

Supporting Information

Hybrid Gold-Conductive Metal Oxide Films for Attenuated Total Reflectance Surface Enhanced Infrared Absorption Spectroscopy

Ian R. Andvaag, Tyler A. Morhart, Osai J. R. Clarke and Ian J. Burgess^{*,†}

[†]Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan, S7N 5C9 Canada

^{*}corresponding author: email (ian.burgess@usask.ca), Phone. +1-306-966-4722.

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Details of modelling calculations

At a high level, we have modelled our system as a series of layers and applied the Fresnel equations to calculate reflectivity and transmissivity as a function of angle or frequency. First, all of the layers have to be defined and assigned a permittivity function whether modelled or experimental. Modelled permittivity functions may be fixed values (frequency invariant), Drude-modelled (for conductors), Lorentz-modelled (for dielectrics), or others. For composite layers containing several interspersed materials, effective medium approximations (EMA, or equivalently, effective medium theory, EMT) may be used. Once permittivities are obtained for each layer, we use a matrix method developed by Ohta and Hatsuo¹ to apply the Fresnel equations and Snell's law to the system of layered materials and calculate the reflectivity and transmissivity.

Basic optical properties

Relative permittivity, ϵ , and complex refractive index, η , are two different ways of encoding the same information. One can convert between the two by: $\eta^2 = \mu\epsilon$, and for the cases considered in this work, the magnetic permeability, μ , equals unity.

The permittivity can be separated into real and imaginary components:

$$\eta = n + i\kappa \quad (1)$$

$$\epsilon = \eta^2 = (n + i\kappa)^2 = n^2 + 2in\kappa - \kappa^2 \quad (2) \quad \epsilon_1$$

$$= n^2 - \kappa^2 \quad (3) \quad \epsilon_2$$

$$= 2n\kappa \quad (4)$$

where ϵ_1 and ϵ_2 are the real and imaginary parts of the permittivity, respectively.

The various forms of expressing the wavelength/frequency of the electromagnetic radiation are explicitly given in Equation 5

$$\lambda = \frac{1}{\nu} = \frac{c}{\nu} = \frac{2\pi c}{\omega} \quad (5)$$

where c is the speed of light in a vacuum.

Lorentz model

The absorbing organic molecule was modelled as a Lorentz oscillator:

$$\epsilon_{\text{lorentz}} = \epsilon_{\infty} + \frac{\omega_p^2}{\omega_r^2 - \omega^2 - i\omega\gamma} \quad (6)$$

where ϵ_{∞} is the relative permittivity off-resonance (i.e. at very high frequency), ω_p is the angular plasma frequency, ω_r is the angular resonant frequency, ω is the angular frequency

of the electric field driving the oscillator (i.e. angular frequency of the incident IR radiation), and γ is the damping factor of the molecular resonance.

Drude model

The permittivity values of metals and conductive metal oxides can be modelled using the Drude model. In this work, the Drude model was used as the function describing the permittivity of IZO films. Electrons in metals are unbound, and thus there is no restoring force causing them to oscillate at some resonant frequency. Therefore, the Drude model is given by the Lorentz model for the special case of $\omega_r = 0$:

$$\epsilon_{Drude} = \epsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\omega\gamma} \quad (7)$$

The plasma frequency, ω_p , is given by:

$$\omega_p = \left(\frac{Ne^2}{\epsilon_0 m^*} \right)^{\frac{1}{2}} \quad (8)$$

where N is the free carrier concentration (density of conduction electrons), e is the elementary charge, ϵ_0 is the permittivity of free space, and m^* is the effective electron mass. The effective mass is a calculated value of an electron's *apparent* mass based on how the electron would be affected by forces applied to it.

Bruggeman Effective Medium Approximation

The permittivity function of the structured metal surface is not accurately described by the permittivity of the bulk metal. Various Effective Medium Approximations (EMAs) have been developed to model the permittivity of a composite structured layer. Examples include the Bruggeman, Maxwell-Garnett and Hunderi EMA models.²

In this work, we have followed Osawa³ and used the Bruggeman EMA, which treats the surface as a collection of metal prolate spheroids in a host medium which fills the spaces between the metal particles. The particles may be coated by a thin uniform layer of some organic molecule. Thus, the Bruggeman EMA effectively combines the permittivity values of the three constituents (metal, organic molecule, host medium) to obtain an effective permittivity of the composite layer. This approximation is valid when the microstructural elements of the layer (in this case, the prolate spheroids) are much smaller than the wavelengths of IR light.

It is not entirely clear how the metal spheroids are arranged within the layer in Osawa's work, so this work assumes that the major semi-axes of the spheroids are parallel to the surface, and thus the layer has a thickness equal to the diameter of the minor semi-axis. Additionally, we assume that within this limitation, the prolate spheroids may adopt any possible rotation.

Granqvist² defines the Bruggeman EMA as:

$$\epsilon_{BR} = \frac{\epsilon_h \left(1 - F + \frac{1}{3}F\alpha\right)}{1 - F - \frac{2}{3}F\alpha} \quad (9)$$

where ϵ_h is the permittivity of the host medium, F is the fractional volume of the layer occupied by metal particles, and α is the polarizability factor of the particles.

The polarizability, α , is a function of the volume ratio of the uncoated to coated particles (Q), the depolarization factors of the core and coated prolate particles (L_1, L_2), and also the permittivity of the metal (ϵ_m) and the dielectric coating (ϵ_d):

$$\alpha = \frac{(\epsilon_d - \epsilon_{BR})[\epsilon_m L_1 + \epsilon_d(1 - L_1)] + Q(\epsilon_m - \epsilon_d)[\epsilon_d(1 - L_1) + \epsilon_{BR} L_2]}{[\epsilon_d L_2 + \epsilon_{BR}(1 - L_1)][\epsilon_m L_1 + \epsilon_d(1 - L_1)] + Q(\epsilon_m - \epsilon_d)(\epsilon_d - \epsilon_{BR})L_2(1 - L_2)} \quad (10)$$

Notice that the Bruggeman permittivity function is a parameter of the polarizability function. Solving eqn (9) for α and then setting the result equal to eqn (10) gives:

$$\frac{3(\epsilon_h - F\epsilon_h + F\epsilon_{BR} - \epsilon_{BR})}{-F(2\epsilon_{BR} + \epsilon_h)} = \frac{(\epsilon_d - \epsilon_{BR})[\epsilon_m L_1 + \epsilon_d(1 - L_1)] + Q(\epsilon_m - \epsilon_d)[\epsilon_d(1 - L_1) + \epsilon_{BR} L_2]}{[\epsilon_d L_2 + \epsilon_{BR}(1 - L_2)][\epsilon_m L_1 + \epsilon_d(1 - L_1)] + Q(\epsilon_m - \epsilon_d)(\epsilon_d - \epsilon_{BR})L_2(1 - L_2)}. \quad (11)$$

It is possible to solve this equation for the Bruggeman permittivity, ϵ_{BR} , but the expression is very lengthy, and is not given here.

To calculate an absorbance spectrum, the Bruggeman permittivity must be also calculated in the absence of the dielectric coating (analyte film.) To calculate the Bruggeman permittivity of a film without dielectric coating, we replaced ϵ_d with ϵ_h .

Prolate ellipsoids are a class of spheroids with dimensions a, b, c where $b = c$ and $a > b$, (*i.e.* where a is the major semi-axis, and b, c are the minor semi-axes). The one-dimensional depolarization factors for major and minor semi-axes of prolate spheroids are given by equations 4.2 and 4.3 in Stoner⁴ (also equations 2.10 and 2.11 in Osborn⁵):

$$L_{major} = \frac{1}{m^2 - 1} \left[\frac{m}{(m^2 - 1)^{\frac{1}{2}}} \ln \left\{ m + (m^2 - 1)^{\frac{1}{2}} \right\} - 1 \right] \quad (12)$$

$$L_{minor} = \frac{1}{2}(1 - L_{major}) \quad (13)$$

where m is the ratio of the long semi-axis to the short semi axis. The depolarization factors given above are only valid for prolate spheroids, the particles may be best modelled by some other geometric solid defined by its own unique depolarization factors but this was not explored in this work. Given our assumption that the particles can adopt any rotation

about the axis normal to the surface, we assume a random distribution of rotational orientations, so the depolarization factor of an average particle is taken to be the arithmetic mean of the depolarization factors along the major and minor semi-axes:

$$L_{eff} = \frac{L_{major} - L_{minor}}{2} \quad (14)$$

Note that this assumption means that the "effective depolarization factor of the collective particles" is independent of direction of the electric field, that is to say the same for s- and p-polarized light.

Ohta's matrix method

Ohta and Hatsu¹ described a method to calculate reflectivity and transmissivity of layered systems using propagation matrices and the Fresnel equations for reflection and transmission coefficients. For each interface in the layered system of interest, a matrix is defined:

$$C_j = \begin{pmatrix} e^{-i\delta_{j-1}} & r_j e^{-i\delta_{j-1}} \\ r_j e^{i\delta_{j-1}} & e^{i\delta_{j-1}} \end{pmatrix} \quad (15)$$

where r is the Fresnel reflection coefficient and δ_{j-1} is the phase shift of the wave after passing through the boundary between the j -th and the $(j+1)$ -th layer with respect to the phase of the wave at the boundary between the $(j-1)$ -th and the j -th layer:

$$\delta_{j-1} = 2\pi n_{j-1} \cos \theta_{j-1} h_{j-1} \quad (16)$$

The subscripts refer to the layer, with $j-1$ referring to the layer on the near side of the interface, with respect to the direction of propagation.

The product of all C_j matrices gives a 2 by 2 matrix with elements:

$$\prod_{j=1}^n C_j = \begin{pmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{pmatrix} \quad (17)$$

And the overall reflection and transmission coefficients across the entire layered system are given by:

$$r = \frac{c_{21}}{c_{11}} \quad (18)$$

$$t = \frac{1}{c_{11}} \prod_{j=1}^n t_j \quad (19)$$

The Fresnel transmission coefficients for s- and p-polarized light at the j -th interface, t_j , are given by⁶:

$$t_{js} = \frac{2\xi_{j-1}}{\xi_j + \xi_{j-1}} \quad (20)$$

$$t_{jp} = \frac{2\eta_j\eta_{j-1}\xi_{j-1}}{\xi_{j-1} + \xi_j} \quad (21)$$

where:

$$\xi_j = |\eta_j \cos \theta_j| \quad (22)$$

Note that the expression for t_{js} in Ohta¹ is incorrect, as is the expression for t_{jp} in Hansen.⁶ Expressing the reflection coefficients in terms of ξ_j (*i.e.* forcing the real and imaginary components of the product $\eta_j \cos \theta_j$ to both be positive) gives the correct root, causing the evanescent wave to decay exponentially as a function of distance from the terminal interface, which is the correct behaviour. If ξ_j is not in quadrant I of the complex plane, the evanescent wave will increase exponentially.

The observable quantities are reflectance (R) and transmittance (T) which are the square moduli of their respective coefficients. However, the cross-sectional area of the beam changes upon refraction, so transmissivity is multiplied by a factor accounting for this change in beam size:

$$R = |r|^2 \quad (23)$$

$$T_s = Re\left(\frac{\eta_{m+1} \cos \theta_{m+1}}{\eta_0 \cos \theta_0}\right) |t_s|^2 \quad (24)$$

$$T_p = Re\left(\frac{\eta_{m+1}^* \cos \theta_{m+1}}{\eta_0^* \cos \theta_0}\right) |t_p|^2 \quad (25)$$

Explanation of Drude model discrepancy in literature

There are two expressions for the Drude model found in the literature. It is not immediately obvious how the parameters of the two expressions are related. The only difference between the two expressions of the Drude model is that ϵ_∞ is factored out and ω_p is defined differently. The following derivation of the relationship between the two expressions assumes that ϵ_∞ is a directly measured parameter, and is therefore the same in both methods. Note that the subscripts “F” and “LR” refer to the different forms of the expressions exemplified by references (for example) given by Franzen⁷ and LeRu,⁸ respectively.

Franzen expression	LeRu expression
$\epsilon = \epsilon_\infty - \frac{\omega_{p,F}^2}{\omega^2 + i\omega\gamma}$	$\epsilon = \epsilon_\infty \left(1 - \frac{\omega_{p,LR}^2}{\omega^2 + i\omega\gamma} \right)$
Solve each expression for ω_p :	
$\omega_{p,F} = \sqrt{\epsilon_\infty \omega^2 + \epsilon_\infty i\omega\gamma - \epsilon \omega^2 + \epsilon i\omega\gamma}$	$\omega_{p,LR} = \epsilon_\infty^{-\frac{1}{2}} \sqrt{\epsilon_\infty \omega^2 + \epsilon_\infty i\omega\gamma - \epsilon \omega^2 + \epsilon i\omega\gamma}$
Therefore,	
$\omega_{p,F} = \epsilon_\infty^{\frac{1}{2}} \omega_{p,LR}$	

In this work, we have used the more common expression defined by Franzen, and therefore all plasma frequencies are given as $\omega_{p,F}$, as defined above.

SEM images of IZO film

The deposited IZO is remarkably flat and featureless, and the plan view SEM features are rather devoid of features and grain boundaries. Figure S1a below shows an SEM image of the IZO film at the edge of the Si substrate. The estimated roughness of the IZO film is $\pm 10\%$ of the film thickness (i.e. ~ 5 nm rms). Figure S1b is an AFM image of a defect in the conductive metal oxide layer.

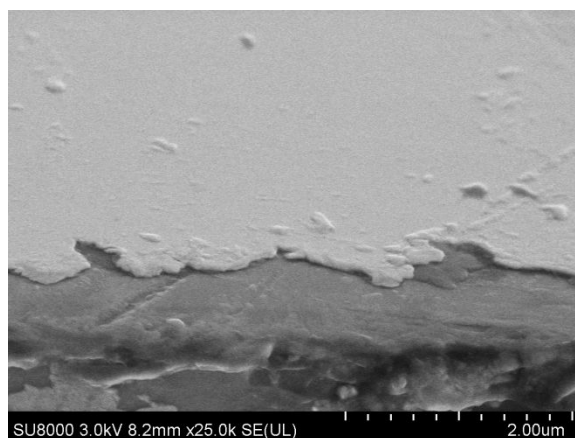


Figure S1a : Tilted SEM image of the IZO film deposited on a Si wafer. The image is taken at the very edge of the deposited film.

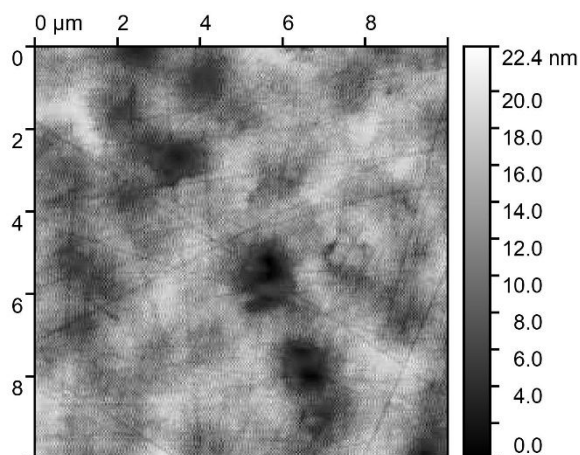


Figure S1b : AFM image of IZO film deposited on a Si wafer.

Cyclic voltammetry of Au electrodeposition

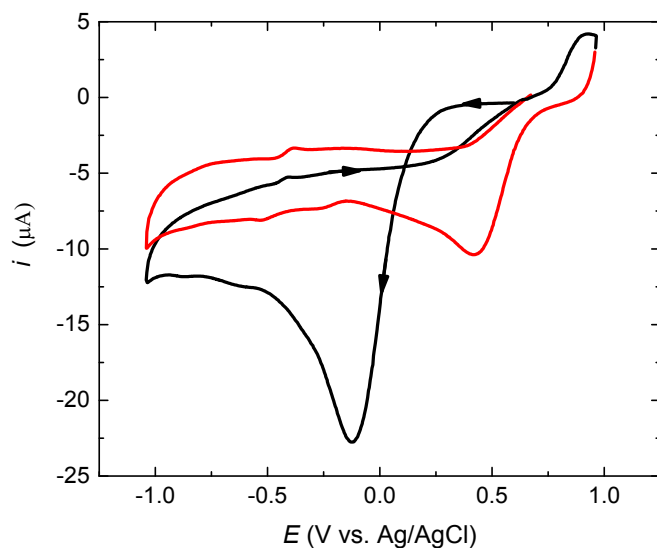


Figure S2. : Cyclic voltammetry was used to follow the electrodeposition of Au onto the IZO film in the spectroelectrochemical cell. The CV shows the first (black line) and second scan (red) at 20 mV/s in an electrolyte consisting of 0.1 M NaF, 0.25 mM KAuCl_4 and 0.1 mM 4-methoxypyridine (MOP).

Evolution of MOP SEIRAS signal with Au deposition

Figure S3 shows the ATR-SEIRA spectra (reference spectrum taken at -0.90 V vs Ag/AgCl and the sample spectrum taken at $+0.30$ V) as a function of the number of Au deposition cycles. The peaks in the spectra can be assigned to 4-methoxypyridine (MOP) as per the discussion in the main part of the paper.

As more gold is deposited with potential cycling, the asymmetry of the peaks increases. This is best illustrated by taking the first derivative of the spectra near an absorption peak (see inset of Fig. S3) for the red and dark blue traces. The positive lobes of the differential spectra were normalized to 1, so the increased negative lobe as deposition proceeded indicates an increase in peak asymmetry.

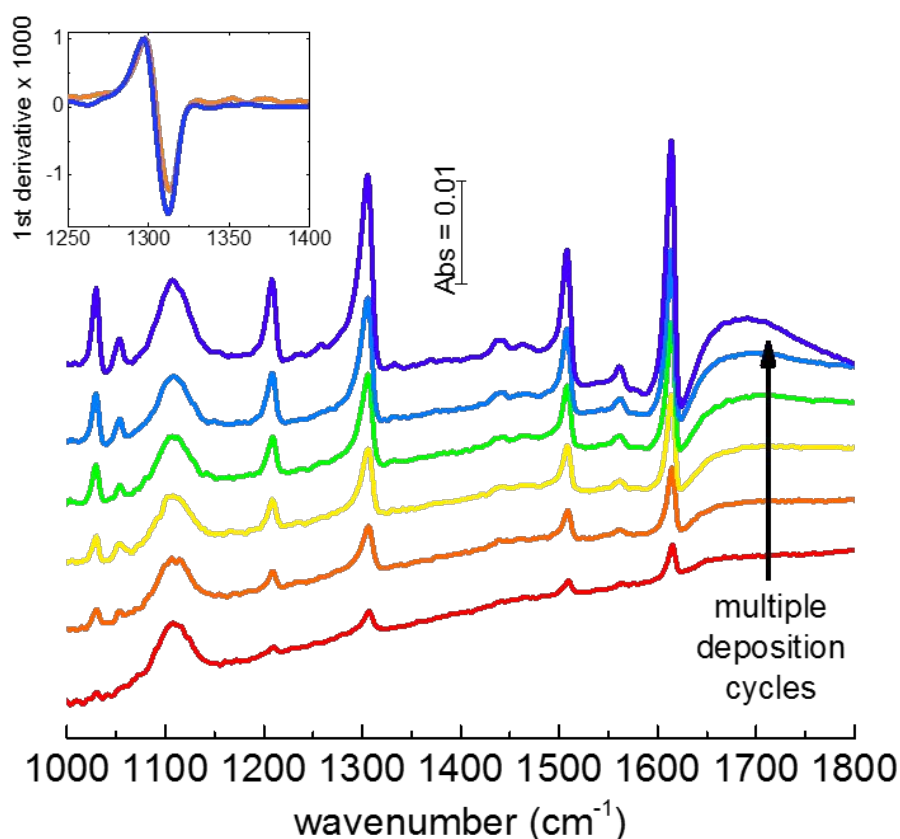


Figure S3 : ATR-SEIRA spectra during the gold deposition process. The electrolyte solution consisted of 0.1 M NaF, 0.25 mM KAuCl₄ and 0.1 mM MOP. The inset shows the first derivative of the 1300 cm⁻¹ peak calculated for the spectra taken after the initial and final deposition cycles.

SEM characterization of electrodeposited Au on IZO films

SEM images of the electrodeposited Au on the IZO/Si substrates were collected in order to evaluate the morphology and coverage of the resulting gold layer. SEM images were collected at different positions within the area defined by the o-ring boundary. The inner diameter of the o-ring in the spectroelectrochemical cell was 6.35 mm.

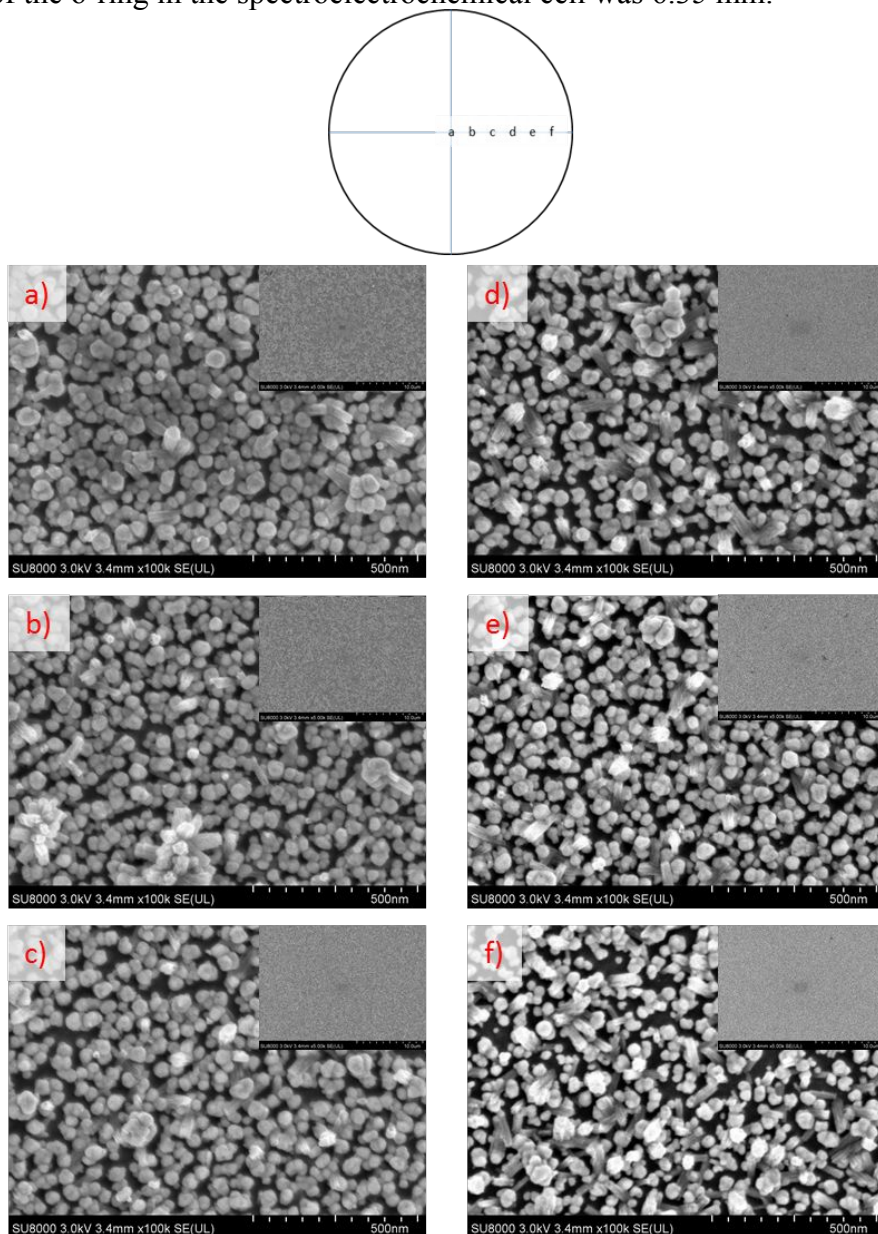


Figure S4: SEM images collected every 0.5 mm radially outward from the centre of the active area of the working electrode, as defined by the boundary of the o-ring. The graphic above illustrates the position of each image with respect to the boundary of the o-ring. The images are representative of the density of deposited gold anywhere along the concentric ring defined by the radius at which the image was taken.

Images S4a to S4f show that the density of the deposited gold is greatest at the centre of the o-ring and decreases slightly as the image area is moved radially away from the middle of the o-ring. Nevertheless, the larger area SEM images (the insets of each figure have a scale bar of 10 μm) show that the surface is free of major defects and voids across the entire surface.

It is important to note that although the percolated network of gold islands looks relatively rough compared to the SEM images of magnetron sputtered gold (*vide infra*), the islands do not occupy the full geometric area of the surface. The less than full coverage of the islands offsets the increased roughness such that the effective surface area of gold for the electrodeposited Au film and the vacuum prepared Au film are within $\sim 20\%$ of each other.

SEM characterization of vacuum-deposited Au on IZO films

Vacuum-deposited Au films are very homogeneous and much flatter than the electrodeposited Au. These surfaces do not provide SEIRAS enhancement when formed on thin layers of IZO.

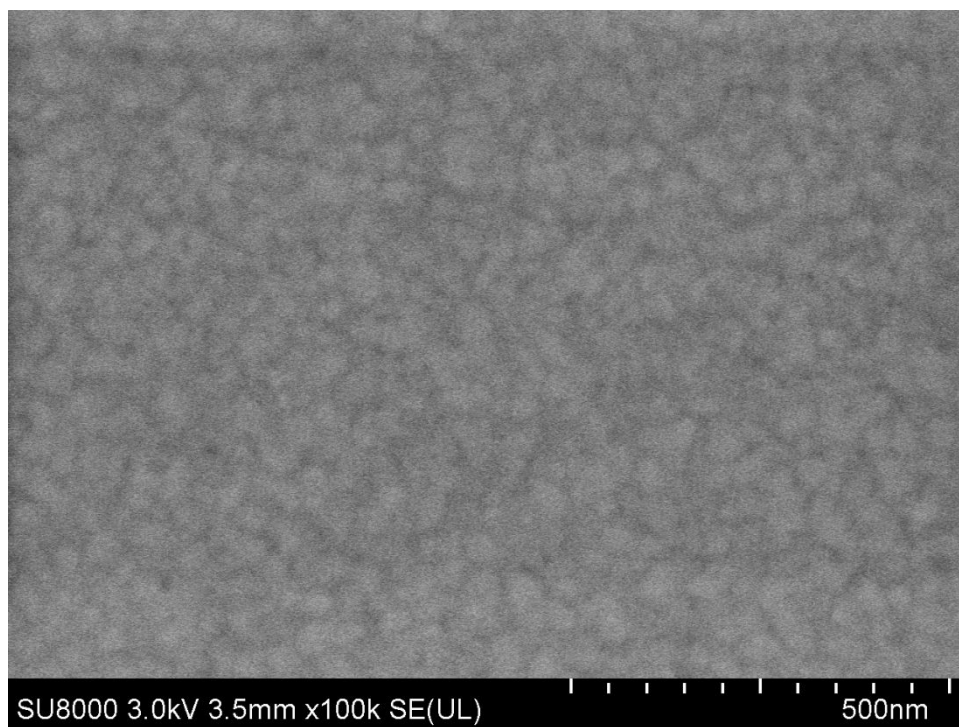


Figure S5: SEM image of 20 nm thick film of Au magnetron sputtered on a 50 nm thick IZO film supported on a Si wafer. The deposition rate was 0.01 nm s^{-1} .

Cyclic voltammetry of electrodeposited Au on IZO in presence of MOP

After the deposition procedure, the cell was disassembled, rinsed, and reassembled with the μ -IRE that had been deposited with Au. The cell was filled with 0.1 mM MOP in an electrolyte of 0.1 M NaF and the potential was cycled from -1 V to + 500 mV at a rate of 20 mV s⁻¹. Fig. S6 shows the relative stability of the CV over ~1 hour of cycling.

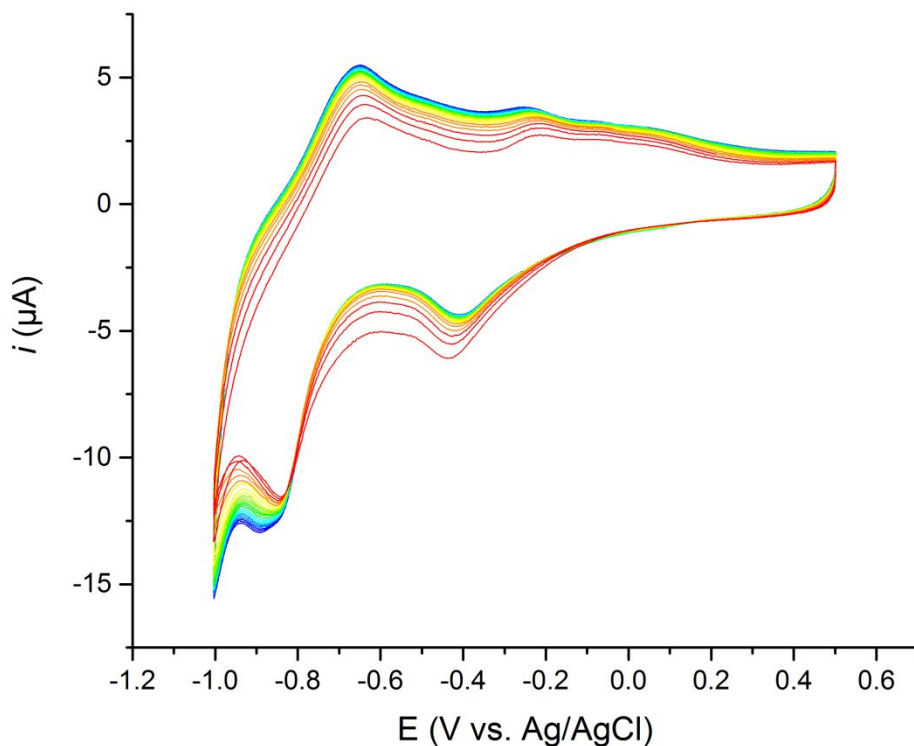


Figure S6. : Cyclic voltammograms over the course of 1 hour of electrodeposited Au wafer on IZO on Si in 0.1 mM MOP. The trace is colour-mapped as a function of time, with early scans appearing in red and late scans appearing in blue.

Calculation of enhancement factor, G

To quantify the enhancement resulting from our ATR-SEIRAS system, it is helpful to compare it to the external reflectance spectrum of our adsorbed analyte on a bulk Au film. A 110 nm thick layer of Au was sputtered onto two glass substrates. One substrate was incubated in a 1 mM solution of 4-MBA in ethanol for 3.5 hours to ensure the formation of a self-assembled monolayer (SAM.) The sample was rinsed with neat ethanol and dried under Ar. To deprotonate the adsorbed 4-MBA, the SAM was immersed in pH 9 NaOH solution for 1 minute and dried with a Kimwipe. An absorbance spectrum was calculated using the unmodified Au layer as the reference spectrum and the deprotonated SAM as the sample spectrum. A grazing angle of incidence of 80° with respect to the surface normal was used to obtain an acceptable SNR.

In order to correct for the experimental differences between the ATR-SEIRAS and external reflectance spectra, Huo et al⁹ define an enhancement factor, G , which accounts for differences in coverage, surface roughness, and polarization:

$$G = \frac{I_{SEIRAS}}{I_{ERS}} C_1 C_2 C_3 \quad (26)$$

I_{SEIRAS} and I_{ERS} are the absorbance intensities of the ATR-SEIRAS (12.9 mAbs as per Fig. 6 in main paper) and external reflectance measurements (this value was found to be 0.2 mAbs). The C_n are correction factors, defined as follows:

- C_1 is the correction factor for surface coverage. Since a SAM is present on the surface for both measurements, we assume $C_1 = 1$.
- C_2 accounts for differences in surface roughness. The surface roughness factors for the Au films used for obtaining I_{SEIRAS} and I_{ERS} were estimated by measuring cyclic voltammograms (Fig. S7) with E limits of -0.3 V and +1.25 V vs sat. Ag/AgCl. The charge required to reduce the oxide layer was determined by integrating the cathodic half scan. The charge per unit area was calculated using the surface area of our working electrode. The roughness factor was determined by dividing the calculated charge per unit area by the charge per unit area of polycrystalline Au, 400 $\mu\text{C cm}^{-2}$ as reported by Angerstein-Kozolowska *et al.*¹⁰

$$R_{ERS} = 1.64$$

$$R_{SEIRAS} = 1.58$$

$$C_2 = \frac{R_{SEIRAS}}{R_{ERS}} = 0.96$$

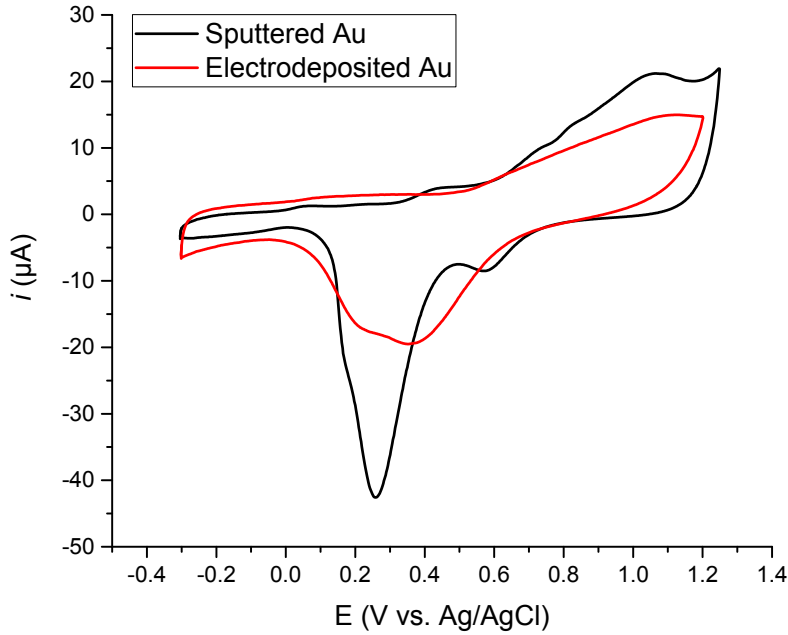


Figure S7. : Cyclic voltammograms of sputtered (black) and electrodeposited (red) Au films on top of a 50 nm thick layer of IZO on Si used to determine surface roughness by integrating the cathodic scan from its beginning at positive potentials to the local extremum at ~ 0 V. The electrolyte is 0.1 M NaF. The geometric area of both working electrodes was 0.32 cm^2 .

- C_3 corrects for any differences in polarization. Since unpolarized light was used for both ATR-SEIRAS and the external reflectance measurements, C_3 is taken to be 1.

This gives an enhancement factor of ~ 60 :

$$G = \frac{I_A}{I_E} C_1 C_2 C_3 C_4 = \frac{12.9}{0.2} * 1 * 0.96 * 1 = 62$$

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