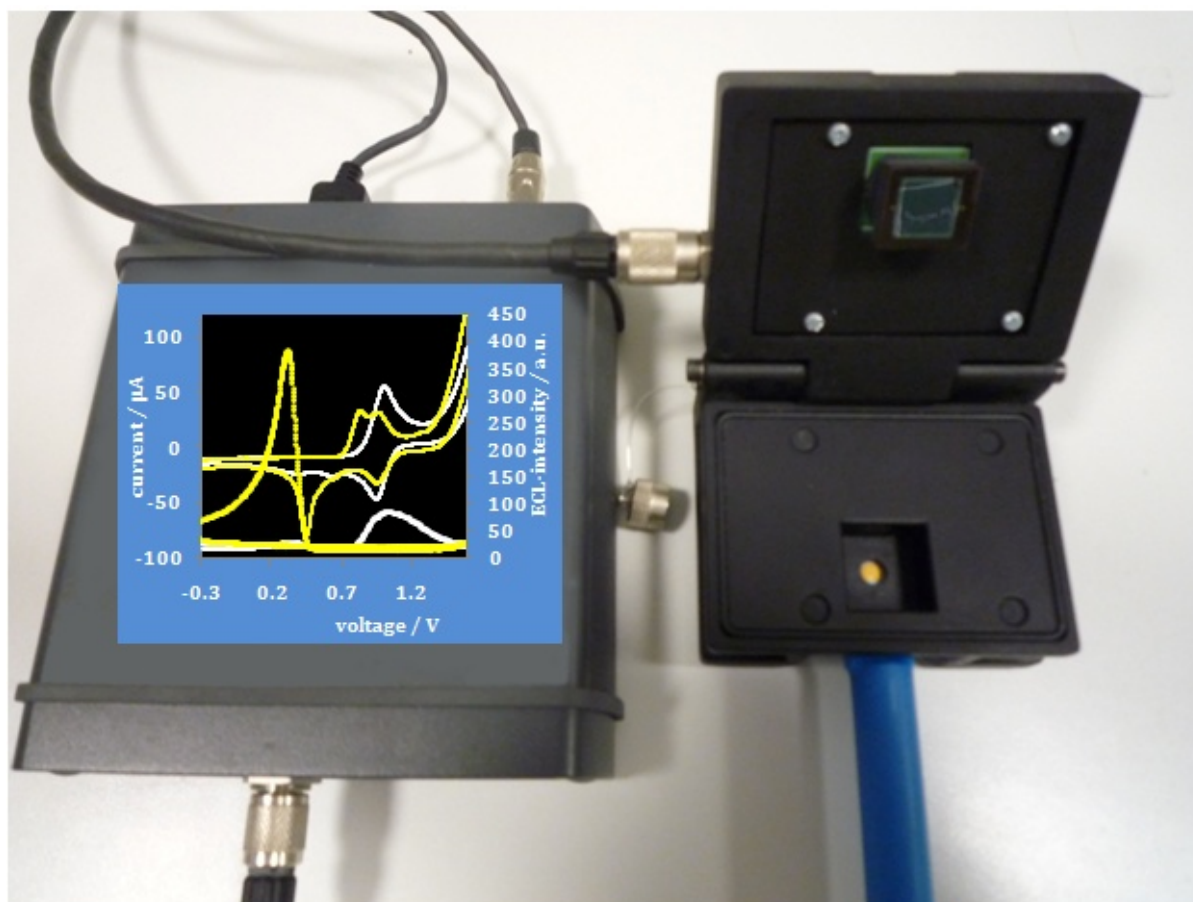
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Abstract Redox reactions on gold- and silver screen-printed electrodes (SPE) can be monitored electrochemically using cyclic voltammetry (CV) and spectroscopically by electrochemical chemiluminescence (ECL). Alongside conventional anionic ECL, cathionic ECL with in-situ generated, finely-dispersed Au as a co-reagent is also presented. Raman spectroscopy is a powerful technique that can be employed for the detection of ultralow concentrations when promoted by an enhancement of the scattering process. Simple in-situ electrochemical modification of the electrode leads to surface-enhanced Raman intensities.



Keywords: graduate education / research, electrochemistry, Raman spectroscopy

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1. Introduction

In the experiments presented here, we used screen-printed electrodes (SPE) [1]. These consist of a ceramic plate as a substrate to which three electrodes - the working, reference and counter electrodes - were applied using screen printing. SPEs made out of numerous different electrode materials are available from a range of companies. We used three different SPEs from Metrohm / DropSens. The two gold-SPEs either boasted an Au-At (high temperature curing ink) or Au-Bt (low-temperature

curing ink) as working electrodes and an Ag/AgCl reference- and an Au-counter electrode. The silver-SPE had silver, Ag and carbon as working, reference and counter electrodes (Figure 1).

Figure 2 shows the three scanning-electron microscope (SEM) images. They clearly show that the Au-Bt-SPE has a more pronounced surface roughness than the Au-At-SPE.

To significantly increase the ECL and Raman intensities, Au-At SPE can be modified simply by electrolysis with an aqueous AuCl_3 solution for 2 s at -1.5 V, while the surfaces of the Au-Bt and Ag SPE can be prepared by potential scanning between -0.4 V and 1.5 V and +0.5 V and -0.5 V, resp. and back.

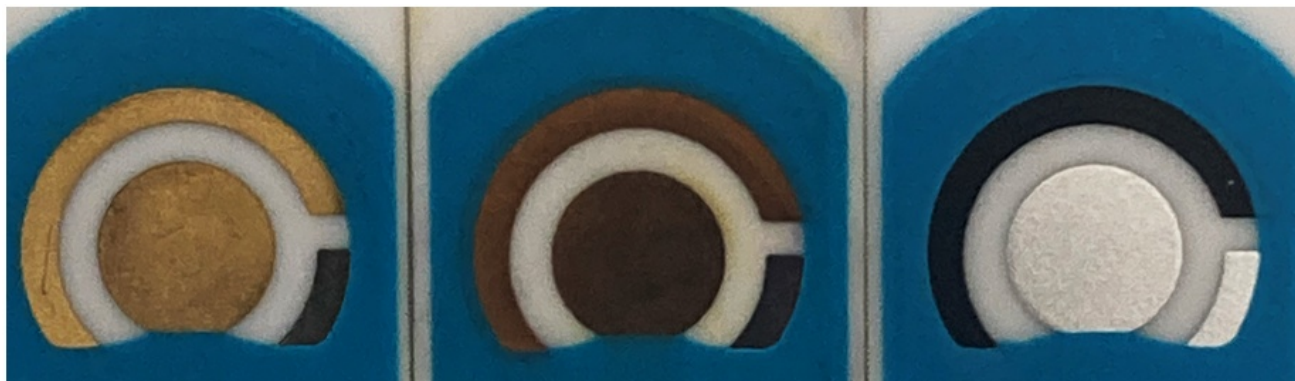


Figure 1. Screen-printed-electrodes: Au-At (left), Au-Bt (middle), Ag (right) with working-electrode (circular), counter electrode (semicircle) and reference electrode (down-right)

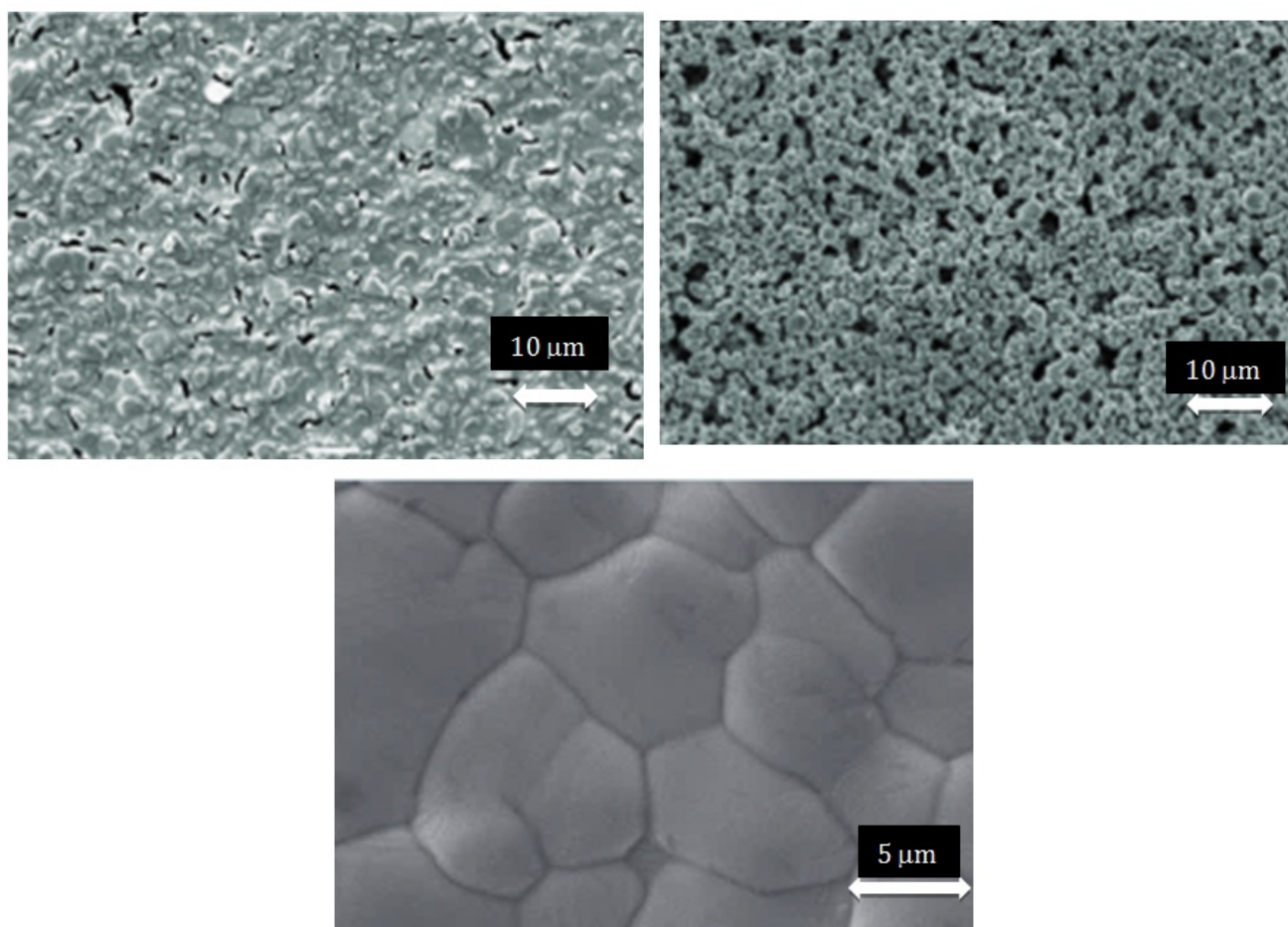


Figure 2. SEM image of the working electrodes used. Top: Au-At, middle: Au-Bt and bottom: Ag (kindly from DropSens)

2. Pedagogical Objectives

Electrochemistry plays an important role in curricula, textbooks, and everyday life, but there exist several problems in learning electrochemistry [2-7]. We do not want to go into the multitude of misunderstandings here, but only point out one point because it is directly related to this article: electrode reactions cannot be identified [2].

We think that the pedagogical benefit of the described experimental procedures lies in the combination of electrochemical and spectroscopic experiments (more information on the important aspects of the primary method used in electrochemistry, cyclic voltammetry, can be found in the supporting information "Cyclic Voltammetry"). The electrode reactions, i.e. anodic and cathodic current peaks, are directly correlated with the emission of light and with a dramatic enhancement of Raman intensities.

The demonstrations of the ECL phenomenon are striking. The importance of stimulating experiences as a motivational aid will not be discussed further here - this has been discussed in detail elsewhere [5]. The phenomenon of both ECL and surface-enhanced Raman spectroscopy plays an important role in analytical chemistry [8,9]: The oxidation of the precious metal gold is surprising for students, the increase in Raman signals after simple electrochemical formation of a finely dispersed surface may also surprise the students. These phenomena can be understood directly from the interpretation of the corresponding CV. The described experiments were conducted in a graduate-level university course in electrochemistry. Until now twenty students performed these experiments at the end of an electrochemistry course for advanced students. The students got the theoretical information in a parallel lecture about physical chemistry, and the students' misconceptions in electrochemistry were treated in different didactic-lectures. Therefore, the students were no freshmen. The experiments were done, and the students wrote down their observations. The teacher provided instructions through lecture and discussion, as students took notes and ask questions. Moreover, the teacher solved problems with respect to spectroscopy and electrochemical concepts. At the end the students had to remind their predictions and explain their observations: What was the purpose of the experiment? What is the role of the used substances? Assume the electrode reactions. Do you see any advantage in the combination of electrochemical processes and spectroscopic observation? Compare the limit of detection of ECL and Raman.

Without empirical background we can resume that high-achieving students enjoyed the experiments, because the combination of two disparate subjects (electrochemistry and spectroscopy) were unusual. But weaker students asserted that the experimental setup is "slightly difficult".

3. Experimental Materials and Procedures

Tris(2,2'-bipyridyl)ruthenium(II) Chloride Hexahydrate (TCI T1655, CAS RN: 50525-27-4), double-distilled water, KCl-solution phosphate buffer (0.1 mol/L), DL-prolin

(Pyrrolidin-2-carbonsäure) (SigmaAldrich171824, CAS RN: 609-36-9), Gold chloride-Hydrat (50% Au) (SigmaAldrich, 50790, CAS RN: 27988-77-8). $K_4[Fe(CN)_6] \cdot 4 H_2O$ (SigmaAldrich, 455989, CAS RN: 14459-95-1)

ECL-potentiostat (STAT-ECL, DropSens). Additional information about this device can be found in the supporting information "STAT-ECL".

Raman spectrometer: AvaRaman (785 nm Laser) from Avantes with a Raman cell for SPE from Metrohm / DropSens. Additional information about this device can be found in the supporting information "AvaRaman".

Screen-printed electrodes: DropSens: AuAt (Au as working electrode, Au as counter electrode, Ag/AgCl as reference electrode), AuBt (Au as working electrode, Au as counter electrode, Ag/AgCl as reference electrode), Ag (Ag as working electrode, Ad as counter electrode, Ag/AgCl as reference electrode).

4. Hazard

Tris(2,2'-bipyridyl)ruthenium(II) Chloride Hexahydrate: This product does not meet the criteria for classification in any hazard class according to Regulation (EC) No 1272/2008.

DL-Prolin: This substance/mixture contains no components considered to be either persistent, bioaccumulative and toxic (PBT), or very persistent and very bioaccumulative at levels of 0.1% or higher. If breathed in, move person into fresh air. If not breathing, give artificial respiration. In case of skin contact, wash off with soap and plenty of water. In case of eye contact, flush eyes with water as a precaution. If swallowed, never give anything by mouth to an unconscious person. Rinse mouth with water.

Gold chloride: Harmful if swallowed. Causes severe skin burns and eye damage. May cause an allergic skin reaction. Do not breathe dusts or mists. Do not eat, drink or smoke when using this product. Wear protective gloves/protective clothing/eye protection/face protection/hearing protection.

Precautionary statements: If swallowed: Call a poison center / doctor if you feel unwell. Take off immediately all contaminated clothing. Rinse skin with water. If in eyes: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

$K_4[Fe(CN)_6]$: Harmful to aquatic life with long lasting effects, contact with acids liberates very toxic gas.

Precautionary statements: Avoid release to the environment. Dispose of contents/container to an approved waste disposal plant.

5. Procedures

The SPE are placed into the ECL- or Raman cell and connected with the cable connector. A 0.1 mmolar solution of $[Ru(bpy)_3]^{2+}$ is mixed with the 1 mmolar aqueous KCl solution. 60 μ L thereof is added to the SPE with an Eppendorf pipette so that all three electrodes are wetted. In the experiment with proline as the co-reagent, a crumb of the powder is stirred in without touching the electrodes.

ECL: The program DropView 8400 is started with scan rate 0.05 V/s, 0.02 V potential increment and amplification factor for ECL: 10.

CV-parameters: Anodic potential scan: Start potential: 0.6 V, reverse potential: 1.6 V, end potential: 0.6 V. Cathodic scan: Start potential: -0.4 V, reverse potential: 1.5 V, end potential: -0.4 V.

Linear sweep parameters: Start potential: 0.5 V, end potential: -0.3 V.

Formation of Ag-electrode: Start potential: -0.5 V, reverse potential: 0.5 V, end potential: -0.5 V.

Formation of Au-Bt-electrode: Start potential: 0 V, reverse potential: 1.6 V, end potential: 0 V.

Electrolysis of the Au-At-electrode with 1 mmol aqueous AuCl₃ solution at -1.5 V for 2 s.

Raman: Integration time: 1 s. CV: Start potential: -0.3 V, reverse potential: 1.7 V, end potential: -0.3 V.

EIS: Solution: K₄Fe(CN)₆ (0.1 mmol/L), potential: 0.05 V, frequency sweep: 100 kHz to 0.1 Hz, AC voltage amplitude: 10 mV.

For synchronizing of potentiostat and Raman and for data handling, see supporting information ("Synchronizing and data handling").

6. Spectroelectrochemistry

Spectroelectrochemistry of electroluminescent substances can be used to show strong correlations between electrochemical reactions on electrodes and changes in absorbance or luminescence adjacent to the electrodes used. This is demonstrated using the well-known substance tris(2,2'-bipyridyl)dichlororuthenium [Ru(bpy)₃]²⁺ [8,9,10]. Electroluminescent substances change emission spectrum depending on their redox state. The combination of electrochemistry and optical spectroscopy results in electrogenerated chemiluminescence (ECL). [Ru(bpy)₃]²⁺ is oxidised to [Ru(bpy)₃]³⁺ at a given potential and reacts with a co-reagent (preferably isopropylamine [4]) forming [Ru(bpy)₃]^{2+*}. This excited singlet state species luminesces around 600nm. This so-called anodic ECL has been

extensively been studied [11]. In contrast, in this paper we will describe a rather unusual form of cathodic ECL of [Ru(bpy)₃]²⁺ using electrochemically-prepared, finely dispersed gold as co-reagent.

Raman scattering, normally low in intensity, can be dramatically enhanced by simply modifying the metal-electrode surface used (surface enhanced Raman spectroscopy SERS). We demonstrate that both electrochemically-activated gold and silver electrodes show a significant increase in Raman scattering.

All methods are easy to perform and do not require the additional ex-situ synthesis of gold or silver nanoparticles.

7. Electrochemical Chemiluminescence

Figure 3 shows the cyclic voltammogram (CV) and the ECL intensity of [Ru(bpy)₃]²⁺ (0.1 mmol in 10 mmol aqueous solution of KCl with and without the co-reagent proline (0.1 mmol)) measured by the STAT-ECL potentiostat/photodiode combination from Metrohm/DropSens whilst simultaneously recording the CV and the ECL curves. Without a co-reagent ECL cannot be observed. In the presence of a co-reactant, however, the ECL intensity increases significantly for the anodic scan, beginning at about 0.9 V. This process is well-known and is described and explained in the literature in detail [9,10].

Cathodic ECL, however, is a relatively new phenomenon [11]. Lu et al observed an increase of the luminescence of [Ru(bpy)₃]²⁺ using Au-nanoparticles (Au-NPs). The authors proposed that Au-NPs and [Ru(bpy)₃]²⁺ are electrochemically oxidised first, and Au-NP⁺ and [Ru(bpy)₃]³⁺ are then formed. In the back scan [Ru(bpy)₃]³⁺ and Au-NP⁺ are reduced to [Ru(bpy)₃]^{2+*} and Au-NP, resulting in luminescence.

We have found that a preparation of Au-NP is not necessary, as the ECL of [Ru(bpy)₃]²⁺ occurs, to a large extent, only if Au electrodes with finely dispersed gold are used. This is ensured by using a commercial Au-Bt SPE, which is simply modified by an electrochemical potential scan between -0.4 V and 1.5 V (Figure 4).

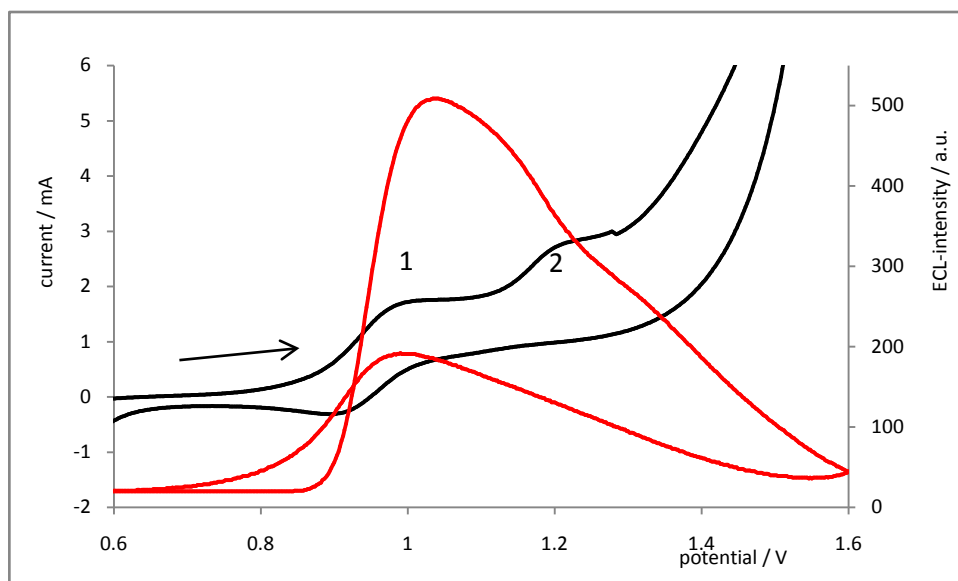


Figure 3. Cyclic voltammogram (black line) and ECL intensity (red line) of [Ru(bpy)₃]²⁺ with proline in 1 mmol KCl on an Au-At-SPE. Scan rate: 0.01 V/s. 1: Oxidation of [Ru(bpy)₃]²⁺, 2: Oxidation of Cl⁻. Arrow indicates scan direction

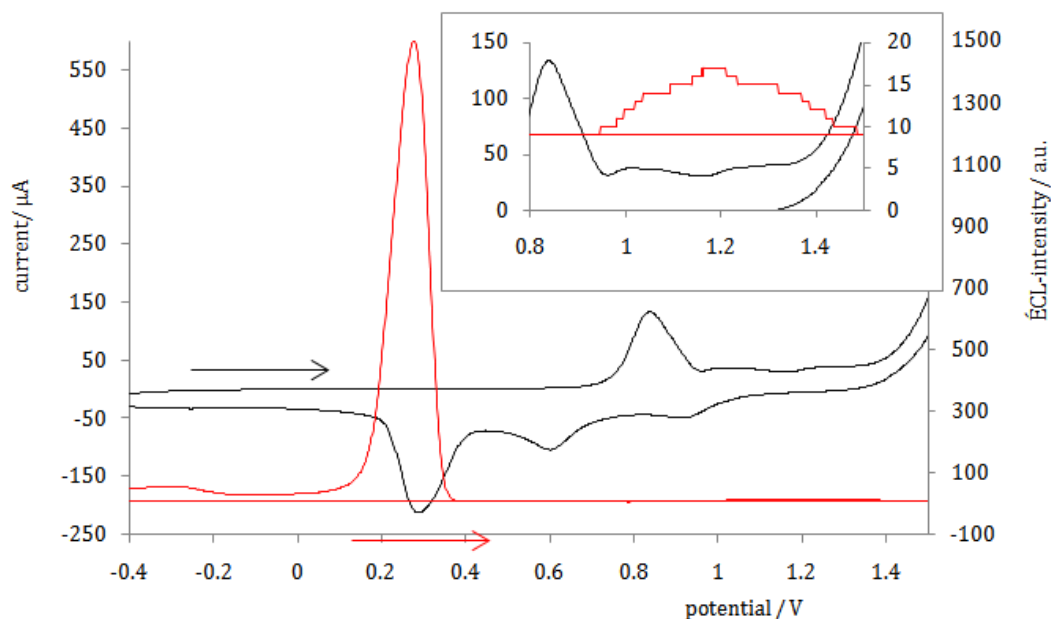


Figure 4. Cyclic voltammogram (black line) and ECL intensity (red line) of $[\text{Ru}(\text{bpy})_3]^{2+}$ at an Au-Bt-SPE. Arrow indicates scan direction. Insert: Enlarged representation of CV and ECL between 0.8V and 1.5 V

Table 1 shows the reactions and the corresponding voltages.

Table 1. Reaction scheme of the anodic and cathodic reactions

anodic scan:	
$\text{Au}^0 \rightarrow \text{Au}^+ + \text{e}^-$ (0.8V)	(1)
$[\text{Ru}(\text{bpy})_3]^{2+} \rightarrow [\text{Ru}(\text{bpy})_3]^{3+} + \text{e}^-$ (1V)	(2)
Au^0 (not oxidized) + $[\text{Ru}(\text{bpy})_3]^{3+} \rightarrow \text{Au}^+ + [\text{Ru}(\text{bpy})_3]^{2+*}$	(3)
$[\text{Ru}(\text{bpy})_3]^{2+*} \rightarrow [\text{Ru}(\text{bpy})_3]^{2+} + \text{h}\nu$	(4)
cathodic scan:	
$[\text{Ru}(\text{bpy})_3]^{3+}$ (not reacted in (3)) + $\text{e}^- \rightarrow [\text{Ru}(\text{bpy})_3]^{2+}$ (0.9V)	(4)
$[\text{Ru}(\text{bpy})_3]^{2+} + \text{Au}^+ \rightarrow [\text{Ru}(\text{bpy})_3]^{3+} + \text{Au}^0$ (0.9V-0.4V)	(5)
$\text{Au}^+ + \text{e}^- \rightarrow \text{Au}^0$ (0.4V)	(6)
$[\text{Ru}(\text{bpy})_3]^{3+} + \text{Au}^0 \rightarrow [\text{Ru}(\text{bpy})_3]^{2+*} + \text{Au}^+$ (0.4V)	(7)
$[\text{Ru}(\text{bpy})_3]^{2+*} \rightarrow [\text{Ru}(\text{bpy})_3]^{2+} + \text{h}\nu$ (0.4V)	(8)

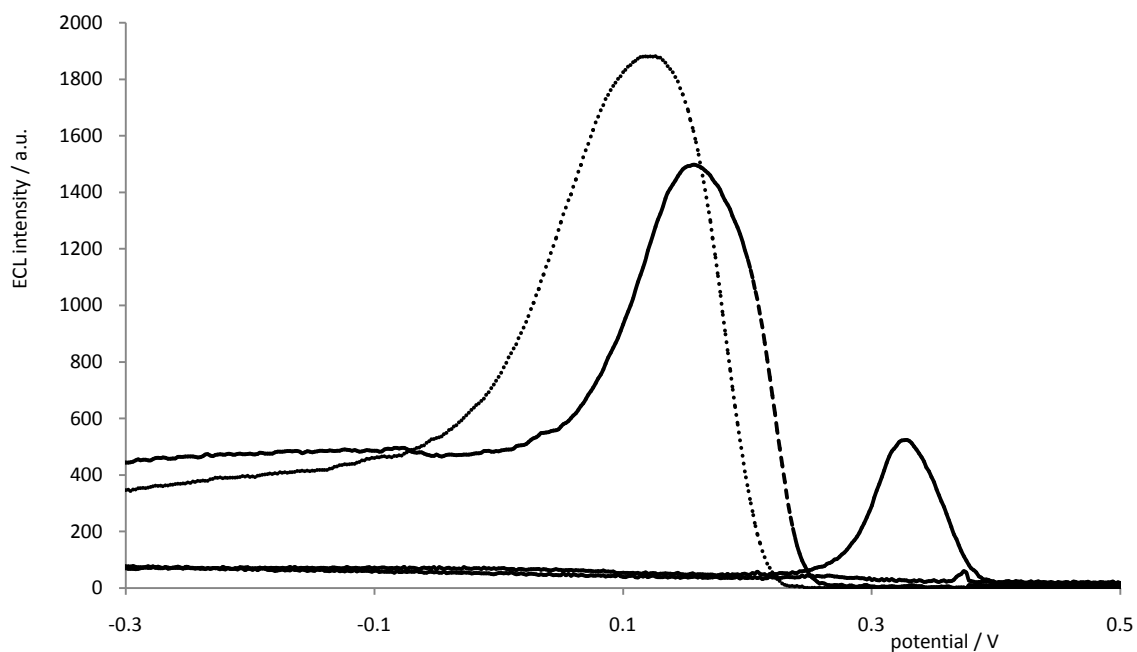


Figure 5. ECL at four different scan rates (0.01 V/s (solid line), 0.05 V/s (dashed line), 0.1 V/s (bold dotted line) and 0.2 V/s (thin dotted line)). Only back scan presented

In the anodic scan a small ECL intensity can be observed (see Figure 3, insert). This is possibly due to the incomplete oxidation of the gold surface, so that a small amount of Au on the surface can react with $[\text{Ru}(\text{bpy})_3]^{3+}$ forming Au^+ and $[\text{Ru}(\text{bpy})_3]^{2+*}$ (eq. 3).

During cathodic scanning, $[\text{Ru}(\text{bpy})_3]^{3+}$ is reduced to $[\text{Ru}(\text{bpy})_3]^{2+}$ at about 0.9 V (eq. 4). To a small extent, the resulting $[\text{Ru}(\text{bpy})_3]^{2+}$ reacts with Au^+ between 0.9 V and 0.5 V (eq. 5). The Au^+ surface, however, is reconstructed to boast finely dispersed Au^0 at about 0.4 V (eq. 6). The released electrons reduce $[\text{Ru}(\text{bpy})_3]^{3+}$ to $[\text{Ru}(\text{bpy})_3]^{2+*}$ (eq. 7), which subsequently luminesces (eq. 8). However, if the scan rate is low, no ECL can be observed because the formation of $[\text{Ru}(\text{bpy})_3]^{2+}$ between 0.9 V and 0.5 V (eq. 5) is completed just before the gold surface is restored. Figure 5 exhibits this type of behaviour

at four different scan rates (0.01 V/s, 0.05 V/s, 0.1 V/s and 0.2 V/s). To date, we cannot explain why no ECL can be observed between 0.9 V and 0.5 V, although $[\text{Ru}(\text{bpy})_3]^{3+}$ is able to react with Au^0 . Perhaps a finely-dispersed Au surface is an important prerequisite for a noticeable electrochemical reaction involving $[\text{Ru}(\text{bpy})_3]^{3+}$ to take place. At 0.4 V, Au^+ is reduced, forming a finely-dispersed Au surface⁵ on which $[\text{Ru}(\text{bpy})_3]^{3+}$ can be reduced (7, 8). The charge conversion of the process between 1 V - 0.8 V for a cathodic scan ≈ 0.06 As, but between 0.45 V - 0.2 V for a cathodic scan ≈ 6.1 As. This means that in contrast to the first process (eq. 4), in the last (eq. 6, 7, 8), a charge conversion with a value that is hundredfold occurs. Therefore, the charge transfer between electrode surface and solution seems to be sufficient to observe an intense ECL.

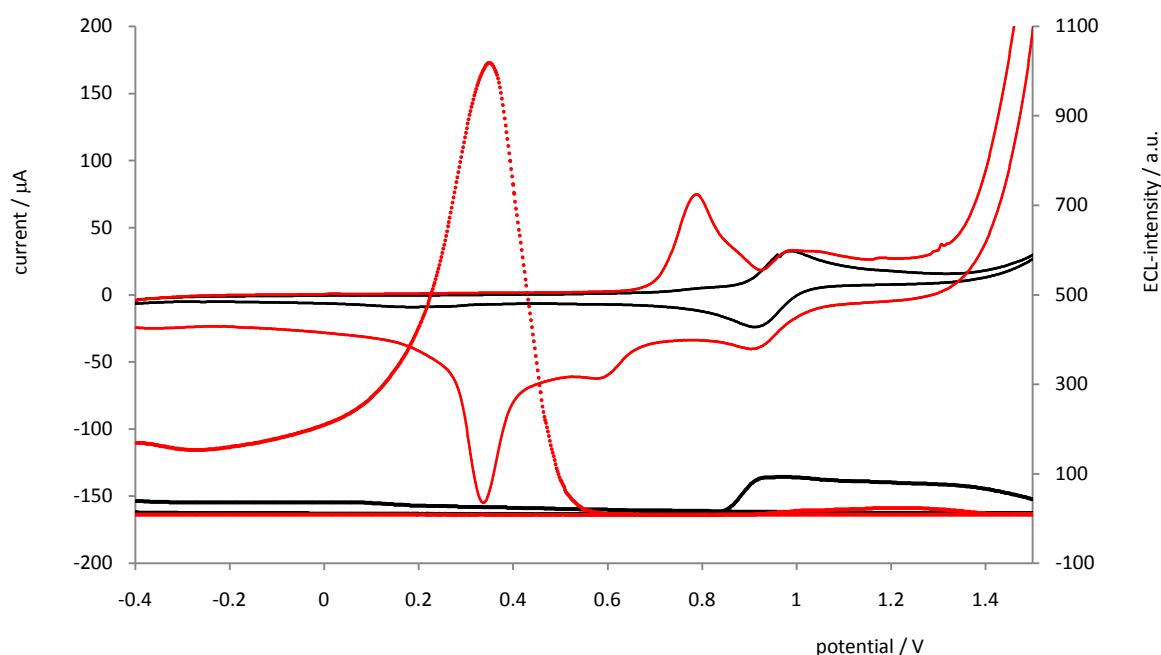


Figure 6. Cyclic voltammograms (black and red solid lines) and ECL intensity (black and red dotted lines). Black lines: Au-At- electrode. Red lines: Au-At-electrode with additional electrolysis with AuCl_3

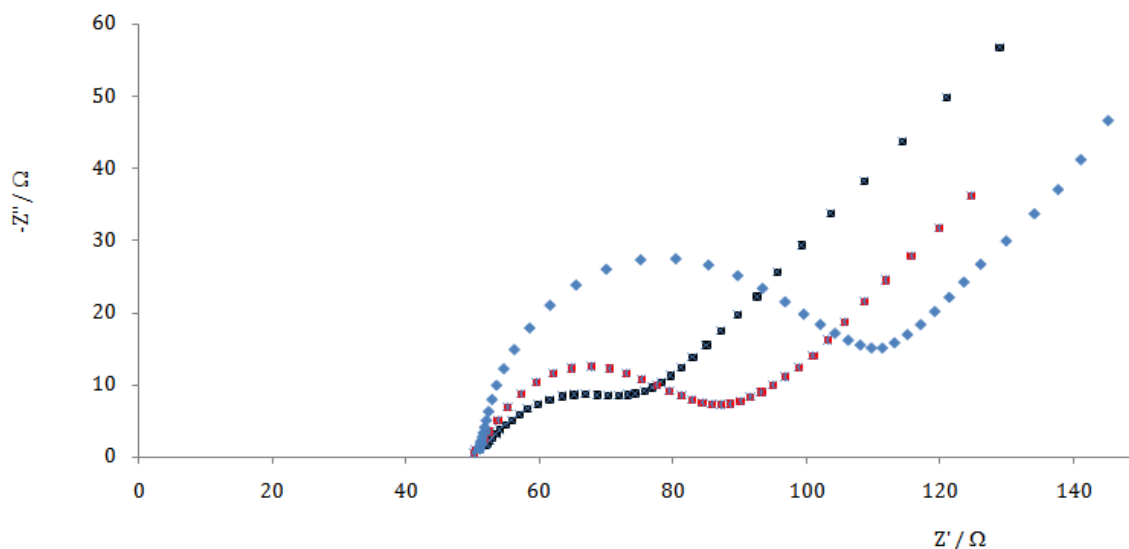


Figure 7. Nyquist diagram of Au-At before (blue points) and after electrolysis with an aqueous solution of AuCl_3 (1 mmol/L) at -1.5 V at two different times. 1s: red points and 2s: black points

A comparison between an Au-Ag SPE with and without electrolysis and an aqueous solution of AuCl_3 is shown in Figure 6. Obviously, the ECL intensity increases when the Au-electrode is covered with Au multilayers by electrolysis.

The Nyquist diagram [12] shows the difference between a non-electrolysed and a stepwise electrolysed gold surface: The semicircles of electrolysed Au each have a smaller radius. This is an indicator of a lower polarising (or faradic) impedance, which means that the electron transfer between the electrode and the substance in the solution is faster on the surface upon which gold has been deposited (In the supporting information details of the Electrochemical impedance spectroscopy "EIS" are listed).

8. Surface-enhanced Raman Spectroscopy (SERS)

Raman spectroscopy is a scattering technique used to detect molecular vibrations when polarisability changes during excitation. Normally, the intensity of the scattered radiation is very low. However, the intensity can be increased dramatically if the analyte is adsorbed on a finely dispersed metallic surface [13]. The theory behind SERS is quite complicated, but there is general consensus that structural features such as shape, size and surface charge lead to plasmonic properties that influence SERS [14].

Here, we demonstrate that an activation of a silver surface can be carried out by initiating an electrochemical oxidation – reduction process between -0.5 V and $+0.5$ V and vice versa. Figure 8 shows the results for $[\text{Ru}(\text{bpy})_3]^{2+}$ in a KCl-solution): Before electrochemical activation, the Raman signals have a low intensity (black line). Activation results in an enhancement factor

$$EF = \frac{I(\text{SERS})}{I(\text{normal})} \approx 1000. \text{ In [15] the surface of silver}$$

was measured before and after electrochemical activation. The SEM images show a significant difference between the pristine and the activated electrode: The latter shows a clear reduction of the silver domains by a factor of about five.

Analogous results were obtained when using the Au-Bt-SPE. Figure 9 shows the results during the potential scan from -0.3 V to 1.7 V and vice versa with the Au-Bt-SPE: Starting with high Raman intensities, the intensities decrease continuously in the anodic scan because the Au surface is increasingly covered with Au^+ . In the reverse backward scan, the intensities increase again and reach the original intensities.

Figure 10 shows the resulting Raman voltammogram for the 1044 cm^{-1} vibration of $[\text{Ru}(\text{bpy})_3]^{2+}$. The increase of the Raman signal in the cathodic scan can correlate with the reduction of the Au^+ surface-forming Au. In addition, the vibration of Au-Cl at 348 cm^{-1} [16] is shown: The intensity increases as soon as the Au surface is oxidised forming Au^+Cl^- .

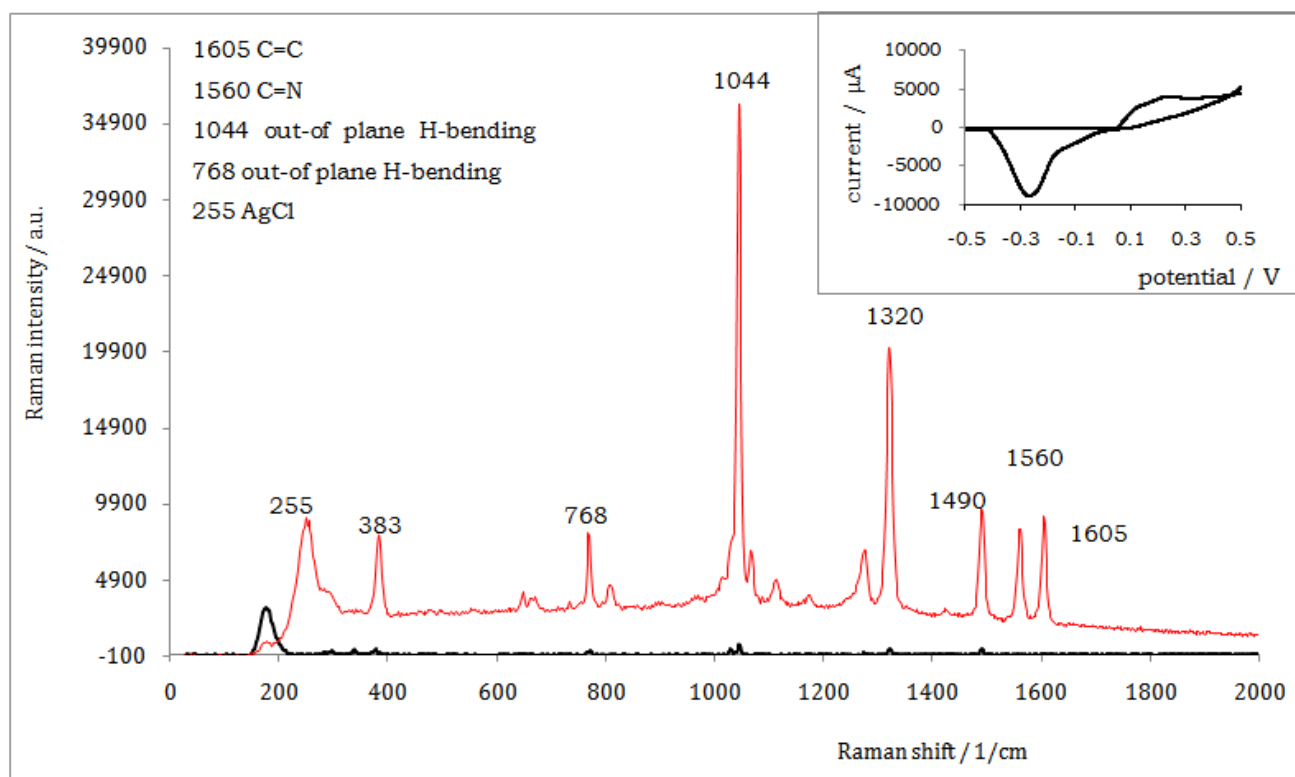


Figure 8. Raman spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ on a silver electrode before (black line) and after electrochemical activation (red line)

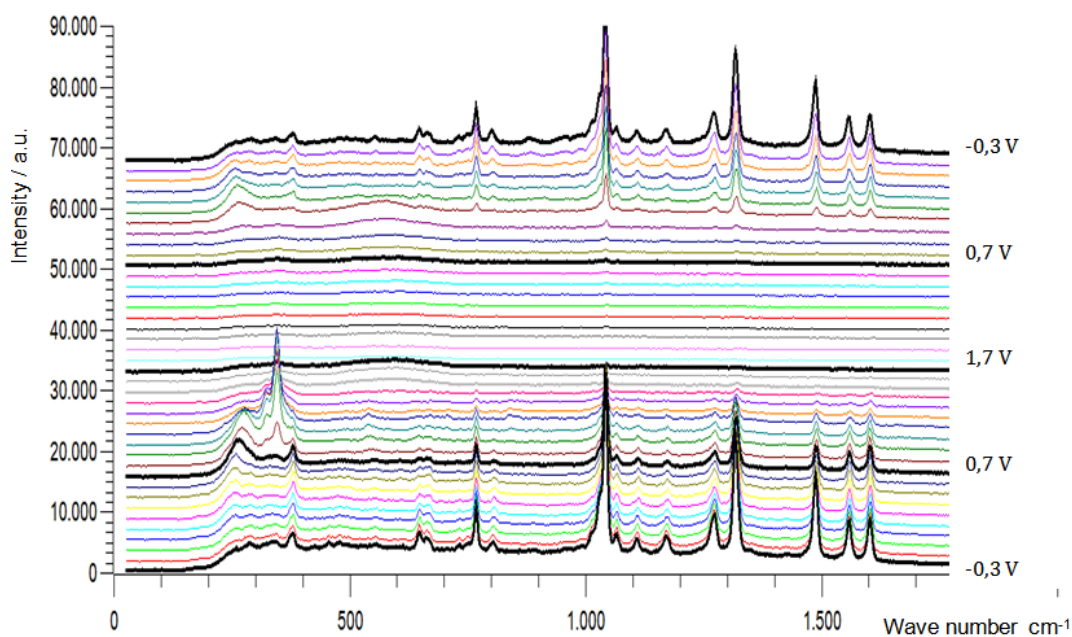


Figure 9. Raman spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ on an Au-Bt-SPE at different potentials

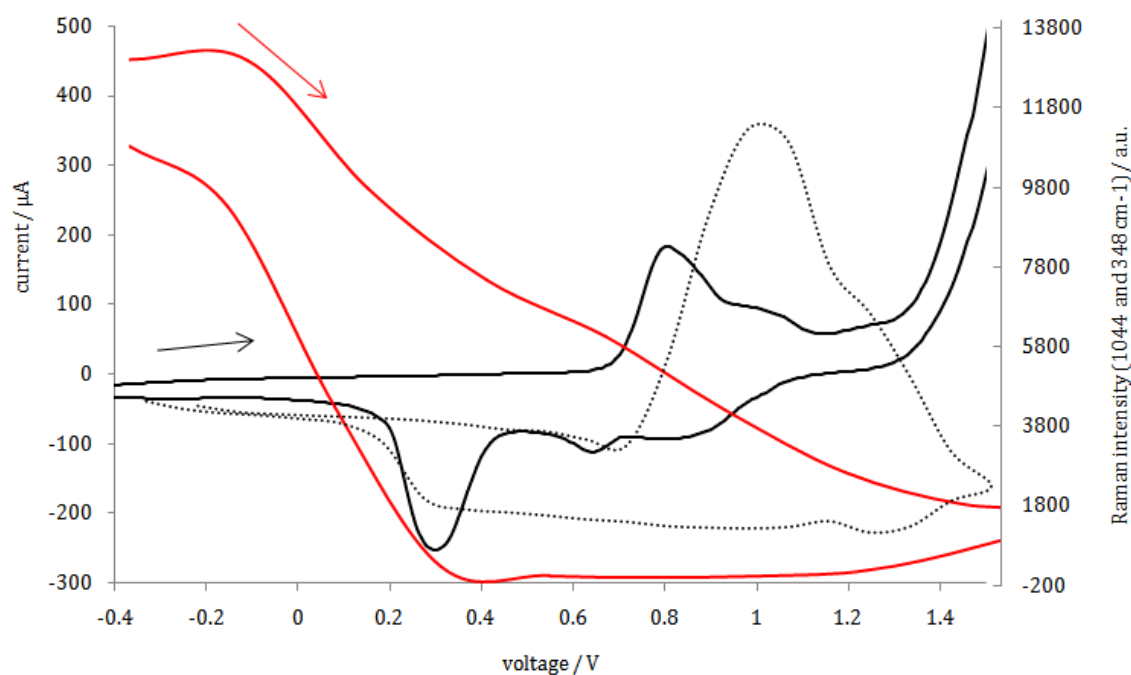


Figure 10. Ramanvoltammogram of the 1044 cm^{-1} vibration of $[\text{Ru}(\text{bpy})_3]^{2+}$ (red line) and 348 cm^{-1} vibration of $[\text{Au}^+\text{Cl}^-]$ (black dotted line) on an Au-Bt-SPE. Black solid line: CV

In conclusion, the in situ electrochemical preparation of gold and silver electrodes results in an enhancement of cathodic ECL and Raman intensities. Further analyses need to be carried out to establish whether chloride is responsible for “roughening” the silver electrode surface when using the salts of other conduction anions.

Supporting Information

In the Supporting Information the reader may find detailed experimental information. In addition, the theory of cyclic voltammetry and electrochemical impedance spectroscopy is explained.

Acknowledgments

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Supporting Information

Cyclic Voltammetry

A CV is obtained by measuring the current between the working and the counter electrode as a function of the potential (normalized to the potential of the reference electrode). To do this, the experimenter uses a three-electrode setup and varies the potential of an electrode (the "working" electrode), which is immersed in an unstirred solution, and measures the resulting current.

A triangular potential sweeps the potential of the working electrode between the starting potential to the switching potential and back again. The scan rate v (in mV/s) is an important parameter, as will be shown below.

The current flows in or out of the working electrode to or from a counter electrode. The potential of the working electrode is controlled versus a reference electrode, e.g., a saturated calomel or a silver/silver chloride electrode. The reference electrode passes no current.

All these requirements can be fulfilled by a potentiostat.

Here are the main points to consider when starting out with CV:

- According to the IUPAC recommendation anodic peaks point upward, cathodic downward.
- The standard redox potential E_0 can be calculated

$$E_0 = \frac{1}{2}\{E_p(\text{cathodic}) + E_p(\text{anodic})\}$$

where E_p are the peak potentials.

- If the current peaks appear to be sliding apart as a function of scan rate, the process is quasi-reversible (or, in an extreme case, irreversible).

Two qualities, parameterized by the standard electron rate constant k_0 and the mass transport to or from the working electrode $m_{\text{transport}}$, determine the CV.

- If $k_0 \gg m_{\text{trans}}$ then the electrode process is reversible and diffusion controlled.
- In the intermediate, the so-called quasi-reversible case, diffusion and electron transfer are in the same order ($k_0 \approx m_{\text{trans}}$).
- The process will be rate-determined if the mass transport is faster than the electron transfer ($k_0 < m_{\text{trans}}$) and the electron transfer is irreversible.

There are three other clues that a cyclic voltammogram provides that indicate that the observed process is reversible.

The first is that the peak currents I_p for the forward and reverse reactions are the same,

$$I_p(\text{red}) / I_p(\text{ox}) = 1$$

The second is that the peak current is proportional to the square root of the scan rate: Reversible processes show a $v^{1/2}$ -dependence of their current peaks according to the Randles-Sevcik equation:

$$I_p = 0.4463nFAC\{FDv/(RT)\}^{1/2}$$

Third, the difference between the electrode potentials at which reduction and oxidation occur is constant at all scan rates: If the positions of the maximum current peaks with regard to their potential do not change as a function of the scan rate, and the heights of the anodic and cathodic peaks appear to be equal, then the process occurring is reversible. If the peaks are about 59 mV apart then the process is a reversible one-electron transfer ($n = 1$):

$$DE_p = E_p(\text{anodic}) - E_p(\text{cathodic}) = 0.059/n$$

With this eq. the experimenter can calculate the number of transferred electrons n .

In the quasi-reversible and the (electrochemical) irreversible case one can see that the current peaks are drifting apart with increasing scan rate up to hundreds of millivolts. Now the kinetic process, i.e. the electron transfer, is determining the electrochemical behavior.

In cyclic voltammetry the scan rate is a means that provides the experimenter with a tool to control the electrochemical process either by electron transfer process or by mass transport: By varying the scan rate we vary the diffusion layer thickness: at slow scan rates, the diffusion layer is thick, while at faster scan rates the diffusion layer is thinner. Since the electrochemical process reflects the competition between the electrode reaction and the diffusion, faster scan rates will favor electrochemical irreversibility (controlled by the electron transfer rate) and the peak potentials will drift apart.

STAT-ECL

The ECL method has the advantage of being sensitive, and the SPE used are cheap (€1-3 each), but the cost of $[\text{Ru}(\text{bpy})_3]^{2+}$ is a disadvantage. With a commercial ECL system the measurements are very fast, the sensitivity is high, but the high price of the device (STAT-ECL) can be off-putting (€10,000: Metrohm/DropSens).

This device can measure different electrochemical procedures such as linear-sweep voltammetry, cyclic voltammetry, and square wave voltammetry, and can simultaneously detect the resulting chemiluminescence signal.

STAT-ECL is a portable potentiostat combined with a specific Electrochemiluminescence (ECL) cell that performs electrogenerated chemiluminescence studies with SPEs. A potentiostat and a Si-Photodiode integrated in the ECL cell (spectral response: 340 – 1100 nm) are combined.

All electrochemical features inclusive the amplification factor of the light intensity can be programmed with the DropView 8400 software from Metrohm/DropSens.

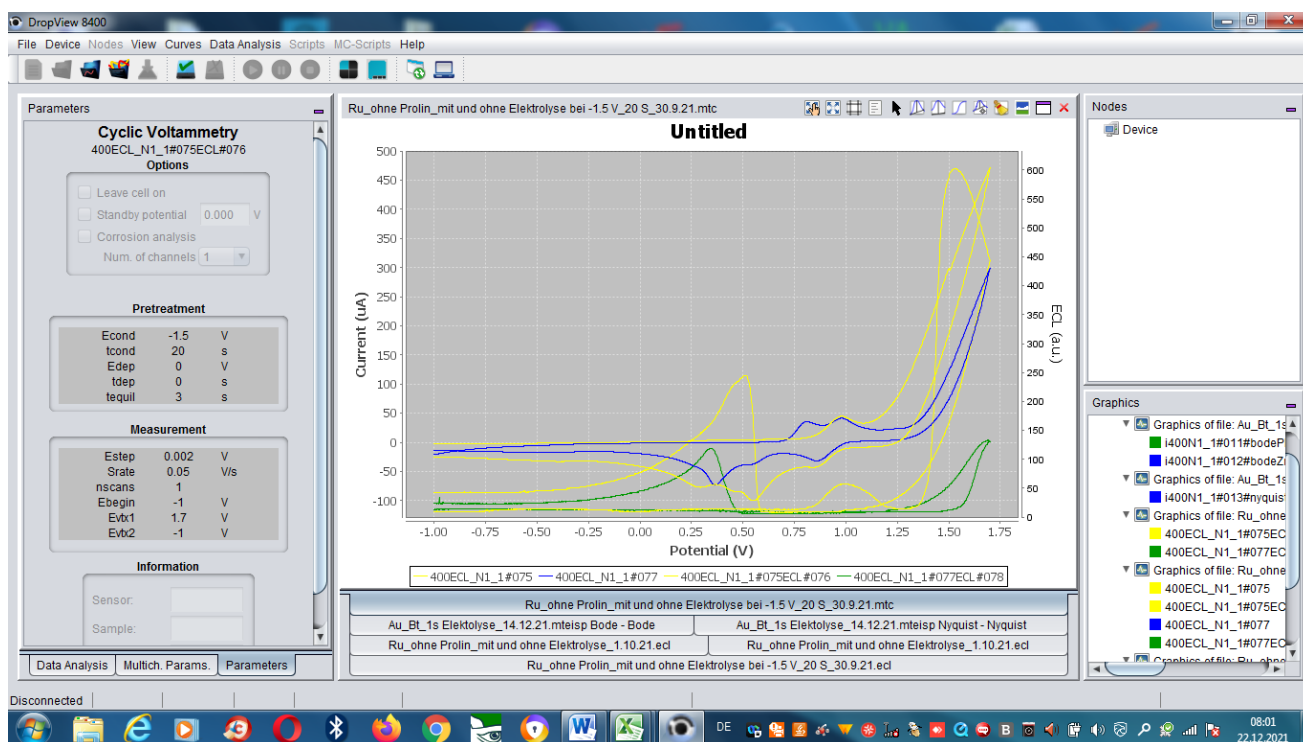


Figure S1. User interface

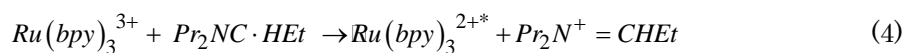
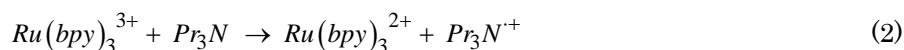


Figure S2. Potentiostat with ECL cell

Reaction Scheme of ECL

In the $[Ru(bpy)_3]^{2+}$ system the ECL-reaction can be expressed in the following way, here with tripropylamine (Pr_3N) as a coreactant:

Scheme: Reaction mechanism ECL



(Pr: propyl, Et: ethyl, hv: energy of the emitted light).

Reaction (1) may be an electrode process or a direct oxidation with an oxidizing agent.

In contrast to the above scheme, there may be a direct oxidation of Pr_3N (sometimes as a competition process).

$Ru(bpy)_3^{2+}$ reacts with the $Pr_2NC \cdot HEt$ radical to form $Ru(bpy)_3^{2+*}$, a species in an excited state that undergoes radiative decay. In addition, Eq. (3) shows that the forming of $Ru(bpy)_3^{2+*}$ with the subsequent emission of light is pH-dependent.

Electrochemical Impedance Spectroscopy (EIS)

Along with other electrochemical measurements such as cyclic voltammetry (CV), square wave voltammetry (SWV) or chronoamperometry (CA), electrochemical impedance spectroscopy (EIS) plays an important role in measuring the characteristics of electrode in electrolyte solutions.

If a potential is applied to an electrode-electrolyte interface, a flow of charge and matter occurs. Without going into details, in EIS the impedance (the resistance of the AC circuit) of the electrochemical system is measured as a function of

the applied frequency. The processes at the electrode, immersed in the solution, can be described with different electrical compounds as resistors (solution resistor, R_s ; charge transfer or polarization resistor, R_p), capacitor (Helmholtz double layer in front of the electrode, C_{dl}), and coil (inductance resulting from the current, which induces an electromotive force that opposes a change in current, L). One of the main purposes of EIS is to describe an electrochemical system through a combination of these passive electric compounds. In contrast to the ohmic resistor, capacitors and coils have a frequency-dependent resistance, which is inversely proportional to the frequency of the first and proportional to the frequency of the latter.

The impedance, Z , is represented as the complex number

$$Z(\omega) = E / I = Z_0 * \exp(j\omega t) = Z_0[\cos(\omega t) + j\sin(\omega t)] = \text{Re}(Z) + j\text{Im}(Z).$$

Re: real part and Im: imaginary part of the impedance.

Therefore

$$\text{Re}(Z) = Z' = Z_0 \cos(\omega t) \text{ and } \text{Im}(Z) = Z'' = Z_0 \sin(\omega t).$$

The modulus of Z is

$$|Z| = \sqrt{(Z')^2 + (Z'')^2}$$

In electrochemistry, a Randles circuit is one of the simplest electrical circuits to describe an electrochemical system. It consists of an electrolyte resistance, R_s , in series with the parallel combination of the double-layer capacitance, C_{dl} , and an impedance of a faradaic (i.e., electron-transfer) reaction, R_p . Sometimes a constant phase element CPE is used instead of an imperfect capacitor, which is in series to R_s or to R_p . The Warburg impedance (Z_W) describes the diffusion. In real electrochemical systems, EIS is more complicated and the Randles circuit may not give appropriate results.

The Nyquist-plot in the following figure is measured with the μ STAT I 400 from Metrohm/DropSens.

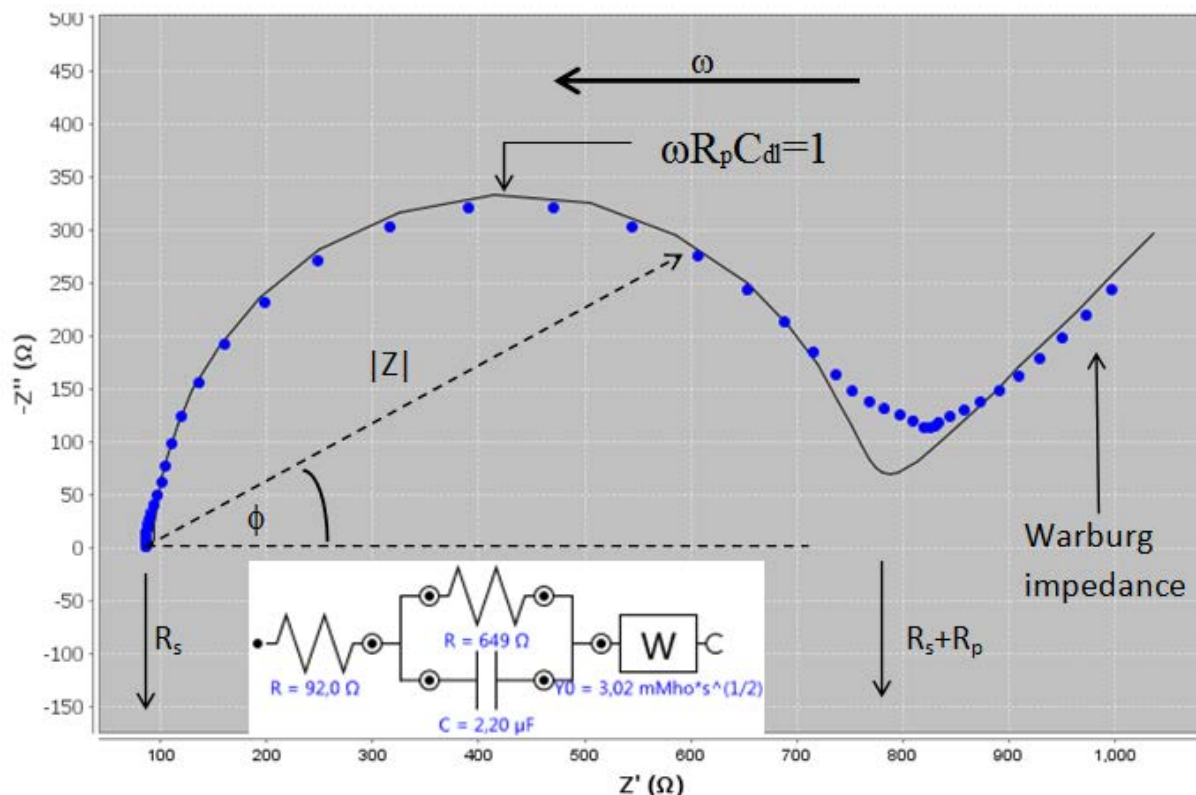


Figure S3. Nyquist diagram (measuring points and fitted curve) with Randles circuit

Figure shows a Nyquist-plot Nyquist diagram. Points: measuring points; solid line: fit with Randles circuit ($R_s = 92 \Omega$, $R_p = 649 \Omega$, $C_{dl} = 2.2 \mu F$, $Y_0(\text{Warburg}) = 3.02 \text{ mSohm}^{-1/2}$), see insert. Note: “Mho” is Ohm written backwards. Y_0 is the admittance (reciprocal of the impedance) multiplied by $\text{sqr}(\omega)$.

Raman Spectrometer

The AvaRaman spectrometer from Avantes is combined with 785 nm laser. The spectrometer is appropriately configured according to the wavelength of the laser.

The AvaRaman system is equipped with a cooling system. Cooling the detector down to -35°C cooling versus ambient, reduces the noise by a factor 2-3, enabling the usage of longer integration times to enhance the detection of small signals. The AvaRaman system used is delivered with the AvaSoft-Raman software.

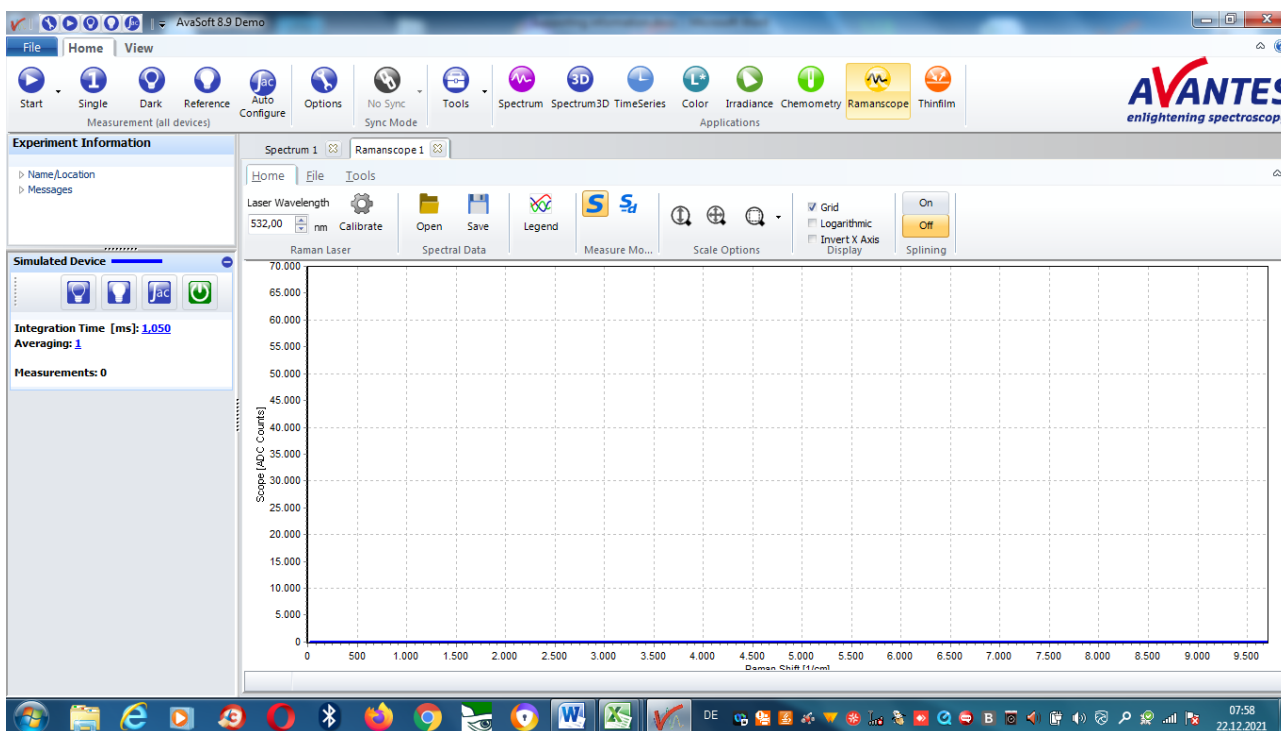


Figure S4. User interface of AvaRaman

Raman Probe

The Raman probe consists of a focusing probe with a $200\ \mu\text{m}$ excitation fiber and $400\ \mu\text{m}$ read fiber (all 1.5 m), focal length 7.5 mm. A manual shutter is included. Figure S5 shows the excitation and read fiber.

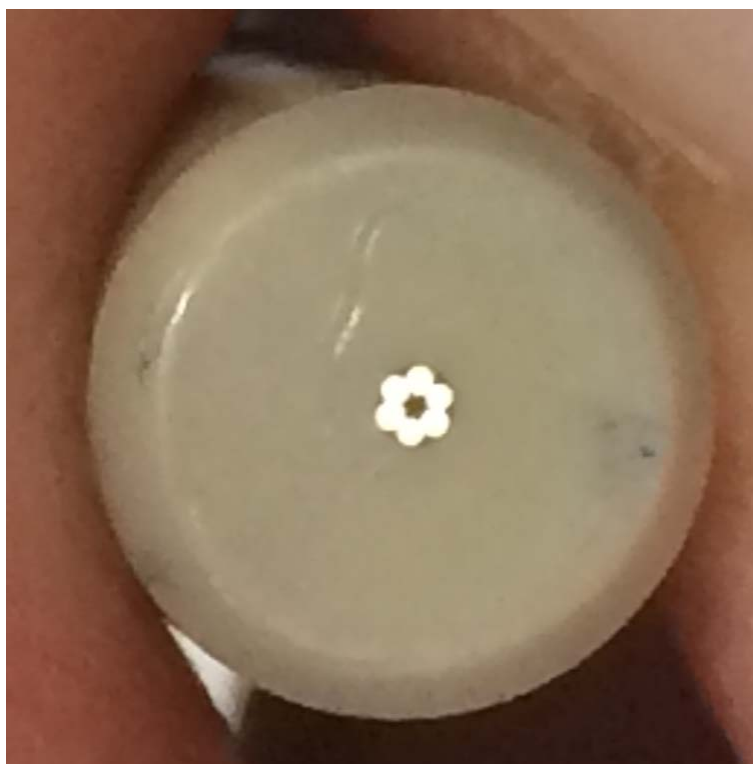


Figure S5. Bifurcated excitation – read fiber. Middle: read fiber, surrounded by six excitation fibers (illuminated)

Raman Cell



Figure S6. Raman cell from Metrohm/DropSens

Figure shows the used Raman cell for SPE (Metrohm/DropSens)

Synchronizing and Data Handling: Ramanvoltammogram

By means of the following figure students are able to connect the different parts of the experiment. In detail, they connect the potentiostat with the three electrodes in the ECL- or Raman cell via a special cable (Metrohm/DropSens).

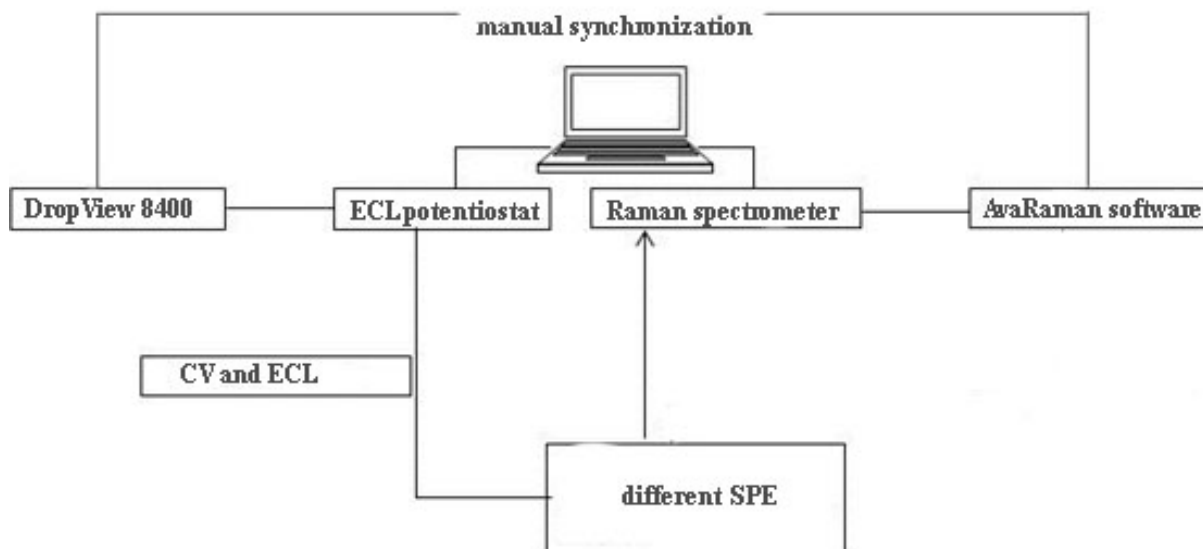


Figure S7. Scheme of the Ramanvoltammogram

The following Figure S8 shows the user interface of the measuring programs (DropView and Ava Raman). After starting the DropView program, students have to set the scan rate, the start-, reverse- and end potential of the CV and the amplification factor of the ECL intensity. The Raman spectrometer software proposes integration time and averaging number of the spectra. With these proposed values no saturation is measured.

The Raman mode is set by the Raman button. Every new integration-time needs a new dark zero adjustment. After clicking the button the Raman intensity becomes zero.

After fixing the values of the cyclic voltammogram (scan rate and scan range, i.e. start, reversal and end values), the potentiostat can be started. After sending the set values to the potentiostat the software sends an equilibration command for about 3 seconds, and the potentiostat begins to run. Immediately, the spectrometer must be started manually.

The CV and spectrometer data must be synchronized. This means that if the potentiostat takes 200 current / voltage couples (+0.5 V \rightarrow -0.5 V \rightarrow +0.5V, scan rate 0.01 V/s) the spectrometer also must record 200 spectra – one per second. The spectrometer used has two options: single and continuous measurement. Here the last must be activated.

After the end of a measurement cycle, all data can be transferred into Excel and displayed separately: voltage against current and Raman intensity against wavenumber. One can separate those Raman data at a given wavenumber that show a maximum change as a function of the applied voltage. Another option may be plotting the whole spectrum against fixed voltages (i.e. the voltage where no reduction or oxidation occurs and the voltage of a current peak). Therefore, one can easily show the difference between the Raman spectra with and without an electrochemical reaction.

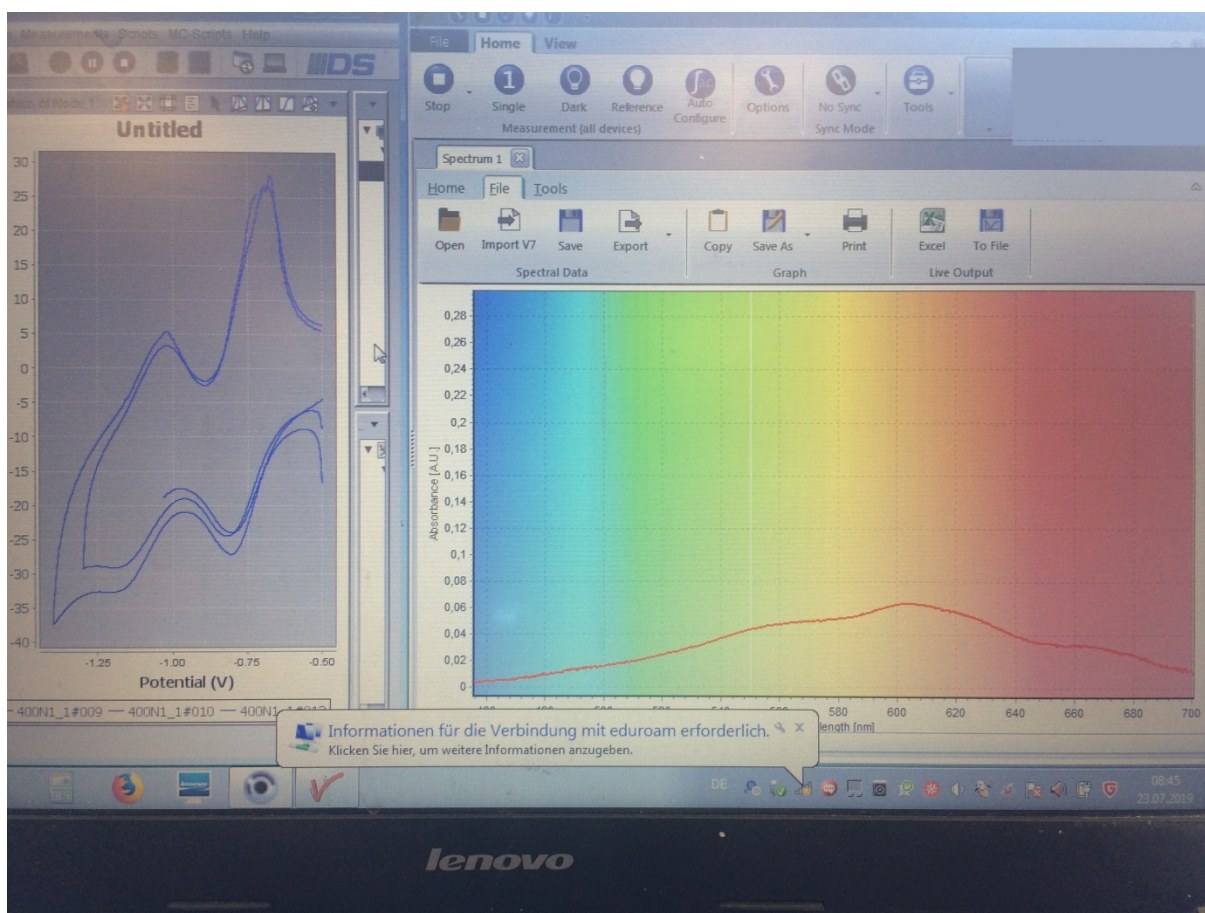


Figure S8. The measuring programs used. Left: Cyclic voltammogram, right: Raman



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