***Supplemental Information***

# Tunable Optical Metamaterial-Based Sensors Enabled by Closed Bipolar Electrochemistry

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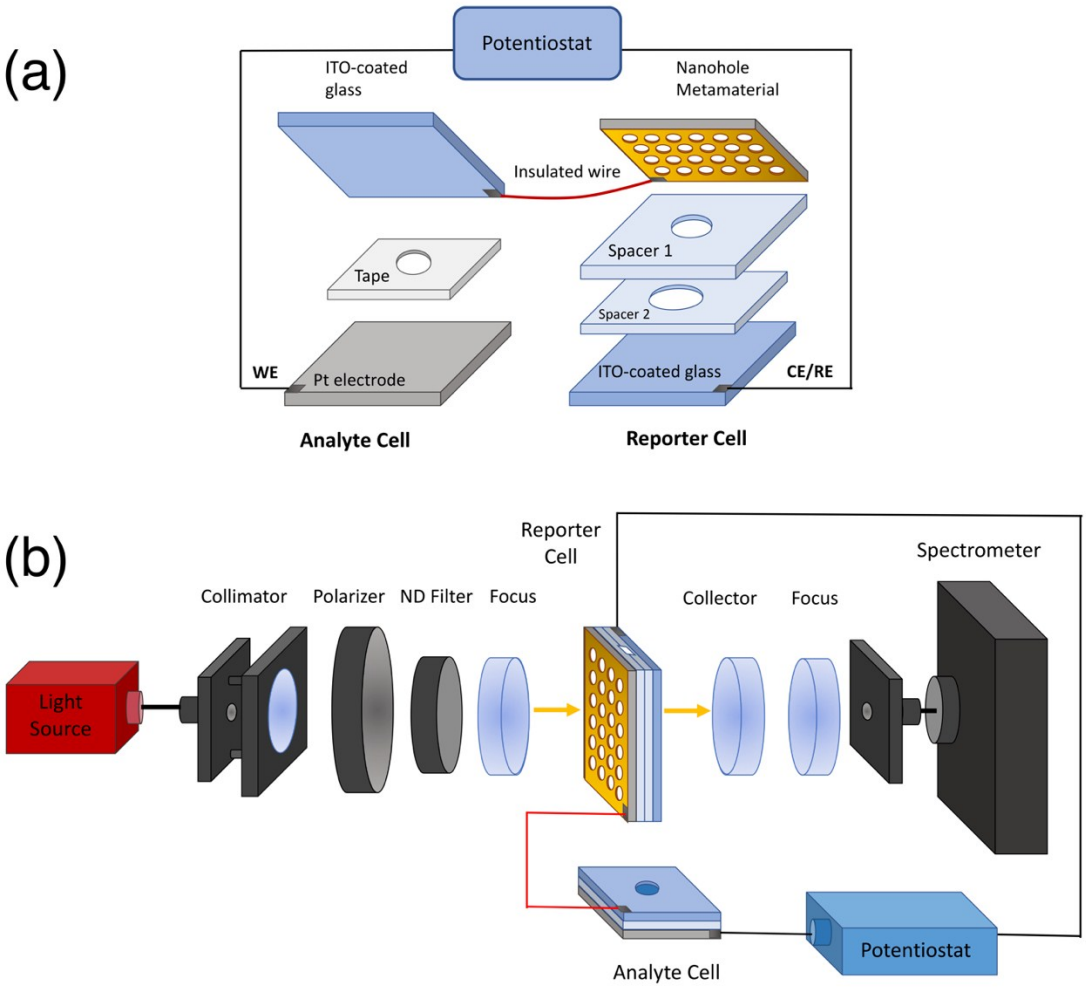


**Figure S1**. (a) Schematic exploded-view illustration of the complete CBE cell. Analyte cell (*left*) is overfilled with analyte solution prior to assembly, while electrodeposition solution is introduced to the reporter cell via syringe. The ITO-coated glass slide of the analyte cell is electrically connected to the nanoaperture metamaterial of the reporter cell, constituting the CBE. (b) Schematic illustration of the custom optical measurement apparatus used to collect *in situ* electrochemically-modulated transmission spectra. Reference spectra were acquired using an unmodified glass slide in place of the nanoaperture metamaterial.

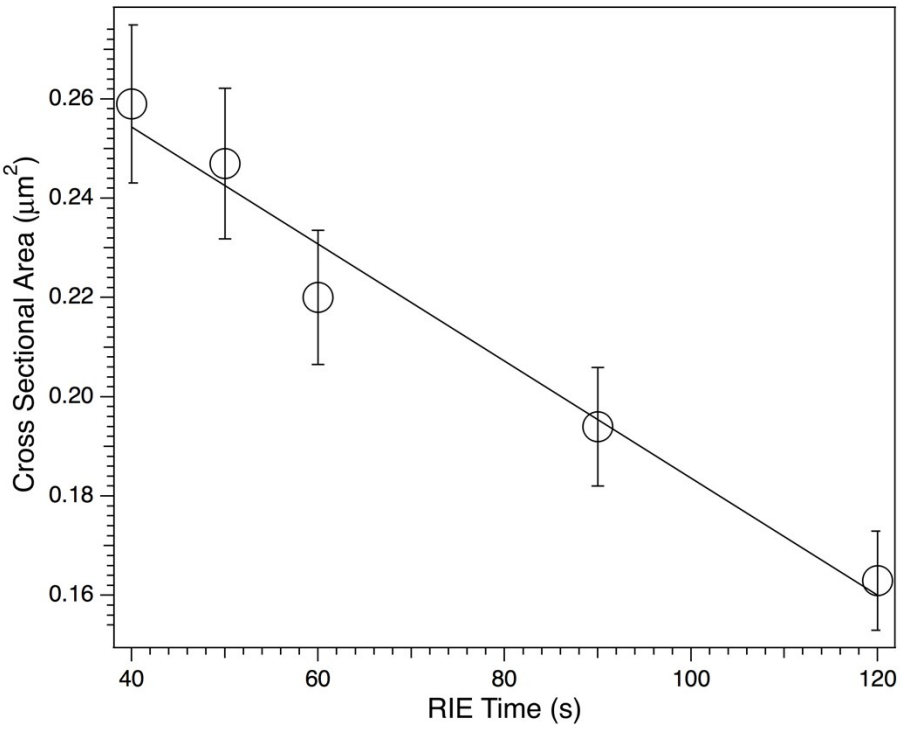


**Figure S2**. Measured cross-sectional area of nanoapertures as a function of RIE etch time. Solid line is a linear fit, and error bars represent uncertainty of the fit parameters.

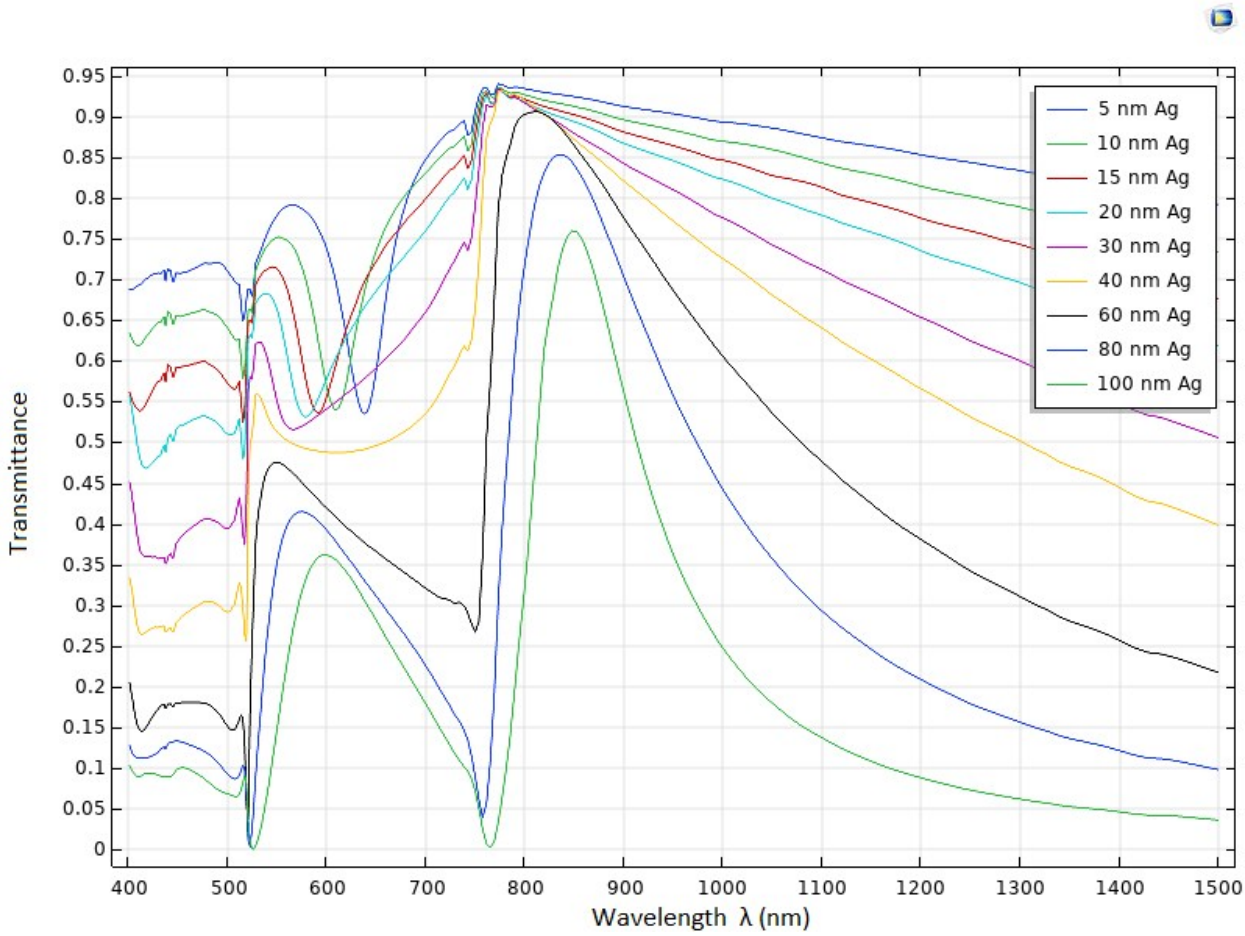


**Figure S3**. Finite-element simulations showing the change in optical response of nanoaperture metamaterials with increasing thickness Ag deposited on them. The simulation models 600-nm spaced hexagonally-packed nanoapertures in a 50 nm Au film on a glass substrate in air. Ag film thickness extends both vertically and horizontally from the Au electrode surface, thus increasing film thickness and decreasing aperture diameter.

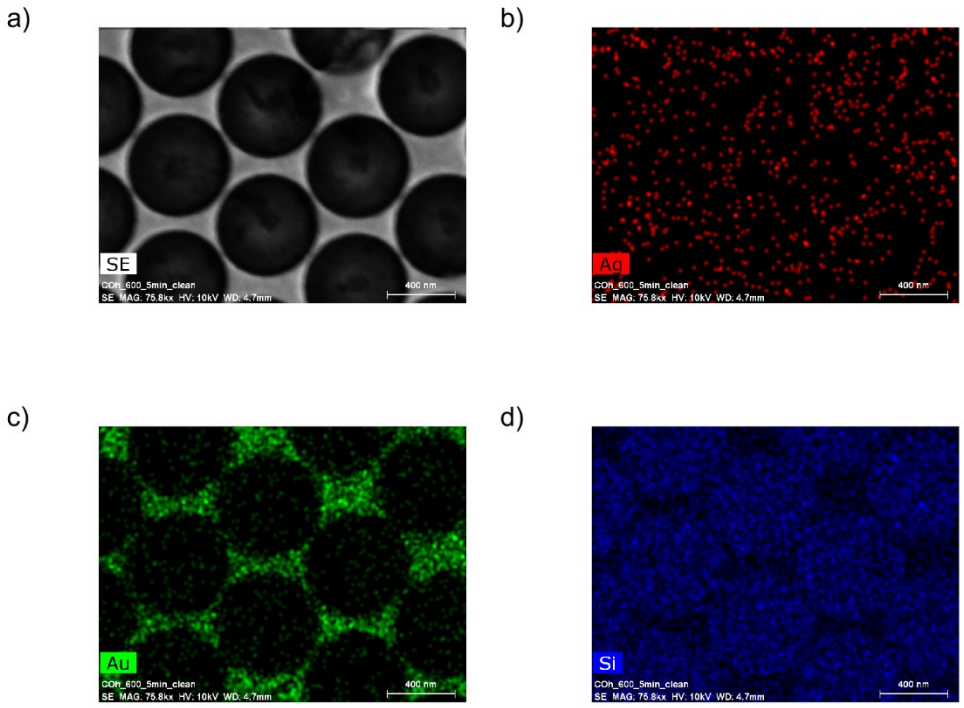


**Figure S4**. EDX images of a pre-deposition (clean) nanoaperture array. (a) Plan view SEM image. (b) Ag EDX image. (c) Au EDX image. (d) Si signal corresponding to the glass substrate in a negative pattern from the metal layers. Scale bars are 400 nm.

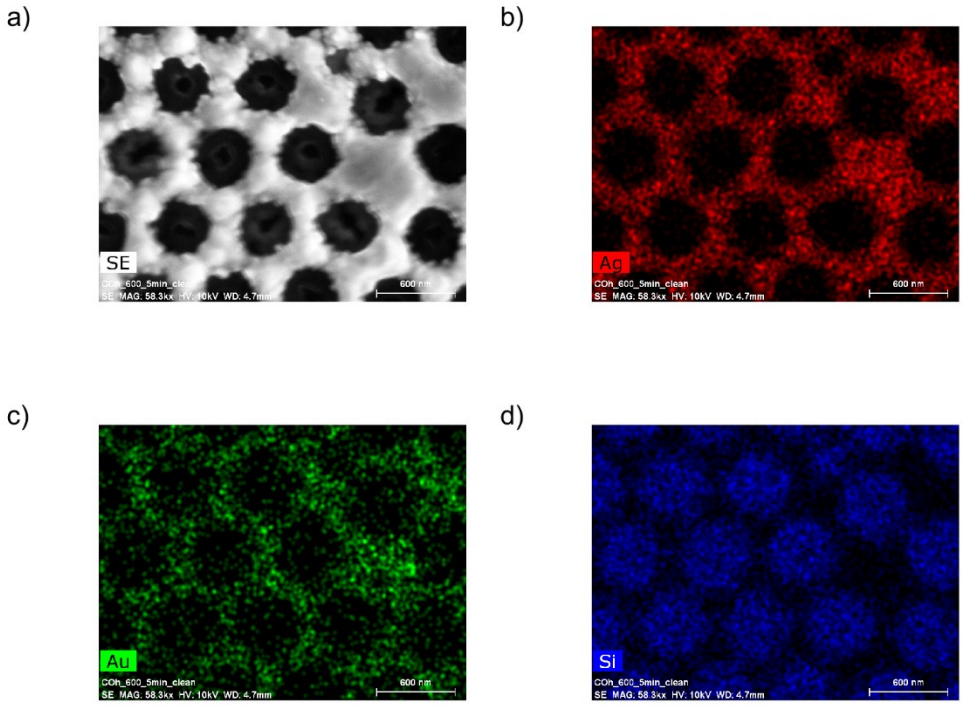


**Figure S5**. EDX images after 5 min Ag deposition. (a) Plan view SEM image. (b) Ag EDX image. (c) Au EDX image. (d) Si signal corresponding to the glass substrate in a negative pattern from the metal layers. Scale bars are 600 nm.