Surface Enhanced Infrared Characterization Using Disordered Slit-Antenna Arrays for the Detection of Electrodeposited Cytochrome C

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Received: 24 March 2021 / Accepted: 5 August 2021 / Published online: 28 August 2021
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Abstract
An approach which allows both electrochemical studies and surface enhanced infrared characterization of electrodeposited Cytochrome C is presented. This approach is based on in-plane disordered arrays of resonant slits engraved in Au substrates using focused ion beam. For light-polarized perpendicular to the slit, the reflectivity spectra of the slit arrays show dips related to the excitation of the slit plasmon resonance, whose position depends on the slit length. Due to the presence of the continuous Au layer around the slits, the very same substrates can be used to perform electrochemical studies. By varying the slit length, we have tuned the plasmon resonance to match the absorption bands of electrodeposited Cytochrome C, demonstrating the detection of minute amounts of this protein, all the way down to a single monolayer.

Keywords Slits · Plasmons · Electrochemical · SEIRA

Introduction
Relating protein function with conformational changes is of great interest in biology. In the case of redox proteins, involved in many essential processes in biology, the combination of electrochemical and spectroscopical measurements can provide this valuable information [1, 2]. Infrared spectroscopy is particularly interesting as it provides a non-destructive, label free, unambiguous identification of local structural protein rearrangements. However, IR cross section is low and a large amount of protein is required to provide a quantifiable and sometimes even detectable signal. Hartsein et al. [3] described that absorption of molecules on metal films can enhance the IR signal on a broad spectral range by nearly two orders of magnitude. This effect, called surface enhanced infrared absorption (SEIRA), strongly depends on the metal-film morphology. A considerable higher signal enhancement can be achieved by using micrometer long plasmonic rods, often referred to as nanoantennas, under resonance conditions [4–6]. In addition to improving the enhancement, these metallic nanoantennas produce sharp plasmonic resonances which can be used to select the spectral region of interest. On the other hand, it is also well known that so-called inverse nanostructures, consisting of slits fabricated in a continuous metallic film, also feature sharp, tunable resonances over the whole mid-IR spectral range. It was recently found that the measured average SEIRA signal of slits is higher compared to their inverse rod structures for the same vibrational layer, showing their advantages for SEIRA experiments over the better-known solid nanoantennas [7, 8]. Moreover, slits present yet another advantage with respect to rods which makes them best suited for the present work: the gold surface surrounding the slits remains conducting and allows combining SEIRA with electrochemical measurements, which is of great interest to study redox proteins [9, 10].

In this work, we present a system based on slit-antenna arrays fabricated by focused ion beam (FIB) out of a continuous Au layer deposited on CaF2 substrates and with in-plane disordered arrangement. Due to the presence of the continuous Au layer around the slits, the very same substrates can be used to perform electrochemical measurements. In addition, the use of FIB as the artificial structuration technique allows us to pre-design at will the size, shape, and in-plane...
arrangement of the antennas, providing therefore with a full control of their IR response. Specifically, we carry out a slit length and concentration dependence study to analyze the enhancement SEIRA capabilities of these slit-antenna arrays. We have first calibrated this system by the use of PMMA as a reference substance, to determine the sensitivity enhancement, and then we have tested these substrates by looking at the IR spectra of Cytochrome C electrochemically oriented on the gold continuous film. The slits were designed to amplify the signal corresponding to the absorption of the Amide I band characteristic of proteins. This soluble redox protein of the respiratory chain has been extensively studied electrochemically [11] and spectroscopically [2] and serves as a good bench mark to test the utility of these microstructured surfaces to study the infrared signal of a monolayer of an electrochemically active protein.

Methods and Materials

Slit Fabrication

Slits were fabricated using focused ion beam (FIB) etching from a continuous 75 nm Au film grown on CaF₂ (111) 1×1 cm² epi polished substrates with a 2-nm-thick Ti adhesion layer between Au and substrate. The thickness of the layers was determined by X−ray reflectometry. Au was grown by magnetron sputtering and Ti by electron beam evaporation at room temperature. A number of different patterns 200×200 μm² in size are fabricated in the central part of the sample, each of them with specific slit lengths and/or concentration. All patterns have an algorithm generated disordered arrangement to minimize order-induced diffraction effects and excitation of propagating plasmons. All slits are 300 nm wide.

Chemical Modification of the Slit-containing Au Film

All used chemicals and materials were purchased from commercial suppliers and employed with any further purification. 4 amino thiophenol (4−ATP), tioctic acid, and horse heart cytochrome C (Cyt C) were purchased from Sigma−Aldrich.

The 1×1 cm² gold-covered CaF₂ substrate containing the slits was immersed for 10 min in piranha solution (3:1 H₂SO₄:H₂O₂) and then thoroughly rinsed with distilled water before exposing to ultraviolet light in a Bioforce UV/Ozone cleaner (Nanoscience) for 30 min. Immediately after, the substrates were immersed in a 10 mM solution (1:1 ethanol:water) of tioctic acid and 4 amino thiophenol (4-ATP) (3:2 molar ratio) and were left overnight to allow for the formation of the mixed self-assembled monolayer (SAM) on the gold surface. The modified electrodes were then rinsed with ethanol to remove physically adsorbed thiols and then with 4 mM phosphate buffer saline (PBS) (pH 7.0) buffer. Cyt C binds to the mixed SAM on the gold film via electrostatic interactions. The chemically modified Au film containing the slits was used as the working electrode where electrochemical and IR measurements were performed.

Cytochrome C Adsorption

The slit-engraved Au modified film was incubated in 0.5 mg mL⁻¹ Cyt C in 4 mM PBS, pH 7.0. In order to adsorb Cyt C, this working electrode was cycled 20 times from −0.1 to +0.3 V vs. Ag/AgCl at a scan rate of 10 mV s⁻¹. After rinsing with 10 mM PBS, pH 7.0, the electrochemical behavior of the immobilized Cyt C was characterized by cyclic voltammetry in 10 mM PBS (pH 7.0) as previously reported Ji and Jin [12].

Electrochemical Measurements

Electrochemical measurements were carried with an Autolab PGTA730 potentiostat controlled by GPES 4.9 software (Eco Chemie, the Netherlands). Cyclic voltammetry was performed in a three electrodes glass cell at 25 °C. The SAM modified Au film containing the slits was employed as the working electrode while a Ag|AgCl (3 M NaCl, from Bioanalytical System Inc.) and a flamed annealed platinum wire were used as a reference and counter electrodes, respectively.

Atomic Force Microscopy Measurements

AFM measurements were done in contact mode in air in an Agilent 5500 using a soft tip from Olympus, OMCL−RC with a spring constant of 0.05 N/m.

FTIR Spectroscopy

The reflectivity spectra were obtained using an IR microscope (Bruker Hyperion) equipped with a liquid nitrogen−cooled MCT detector, polarizers and a reflecting 15×Schwarzchild objective. The microscope was coupled to a FTIR spectrometer (Bruker Vertex 70). Absorption spectra of Cyt C, 4 mM in D₂O solution, were obtained in an IR setup from Pike Instruments using a home-made dismountable transmission cell with two CaF₂ windows.

Results and Discussion

Characterization of the Slit-engraved Au Film

Figure 1 shows a sketch of the 1×1 cm² sample and AFM images of some representative patterns with different slit...
length and concentration. In order to minimize inter-slit interaction while maintaining a quality level of measured IR signal five of the patterns have a low slit concentration with the same number of slits, 1408, in the 200×200 μm² patterned area, which corresponds to a percentage of area covered by the slits of around 2.2% (Fig. 1a and b). Each of these patterns had a different slit length, namely 1.7, 1.9, 2.1, 2.3, and 2.5 μm. In addition, two more patterns are fabricated, with a 2.1-μm slit length and higher slit concentration. In particular, 2468 and 5403 slits in the patterned area, which corresponds to a percentage of area covered by the slits of 3.9% (Fig. 1c) and 8.1% (Fig. 1d), respectively.

The sample prepared shows a continuous and well adhered 72–nm–thick gold layer on top of the CaF₂ surface that allows using the substrate as a working electrode to perform systematic, repetitive, and reproducible electrochemical measurements.

**Electrochemical Adsorption of Cytochrome C**

Cyt C was adsorbed to the Au surface by immersing it in a solution containing 0.5 mg mL⁻¹ of the protein and subjecting the electrode to 20 electrochemical cycles from −0.1 to +0.3 V vs. Ag/AgCl [12].

Figure 2 shows the AFM images of the patterned surface after the Cytochrome was electrochemically deposited. Panel a shows that the height of the slits is 10 nm less than before protein deposition, indicating that a thin layer of protein might be deposited at the bottom of the slit. The AFM tip cannot access the surface of the slit walls, but the width of the slit is comparable to the one measured before protein deposition, indicating that, at most, a thin layer of protein is lining the walls and that the slit is mostly devoid of protein. The topography of the flat gold regions shown in panel 2b indicates that the surface is fully and homogeneously covered by the protein. The roughness of about 3 nm observed corresponds well with the diameter of the monomeric protein.

Figure 2c shows the cyclic voltamogram obtained after the protein oriented and adsorbed to the surface. The position of the peaks observed is the one expected for the oxidation and reduction of the protein occurring by direct electron transfer from the electrode surface. Measuring the area under the oxidation peak allows estimating the amount of electrons transferred during the process, which is associated to the amount of protein adsorbed. The quantitative analysis confirmed that it corresponds to approximately one monolayer of protein being present on the surface of the electrode.

**Infrared Reflectivity Characterization and Sensitivity Calibration of the Slit-engraved Au Film**

In Fig. 3a, we show a sketch of the used experimental setup. An IR microscope connected to the FTIR spectrometer allows measuring reflectivity spectra in the IR range of every
slit pattern without getting signal from the others. The slit is a plasmonic element which has resonant modes that can be excited with light-polarized either parallel or perpendicular to it, the perpendicular polarization mode appearing at longer wavelengths than the parallel one [13, 14]. As an example, in Fig. 3b, we present the reflectivity spectra for slit-engraved regions with different slit lengths, 2.2% slit concentration, and light-polarized perpendicular to the slit. As it can be seen, the spectra show a dip corresponding to the excitation of the plasmon resonance. The position of the dip depends on the slit length, shifting to lower energies as the slit length increases [15], a property exploited in the present work to tune the resonance to the spectral region of the Amide I band. On the other hand, for light-polarized parallel to the slit, no resonance is excited in any of the arrays in the considered spectral range, as it can be seen in the reflectivity spectrum of the 1.7-μm long slits, represented with a dashed line.

This work is oriented to the detection of a single monolayer of protein, a challenging amount for IR spectroscopies...
and from which no signal was detected in the unpatterned regions of the Au film. Therefore, before analyzing the effect of the Cytochrome adsorption on the resonant reflectivity spectra of the slits arrays, we have characterized the SEIRA enhancement capabilities of the arrays by studying a layer of PMMA deposited by spin coating on top of the Au film. PMMA is a very convenient material for this purpose, since it has an intense absorption band at 1730 \( \text{cm}^{-1} \), which falls within the spectral range considered here. For 30-nm-thick PMMA films, this absorption can be detected in the unpatterned regions of the Au film and can therefore be used to quantify the increase of the band signal due to the slit resonance. In Fig. 4, we present the slit length dependence of the reflectivity for the light polarization perpendicular to the long slit axis of the patterns with 2.2% slit concentration after PMMA deposition. The effect of depositing the PMMA layers is twofold, on the one hand there is a red shift of the slit resonance due to the change in the permittivity of the region surrounding the slit and, on the other, additional features appear at the position of the PMMA bands. As observed, the intensity and spectral shape of these features depend on the slit length.

To highlight these features, the difference between the experimental reflectivity spectra and a baseline spectra obtained smoothing the experimental ones (\( R_{\text{BL}} \) \cite{16, 17}), is presented in Fig. 5 in the spectral region around the 1730 \( \text{cm}^{-1} \) absorption band. In the same figure, we also present the spectrum of the difference (multiplied by 10) measured in the unpatterned regions of the Au film. This spectrum shows a dip at the position of the PMMA absorption band. On the other hand, the spectra of the slits regions are more complex, showing the specific properties related to the resonant SEIRA substrates. In particular, the PMMA-related feature has a spectral shape and intensity (difference between the maximum and minimum of the signal) which depends on the slit length. This

![Fig. 3](image)

**Fig. 3** a Sketch of the experimental setup. An IR microscope connected to a FTIR spectrometer allows measuring the different slits patterns. The relative orientation of the light polarization with respect to the main axis of the slits determines the excitation of the slit resonance in the considered spectral range. In this case, the slit resonance is excited by using light-polarized perpendicular to the slits. b Reflectivity spectra for light-polarized perpendicular to the slit for different slit lengths and 2.2% slit concentration. For the 1.7-\( \mu \)m long slit, also the spectrum for light parallel to the slit is shown (dashed line).

![Fig. 4](image)

**Fig. 4** Reflectivity spectra for light-polarized perpendicular to the slit long axis for different slit lengths and 2.2% slit concentration after PMMA deposition. Inset: transmission spectrum of a PMMA layer.
can be clearly seen in Fig. 5b, where we depict this intensity, normalized to the intensity of the unpatterned region of the Au film, as a function of slit length. This ratio represents the enhancement of the signal and its slit length dependence is related to the evolution of the electromagnetic field intensity in the region around the slit at the frequency of the 1730 cm\(^{-1}\) absorption band. This field is maximum when the slit resonance is tuned to the frequency of the band and decreases as the frequency of the resonance is detuned from it. As it can be seen, the signal enhancement reaches values of up to 30 for 1.7-μm long slits. This makes this system therefore promising for the intended detection of the single monolayer of protein.

The results discussed in the preceding paragraphs correspond to patterns with a very low slit concentration. To determine to what extent the increase in slit density affects the enhancement, in Fig. 6 we present the spectra of the reflectivity with the light-polarized perpendicular to the slit after baseline subtraction for different slit concentrations and 2.1-μm slit length. They were obtained from the spectra shown on the upper-left inset. The enhancements are presented in the upper-right inset of Fig. 6 as a function of slit concentration, reaching factors up to 50 for the largest concentration. As it can be seen, the enhancement increases with slit density, but it does not follow a linear trend as the slit density does (shown by the dashed red line of the figure).

![Fig. 5](image1.jpg)  
**Fig. 5** a Spectra of the reflectivity after baseline subtraction. For clarity, the spectra have been displaced along the y-axis. The arrow represents the intensity of the PMMA-related feature. b Intensity of the 1730 cm\(^{-1}\) feature normalized to the intensity of the unpatterned region of the Au film as a function of the slit length. The dotted line is a guide to the eye.

![Fig. 6](image2.jpg)  
**Fig. 6** Spectra of the reflectivity after baseline subtraction of the structures shown on the upper-left inset. For clarity the spectra have been displaced along the y-axis. Upper-left inset: reflectivity spectra for light-polarized perpendicular to the slit long axis (2.1-μm slit length) for different slits concentrations: 2.2%, 3.9% and 8.5% after PMMA deposition. Upper-right inset: Intensity of the 1730 cm\(^{-1}\) feature normalized to the intensity of the unpatterned region of the Au film as a function of the slit concentration. The dashed black line is a guide to the eye, whereas the dashed red line represents the expected increase of the enhancement assuming a linear dependence with the slit density.
rather staying below this straight line. This indicates that, even though the enhancement increases with the number of slits, as one would intuitively think, since the slits act as electromagnetic field enhancers, it occurs in a gradually slower fashion as the slit concentration increases. This is probably due to inter-slit interaction effects that modify the electromagnetic field distribution from that of an ensemble of non-interacting slits, reducing the intensity of the field. An additional indication of this inter-slit interaction effect can be also inferred from the reflectivity spectra. In this case, the position of the resonance changes with the slit concentration, and the intensity of the resonance does not follow a linear trend as the slit density does, but rather lies below this straight line, in a similar way as does the enhancement. These two effects are a clear indication of the increase of inter-slit interactions with slit concentration, which as far as SEIRA enhancement is concerned, results in a sublinear dependence of the enhancement with the slit concentration.

**Infrared Reflectivity Characterization of the Slit-engraved Au Film with a Layer Cytochrome C Adsorbed**

As we have already mentioned, the electrochemical adsorption of a monolayer of Cyt C on top of the Au surface does not produce any characteristic structure on the reflectivity spectrum of the unpatterned regions of the Au film. Similarly, when the light is polarized along the slit, and due to the absence of any resonance excitation, the reflectivity spectra of all the slits arrays do not show additional structures either. On the other hand, when the slit resonance is excited (light-polarized perpendicular to the slits), the spectra show some structure characteristic of the deposited protein layer. This structure is clearly seen in Fig. 7a, where we present the spectra after base line substation (SEIRA signal) in the region around Amide I band (1700–1600 cm⁻¹). As observed, the shape of the SEIRA signal is different from that of the absorbance spectrum of Cyt C shown on top of the figure, which consists on a main characteristic peak at 1656 cm⁻¹. On the other hand, the SEIRA signal has the characteristic shape of the features observed in resonant SEIRA substrates and its intensity depends on the slit length. This can be clearly seen in Fig. 7b, where we depict the SEIRA intensity as a function of slit length. The maximum of the intensity occurs for a slit length which has its resonance tuned to the frequency of the band, in this case for 1.9–μm long slits.

Besides, and similarly to the results for PMMA, the slit concentration dependence of the Cytochrome features increases with the slit density, but not in a linear fashion as can be observed in Fig. 8 where we present the signal for the two extreme cases.

![Fig. 7](image)

Altogether, these results demonstrate the detection of minute amounts of electrochemically deposited Cyt C, all the way down to a single monolayer, thanks to the use of disordered arrays of resonant slit antennas in a gold film, amounts undetectable in the absence of such antennas. These SEIRA substrates, previously calibrated using PMMA layers, allow spectrally tuning the position of the resonance to match the absorption peak of the substance to be detected. Slit concentration can also be optimized, with larger sensitivities obtained for larger concentrations. This parameter of course finds an upper limit when inter-slit interactions set in, strongly affecting spectral position of the features and...
the electromagnetic field enhancement at resonance, with a gradual reduction of the expected sensitivity enhancement due to these interactions.

The disordered arrangement simplifies the interpretation of the results as only plasmonic resonances localized in the antennas are excited. In addition, the continuous nature of the Au film surrounding the slits make it possible electrochemical experiments, required in the deposition of the selected Cyt C protein.

**Summary and Conclusion**

In summary, an analysis of the effect that random arrays of slits patterned on a 72−nm-thick Au layer have on the reflectivity signal of the Amide I band of a monolayer of Cytochrome C electrodeposited on the Au layer is presented. Due to the plasmon slit resonance, the single monolayer Cytochrome−related signal becomes detectable and its intensity depends on the slit length and slit concentration. This proposed SEIRA substrate can be regarded as an alternative to both ordered arrays of slits, which produce strong enhancements of the electromagnetic field but in a very narrow spectral range, and to typical SEIRA substrates based in a granular deposits of Au, with very little or none reproducibility of the detailed morphologies of the random granules. In our proposed substrates, the Au film between the slits still offers enough continuous coverage so that electrochemical experiments can be carried out. Besides, this substrate may also allow to perform in situ electrochemical studies in small areas by measuring the reflectivity from the bottom side.

**Funding** Open Access funding provided thanks to the CRUE-CSIC agreement with Springer Nature. We acknowledge financial support from MINECO through projects AMES (MAT 2014−58860−P), Quantum Spin Plasmonics (FIS2015−72035−EXP), MIRNAS (MAT2017−84009−R), and Comunidad de Madrid through project SINOPHOS−CM (S2018/BAA−4403). We acknowledge the service from the MiNa Laboratory at IMN and funding from MINECO under project CSIC13−4E−1794 and from CM under project S2013/ICE−2822 (Space−Tec), both with support from EU (FEDER, FSE).

**Data Availability** The data/materials that support the findings of this study are available from the corresponding author upon reasonable request.

**Declarations**

**Ethics Approval** Not applicable.

**Consent to Participate** Not applicable.

**Consent for Publication** Not applicable.

**Conflict of interest** The authors declare no competing interests.

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