

Plasmonic electrocatalysis: energetic carriers enhance electrochemistry

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Surface plasmons and electrochemistry both occur on metal surfaces – it is therefore natural to combine them in the same platform [1-5]. Motivations for the combination include (i) realising a multimodal biosensor (electrochemical and optical), (ii) using SPPs to probe the electrochemical double layer or to probe electrochemical activity, thus revealing complementary information on redox reactions, or (iii) using SPPs to pump electrochemical reactions by creating non-equilibrium energetic electrons and holes in a working electrode through the absorption of SPPs thereon. The latter is of particular interest as it may yield novel redox reaction pathways that may be inaccessible thermally - plasmonic electrocatalysis.

We report a Au stripe waveguide along which infrared ($\lambda_0 \sim 1350$ nm) surface plasmon polaritons (SPPs) propagate, operating simultaneously as an electrochemical working electrode. Cyclic voltammograms obtained under SPP excitation enable oxidative processes involving energetic holes to be investigated separately from reductive processes involving energetic electrons (Fig. 1, left panel). Under SPP excitation, redox currents increase by $10\times$ (Fig. 1, right panel), redox potentials decrease by $\sim 2\times$ and split in correlation with photon energy, and the charge transfer resistance drops by $\sim 2\times$ as measured using electrochemical impedance spectroscopy. The temperature of the working electrode was monitored *in situ* ruling out thermal effects. Chronoamperometry measurements with SPPs modulated at 600 Hz yield a commensurately-modulated current response, ruling out thermally-enhanced mass transport. Our observations indicate opening of optically-controlled non-equilibrium redox channels associated with energetic carrier transfer to the redox species (potassium ferrocyanide).

SPPs propagating along the working electrode are also sensitive to changes in local refractive index, which follow changes in the concentration of reduced and oxidised species near the working electrode. The real-time response of the output optical power from a waveguide working electrode is proportional to the time convolution of the electrochemical current density. Convolutional voltammetry yields complementary results to conventional voltammetry, and can be used to determine the diffusion constant, bulk concentration and the number of transferred electrons of electroactive species. The output optical power remains proportional to the time convolution of the current density, even when the latter is significantly enhanced by the transfer of energetic carriers - SPPs on a waveguide working electrode are thus simultaneously useful as a pump and a probe of electrochemical activity.

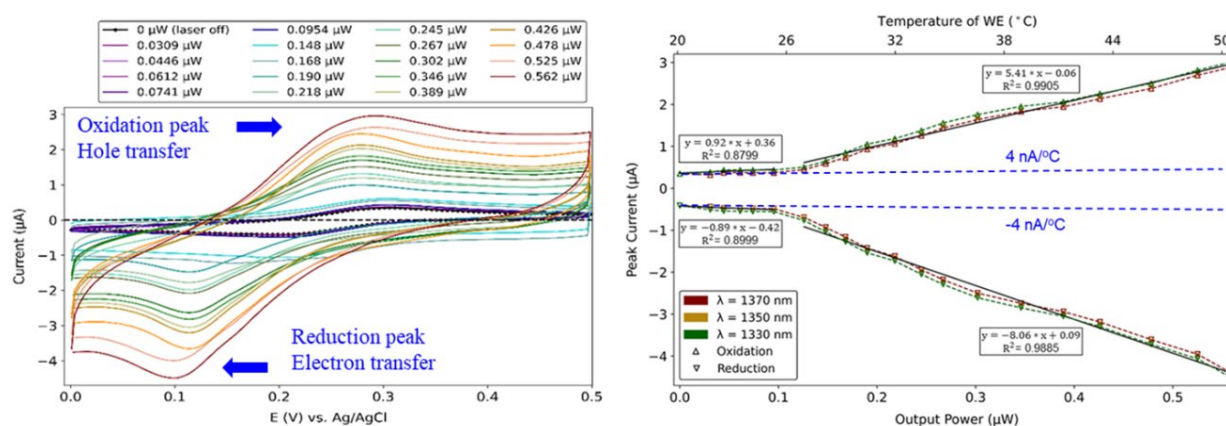


Fig. 1 Left: CV curves obtained on a Au WE, in 0.5 mM $K_3[Fe(CN)_6]$ + 100 mM KNO_3 electrolyte, at a scan rate of 100 mV/s, for increasing output optical power (legend) at $\lambda_0 = 1350$ nm. The incident optical power ranged from 0 to 6.3 mW. The reference CV curve (laser off) is plotted as black dots. Right: Redox current peaks vs. output optical power, from CV curves measured at $\lambda_0 = 1330, 1350$ and 1370 nm. Linear models of the peak redox currents at $\lambda_0 = 1350$ nm are plotted as solid black lines (slopes have units of A/W). Linear thermal trends, measured independently, are added as the blue dashed lines.

References

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