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# Electrochemical surface oxidation enhanced Raman scattering

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ABSTRACT

In this work, an unexpected enhancement of the Raman signal for uric acid during the electrochemical oxidation of a silver electrode is presented. This behavior cannot be easily explained using classical models of Surface Enhanced Raman Scattering (SERS). Time resolved Raman spectroelectrochemistry is used to study this interesting process strongly dependent on the experimental conditions. The new phenomenon was observed in different molecules and was found to be reproducible and robust, allowing us to use this methodology for the determination of citric acid. The enhancement of the Raman signal only takes place when a potential is applied to the electrode and therefore, this new phenomenon can be denoted as Electrochemical Surface Oxidation Enhanced Raman Scattering (EC-SOERS). In this work, EC-SOERS is presented not only as an alternative to SERS for detection of molecules but also as a reproducible process that can be used for quantitative analysis.

## 1. Introduction

Silver roughened electrode [1] is one of the most used substrates in Surface Enhanced Raman Scattering (SERS), due to its plasmonic properties [2,3] and the ease of preparation. The roughening process is widely known in literature and implies the surface oxidation (Ag dissolution) and the subsequent $Ag^+$ reduction on the electrode. During this process, formation of Ag nanoparticles (NPs) [4–6], responsible for the SERS electromagnetic effect, takes place. This deposition yields a much higher area and a nanostructured roughened surface, which modifies its optical properties, and ultimately, modulate the SERS behavior [7]. A number of works propose different ways to generate roughened silver substrates, from using cyclic voltammetry (CV) to applying a step potential program [8,9]. Most of the cases include the presence of chloride ($Cl^-$) or other halide, which allows getting higher silver dissolution and promoting the nanostructuration after the reduction stage [8,9]. Despite this process has been widely characterized in literature [10,11], its dynamic evolution in presence of a Raman probe molecule has been scarcely studied.

SERS has been widely used for analysis, not only by using Raman spectroscopic signal but also by combining this one with electrochemistry to quantify different analytes at a controlled potential [12,13]. In the present work, time-resolved Raman spectroelectrochemistry [14–17] (TR-Raman SEC) is used to follow the roughening process of silver with a Raman probe molecule in the electrolytic solution, being possible to detect transient processes [18–20]. Thus, SERS SEC system allows both, the electrochemical investigation and also the simultaneous SERS data, and therefore presents wide applicability in target molecules analysis with low limit of detection. Interestingly, when using uric acid (UA) as a probe molecule, it was found a special and unexpected enhancement of the Raman signal at the electrochemical oxidation stage of a silver substrate. Thus, an equivalent process to SERS is observed, that can be denoted as Surface Oxidation Enhanced Raman Scattering (SOERS). Unlike classical SERS, this effect was only observed during the electrochemical oxidation of the silver electrode surface. Therefore, it should be denoted as Electrochemical-SOERS (EC-SOERS). This effect was potential dependent and exclusively observed for particular experimental conditions. To the best of our knowledge, this is the first time that such behavior is reported in the literature. This result, in principle, does not match any classical SERS result reported in bibliography, which suggests the loss of the Raman signal during silver oxidation [21–23].

In order to illustrate the usefulness of EC-SOERS for analysis, citric acid was selected as target analyte. This compound is used extensively in the manufacturing of carbonated beverages, fruit and

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vegetable drinks, cheeses and other dairy products. It is also a natural component of many fruits and vegetables, and also an important component of certain corporal fluids [24–26]. One of the main advantages of using TR-Raman SEC as analytical technique is the intrinsic trilinear character of the responses obtained by SEC that can be used for multi-way data [27]. Thus, using PARAFAC as a chemometric tool, Raman SEC data could provide information about both the concentration of a test sample and the evolution of the spectra during a voltammetric experiment.

This work is a first approach to this interesting enhancement of the Raman signal during the oxidation of a silver electrode that, as is demonstrated, can be used for analytical purposes.

## 2. Experimental

### 2.1. Reagents and materials

Perchloric acid ($HClO_4$, 60%, reagent, Sigma-Aldrich), uric acid (UA, 99+%, reagent, ACROS Organics), potassium chloride (KCl, 99+%, reagent, ACROS Organics), pyridine (Py, 99.5%, analysis, Merck), benzoic acid (BzA, 99.5%, PA, Panreac) and potassium cyanide (KCN, 99%, PRS, Panreac) were used. All solutions were prepared using ultrapure water obtained from a Millipore DirectQ purification system provided by Millipore (18.2 MΩ cm resistivity at 25 °C).

### 2.2. Instrumentation

*Raman spectroelectrochemistry. In situ* time-resolved Raman spectroelectrochemistry (TR-Raman-SEC) was performed by using a SPELEC RAMAN instrument (DropSens), which integrates a laser source of 785 nm. Laser Power in all experiments was 80 mW (254 W $cm^{-2}$). This instrument was connected to a bifurcated reflection probe (DRP-RAMANPROBE, Dropsens). Two Raman spectroelectrochemical cells were employed: a commercial cell for screen-printed electrodes (DRP-RAMANCELL, Dropsens) [12], and a home-made cell to carry out those experiments using a customized silver disk electrode. DropView SPELEC software (Dropsens) was used to control the instrument, which allows getting real-time and synchronized spectroelectrochemical data.

A home-made customized silver disk electrode was used as a working electrode. This consisted in a silver disk inserted in Teflon. In this experimental set-up, a home-made Ag/AgCl electrode and a platinum wire were used as reference and counter electrodes, respectively. Screen-printed silver electrodes (DRP-C013, DropSens) were also used for some experiments. These devices consist of a flat ceramic card on which a three-electrode system comprising the electrochemical cell is screen-printed. The working silver electrode is circular with a diameter of 1.6 mm, the auxiliary electrode is made of carbon and a silver paint acts as a pseudoreference.

*UV–vis spectroscopy.* UV–vis absorption experiments were carried out using an UV–vis spectrophotometer Cary 50 Conc (Viarian). Solutions were sampled using a standard quartz cuvette 10 × 10 mm.

*SEM microscopy.* A JEOL 6610LV scanning electron microscope (SEM) was used to characterize the working silver electrodes at various stages of the electrochemical activation. Images were recorded with the secondary electron detector and using an accelerated voltage of 20 kV.

*Electrochemical impedance spectroscopy (EIS).* An Autolab PGSTAT 302N potentiostat equipped with a FRA module of impedance was used to carry out the EIS experiments. Differential capacitances were obtained by measuring the real (Z′) and imaginary (Z″) components of the impedance at 20 constant frequencies ranging from 0.1 Hz to 1000 Hz, with the potential being stepped in a sequence of 0.025 V and 0.05 V, from +0.10 V to −0.55 V vs Ag/AgCl.

## 3. Results and discussion

### 3.1. Electrochemical Surface Oxidation Enhanced Raman Scattering (EC-SOERS)

In an attempt to obtain suitable information about the appearance of an EC-SOERS signal during the electrochemical oxidation of a silver substrate, UA Raman response was evaluated in acidic media, using TR-Raman SEC. To achieve this, a linear sweep voltammetry (LSV) along a proper potential window was applied, recording simultaneously the Raman response with a high time-resolution. Fig. 1 presents the Raman spectra for UA 0.2 mM recorded during a LSV experiment and the evolution of the Raman intensity at 641 $cm^{-1}$ as a function of the applied potential for two different electrolytic media ($HClO_4$ 0.1 M and $HClO_4$ 0.1 M + KCl $5\cdot10^{-3}$ M), scanning the potential from +0.1 V to +0.55 V. For simplicity in the terminology, this plot will be called voltaRamangram because it represents the evolution of the Raman intensity at a specific Raman shift as a function of the applied potential in a voltammetric experiment.

As can be observed in Fig. 1a, when the LSV is carried out in $HClO_4$ 0.1 M ($HClO_4$), there is no appreciable peaks in the Raman spectrum corresponding to UA in the whole potential window, fact corroborated in the voltaRamangram at 641 $cm^{-1}$ for UA in this media (blue curve in Fig. 1d). However, when some small amount of $Cl^-$ is added ($5\cdot10^{-3}$ M), unexpectedly, significant unusual Raman signal were observed (Fig. 1b) corresponding unmistakably to uric acid spectrum [28,29].

Fig. 1b shows the Raman spectra for UA 0.2 mM + $HClO_4$ 0.1 M + KCl $5\cdot10^{-3}$ M ($HClO_4$/KCl) recorded at different potentials during the LSV (Table S1 shows the band assignments, and Fig. S1 shows a comparison of UA Raman spectra under different experimental conditions). Interestingly, the enhancement of the Raman signal appeared at the oxidation stage of the silver roughening process (red curve in Fig. 1d), which does not match any previous SERS results during a spectroelectrochemical experiment. A closer look at Fig. 1d shows an increment of the Raman intensity above +0.20 V in the anodic direction, reaching a maximum around +0.50 V. Finally, red curve in Fig. 1c reveals that the increment of Raman signal is closely related with the LSV which support that oxidation products should be responsible for such singular effect.

More interesting results were obtained by recording the Raman spectra during a chronoamperometry (CA). Fig. 2 displays two SEC experiments at fixed potentials, collecting both Raman spectra and transient current responses simultaneously. In a first experiment, the potential was kept at +0.40 V for 60 s. In a second experiment, a potential of +0.40 V was applied for 30 s, time at which the electrode was left at open circuit potential (OCP) and the Raman spectra were recorded for other 30 s (Fig. 2b).

The Raman intensity for UA at 641 $cm^{-1}$ as a function of time (chronoRamangram) for the two experiments is represented in Fig. 2. As can be observed, the application of +0.40 V provoked the increment of the Raman intensity during the whole experiment. These CA experiments corroborate the responses observed in Fig. 1d, the anodic polarization (oxidation) of the electrode yields the increment of the UA Raman signal in these electrolytic conditions, in contrast to the typical SERS response that usually is observed at cathodic potentials [9,28–30]. It is noteworthy that Raman signal is lost at OCP (Fig. 2b), indicating that the phenomenon is potential dependent.

Different experiments using commercial silver screen printed