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# Use of polarization-dependent SERS from scratched gold films to monitor the electrochemically-driven desorption and readsorption of cysteine

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ABSTRACT

The electrochemically-driven desorption and readsorption of cysteine, on scratched gold surfaces placed in a highly concentrated cysteine solution, was investigated. The ordinary Raman signal from cysteine in solution was significant relative to the SERS signal from adsorbed cysteine. However, the SERS signal was isolated from the ordinary Raman background by subtracting the signal obtained with the incident laser light polarized along the scratch (ordinary Raman) from the signal obtained with it polarized across the scratch (ordinary Raman + SERS). The method described here is applicable to other electrochemical systems where signal from solution-phase species can interfere with, or even overwhelm, signal from the adsorbate. For example, it may be used in SERS studies of water or ionic liquid structure in the double-layer region.

## 1. Introduction

Raman scattering is the inelastic collision of a photon with a molecule [1]. The intensity of Raman-scattered light is commonly enhanced by five or six orders of magnitude when the molecule is adsorbed on a nanostructured, free-electron metal [2]. This effect is known as surface-enhanced Raman scattering (SERS) [2]. It results from the concentration of electric field in certain regions at the surface of the nanostructured metal ("hot-spots") by surface plasmon (SP) activity [3,4].

When a SERS experiment is conducted in an electrochemical cell (i.e., when SERS occurs from an electrode placed in contact with an aqueous solution of electrolyte), the intensity of SERS from an adsorbate is generally orders of magnitude larger than the intensity of ordinary Raman scattering from species dissolved in the electrolyte solution.

Yet there are situations where solution-phase species (analyte, solvent or contaminant) produce a background that will interfere with, or even overwhelm, SERS from the adsorbate. One example lies in experiments directed toward understanding water structure at the interface between electrodes and solutions. SERS is well suited for this purpose, as surface-enhancement yields a disproportionately strong signal from the double-layer region compared to that obtained from the bulk solution. However, the number of bulk water molecules probed is much larger than the number of adsorbed water molecules probed because the pathlength through which laser light travels is much greater for the bulk. This difference in the number of water molecules is larger than the gain in Raman signal from the surface-enhancement effect; hence, bulk water constitutes a serious interference.

One method of eliminating signal from the bulk is to record the (ordinary Raman) spectrum at a reference applied potential where SERS is minimized, then subtract it from a signal that contains a SERS component from the double-layer region and an ordinary Raman component from the bulk. This method was used by Tian and coworkers in, for example, Refs. [5,6]. The (ordinary Raman) background signal is acquired at potentials where the species under investigation by SERS is desorbed.

Polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) is a technique which may also be used to eliminate signal from the bulk in spectroelectrochemical experiments. It has been employed by Lipkowski and coworkers to study the structure of lipid bilayers on electrode surfaces [7,8]. During data processing, *s*-polarized reflectivity is subtracted from *p*-polarized reflectivity, and this difference is divided by the sum of the two [9]. Baseline correction of the spectrum obtained from the covered surface may then be carried out using the spectrum of the uncovered surface [9]. Only anisotropic signals survive the subtraction, thus background signal from free-floating molecules, which possess a random orientation, is eliminated.

Recently, we have introduced a new SERS-based method of background-signal elimination that takes advantage of the anisotropy associated with linear scratches on gold surfaces [10]. It is

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based on the idea that SERS may be turned on-and-off by polarizing light across-and-along the linear nanostructures that comprise the scratch. Our background elimination technique is similar, in its implementation, to the one employed by the Tian group in Refs. [5,6]: an ordinary Raman background signal is again subtracted from a signal that contains a SERS component and an ordinary Raman background component. Instead of using an applied potential to turn SERS on-and-off, however, we use a polarization effect to accomplish the on-and-off switching as is done in PM-IRRAS. A detailed description of our technique is given in Section 3 below.

In Section 4 we report application of our technique in a study of the potential-dependent adsorption characteristics of cysteine on scratched gold surfaces placed in a concentrated solution that provides significant spectral interference. It was possible to extract information about the adsorption characteristics of the molecule from the SERS component of the scattered light, in spite of a strong ordinary Raman component from solution-phase cysteine, using our background-signal elimination method.

## 2. Experimental section

Glass slides, plated with a 5 nm chromium adhesion layer and then a 100 nm thick layer of gold, were purchased from Evaporated Metal Films (EMF). Scratches were made in the gold by running a 10 μm metallic tip along the surface. AFM has been used to characterize the morphology of scratches made in this way: images and line-scan topographical data have been published elsewhere [11,12].

A scratched gold slide was placed at the bottom of a custom-made Teflon spectroelectrochemical cell. The cell was then filled with an aqueous solution 0.9 M in DL-cysteine (97% pure from Aldrich), 0.2 M in $NaClO_4$ and 0.5 M in NaOH. Water used as the solvent for this solution was acquired ultra-pure (18.2 MΩ cm) from a Barnstead NANOpure Diamond purification system. The pH of the final cysteine + $NaClO_4$ + NaOH solution was measured to be 8.47.

The scratched gold film acted as our working electrode and a circular platinum wire acted as our counter electrode. We used another platinum wire as a pseudo-reference electrode; however, potentials were later corrected to their saturated calomel electrode (SCE) reference equivalents. All potentials reported in this work are relative to an SCE. Potentials were applied to the electrochemical system using a Hokuto Denko Limited potentiostat/galvanostat, model HAB-151. Cyclic voltammograms obtained for a similar system, but with a much lower concentration of cysteine in solution, have been published elsewhere [13].

An Olympus BHT optical microscope was used to focus laser light through the cysteine solution and onto the scratched gold surface, then to collect backscattered light. Linearly-polarized laser light with a wavelength of 632.8 nm was provided by a 35 mW He–Ne laser from Melles Griot. A ½-wave plate was placed between the light source and the microscope's optical inlet; it allowed us to rotate the polarization of the incident beam relative to the direction of the scratch. This rotation was calibrated at the position of the sample. An Olympus MS Plan 50× ultra-long working distance (ULWD) microscope objective, with a numerical aperture of 0.55, focused the incident beam through the cysteine solution and onto the scratched gold slide. The laser spot diameter was set approximately equal to the width of a scratch: 10 μm. Backscattered light was collected by this same microscope objective, and directed out of the microscope. A Kaiser super-notch filter was placed between the microscope's optical outlet and the spectrometer; it removed most of the reflected and Rayleigh-scattered light. The remaining light, including Raman-scattered light, was separated according to wavelength by a Kaiser Holospec *f*/1.4 spectrograph and then detected by an Andor DV-401-BV CCD. A diagram of our spectroscopic setup has been published elsewhere [10].

Acquisition time used to obtain $S_\perp$, $S_{||}$, $I_\perp$ and $I_{||}$ for cysteine was 180 s; acquisition time used to obtain $I'_\perp$ and $I'_{||}$ for perchlorate was 150 s. The quantities $S_\perp$, $S_{||}$, $I_\perp$, $I_{||}$, $I'_\perp$ and $I'_{||}$ are defined in Section 3 below.

The 55 nm gold nanoparticles that were used in one of our control experiments (see Section 4) were prepared according to the method described in Section 2.1.1 of Ref. [14].

## 3. Background subtraction method

Unidirectional scratches in a gold film exhibit polarization-dependent SERS [10–12]. Oxazine 720, a laser dye with a large Raman cross-section, was applied to the substrate for use as a probe molecule in our previous work in this area. The SERS spectrum of this dye was stronger when acquired with the incident beam polarized across the scratch than it was when acquired with the incident beam polarized along the scratch, i.e., the perpendicular-geometry spectrum ($S_\perp$) was stronger than the parallel-geometry spectrum ($S_{||}$). This result is illustrated in Fig. 1 (as well as in Fig. 4 of Ref. [10]). It may be rationalized, simply, by noting that a rough nanostructured surface is necessary for SERS to occur by the electromagnetic mechanism [2,15]; and that the incident light encounters a rough surface when it is polarized across the scratch, but a smooth surface when it is polarized along the scratch.

Fig. 1 (and Fig. 4 in Ref. [10]) shows that peak intensities in the parallel-geometry spectrum are nonzero. There are two reasons for this. First, some features in the scratched area lie at an angle to the overall direction of the scratch. These may be regarded as defects in the structure, and they provide surface-roughness during parallel irradiation. Second, error in the alignment of the polarization of the incident beam, relative to scratch direction, yields a weak signal because some roughness is then present during (what is supposed to be) the parallel-geometry experiment.

The use of this polarization dependence to eliminate solution-phase interference signals from the SERS spectrum of an adsorbed analyte was then suggested [10]. The main concept is to subtract the parallel-geometry spectrum ($S_{||}$, which contains the ordinary Raman spectrum of solution-phase species) from the perpendicular-geometry spectrum ($S_\perp$, which contains both the ordinary

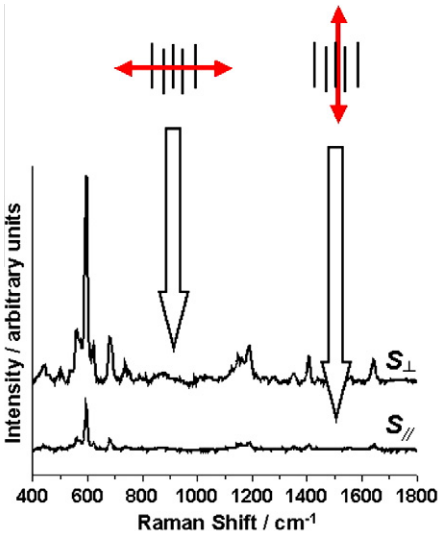

**Fig. 1.** The SERS spectrum obtained when incident light is polarized across a unidirectional scratch ($S_\perp$) is stronger than the one obtained when it is polarized along the scratch ($S_{||}$). The spectra shown are from oxazine 720, which was added to the surface for use as a probe molecule in our earlier experiments.