Plasmonic-based imaging of local square wave voltammetry

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Supporting Information

1. Constant α and β

α, is the surface charge density change for a given plasmonic response (shift in the surface plasmon resonance angle, θ_R, in mdeg), which is given by[1].

$$\alpha = -\frac{ed_m n_e \varepsilon_2 (\varepsilon_1 + \varepsilon_m)^2 \sin(2\theta_R)}{\varepsilon_1^2 (\varepsilon_m - 1)} \qquad (1)$$

where e is electron charge, d_m, n_e and ε_m are the thickness, electron density and real part of the dielectric constant of the metal film, ε_1 anad ε_2 are the dielectric constants of the prism and medium on top of the metal film, respectively. In the present case, ε_1=1.77 (water), ε_2 =2.29 (BK7 prism), d_m=47 nm, n_e=5.9x10^{-28} m^{-3} and ε_m=-11.7 for the Au film, θ_R=72°, and the calculated α_{cal}=28 C.$m^{-2}$$deg^{-1}$. We also calibrated α, experimentally by measuring surface

plasmon resonance angle shift for a given change of surface charge density, and found that α_{exp} = 47 C.m^{-2}deg^{-1}, which is really close to theoretic value.

β is the constant to Faradaic current change for a given plasmonic response, which is expressed as[2]

$$\beta = B\left(\alpha_R D_R^{-\frac{1}{2}} - \alpha_O D_O^{-\frac{1}{2}}\right)\left(nF\pi^{\frac{1}{2}}\right)^{-1} \quad (2)$$

where B measures the sensitivity of the SPR angle to a change in the bulk index of refraction, α_O and α_R are the changes in the local refractive index per unit concentration for the oxidized and reduced molecules, respectively, n is number of electrons transferred per reaction, F is Faraday constant, and D_O and D_R are the diffusion coefficients of the reaction species.

β is obtained from independent calibration experiment. The redox complex in the oxidized state and reduced state at 10mM concentration was injected into the flow cell, and the SPR response was determined and used to calculate α_O and α_R. Because $D_R = D_O = 5.3*10^{-10}$cm2/s, we have =-9.21*10^{-6} m mM Deg^{-1} S$^{-1/2}$.

2. SWV of $[Fe(CN)_6]^{3/4}$.

SWV measurement was carried out also in 10 mM $[Fe(CN)_6]^{3/4-}$ + 0.2M NaF solution by applying a potential waveform composed of square waves with a step height of 5 mV and frequency of 10 Hz superimposed on a linearly sweeping potential from +0.1 V to +0.4 V. The plasmonic response and the plasmonic-based current density vs. potential are plotted in Figure S1a, and SWVs obtained from the current at the end of each potential step are shown in Figures

S1b (PECI method) and c (conventional method). Quantitative agreement of the plasmonic-based SWV with the conventional SWV for $[Fe(CN)_6]^{3/4-}$ further validates the plasmonic imaging of SWV.

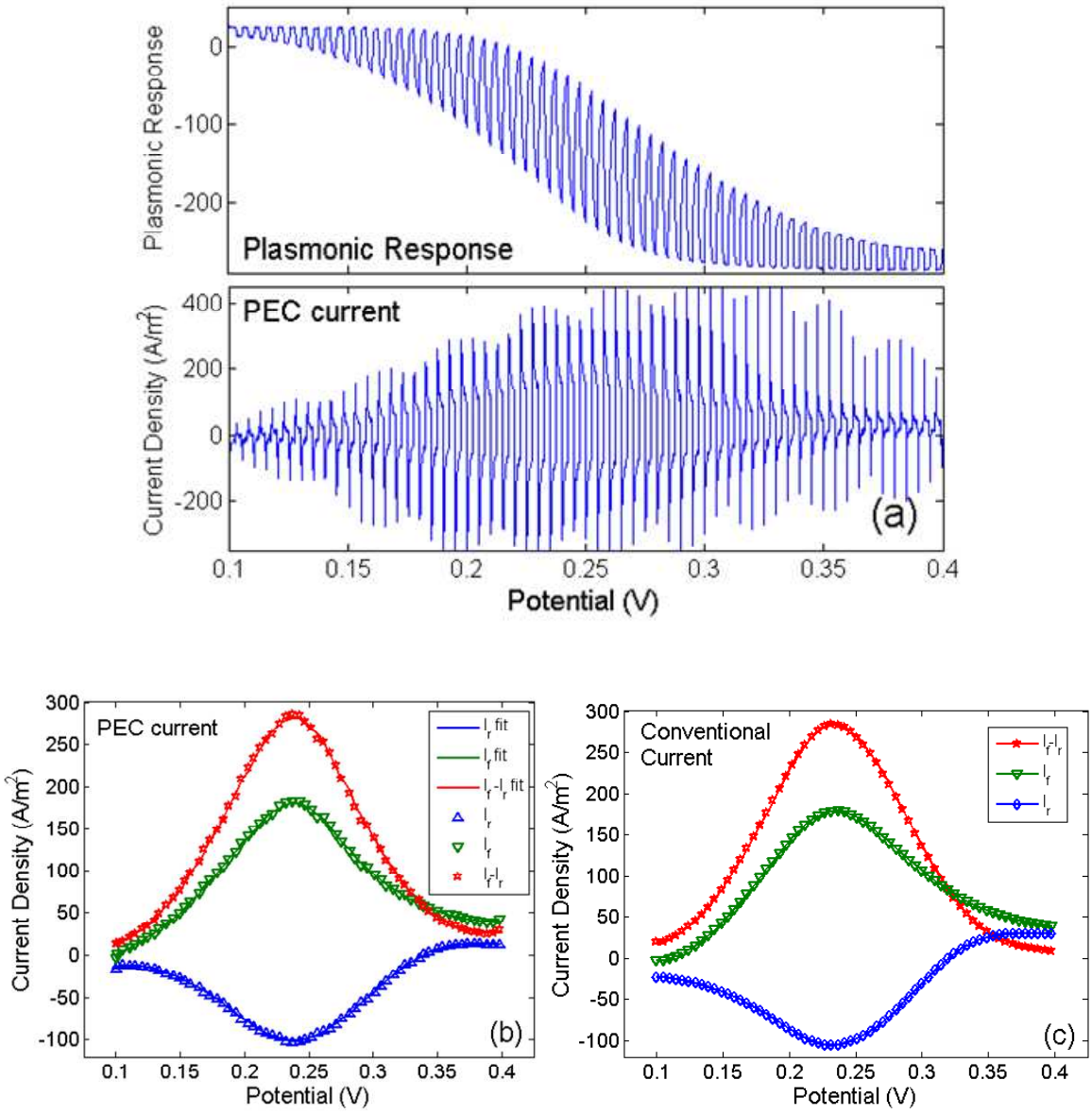

Figure S1. (a) Top: Plasmonic response vs. potential in10mM $[Fe(CN)_6]^{3/4-}$. Bottom: Transient plasmonic-based electrochemical current (PEC) vs. potential. (b) and (c) Plasmonic-based and conventional SWV, where I_f, I_r and I_f-I_r are forward, reverse and difference current.

3. Video S-1.

Current image video of SWV of 20 mM $[Fe(CN)_6]^{3/4-}$ + 0.2 M NaF electrolyte. The experiment conditions were described in the manuscript. The images in Figure 3(c)-(f) are the snapshots of this video. The right top corner has indicated the potential of the frame which is displaying. The scale bar shows the current density of the image, the unit of scan bar is A/m^2. The left top corner shows the frame number.

From video we can easily distinguish the current densities at different locations, the thiol covered area always has small current in entire potential sweep process while the Au area has different current density at different potential. At small potential, there is no contrast throughout the whole surface, because no measurable redox reaction happened on surface. When potential is bigger than +0.18V, the current density between bare Au and thiol covered area has big difference indicates that the redox reaction happened only on the bare Au area. When potential is higher than +0.4V, the contrast disappeared because the forward current is equal to the reversed current (diffusion controlled reaction). Note that the SWV current video is taking at the same time when experiment is processed, no scanning process is needed. Please find more detailed description in manuscript.

References

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