Supporting Information

Structure of Interfacial Water on Gold Electrodes during Hydrogen Evolution in Alkaline Medium: A Spectroscopic Study through Isotopic Dilution

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Rayleigh Range of Raman spectrometer

If the beam focused onto the sample by the microscope objective is assumed to be Gaussian, the beam waist equivalent to half of the diffraction-limited focal spot size is $w_0 = \frac{1}{2}\left(\frac{1.22\lambda}{NA}\right)$. The Rayleigh range, z_0, is the distance over which the intensity of the beam is significant enough. For NA = 0.50 and λ = 633 nm, Gaussian beam physics gives:

$$z_0 = \frac{\pi w_0^2}{\lambda} = \frac{\pi}{4\lambda}\left(\frac{1.22\lambda}{NA}\right)^2 = 2960\, nm\ (\sim 3\ \mu m)$$

Penetration depth in ATR-IR prism

The ATR-IR prism uses ~20 nm Au layer coating on top of the ATR crystal. The penetration depth (*d*) of Au in the IR frequency range 4000 cm^{-1} to 1000 cm^{-1} is ~ 24 nm when calculated according to the equation: $d = \frac{\lambda_0}{2\Pi \mathrm{Im}\ (n)}$, where Im(n)[1] is the imaginary part of the refractive index of Si prism, which is wavelength dependent. Hence the evanescent field reaches the Au-electrolyte interface considerably weakened, and its intensity will continue decreasing exponentially as it penetrates into the electrolyte, although less strongly than within the metal film. An exact quantitative determination of the penetration depth into the electrolyte would require the use of a three-layer model and of effective medium theory to calculate an effective refraction index for the thin layer between the infrared window and the electrolyte. An educated guess is that this will lie between some nanometres and some tens of nanometres.

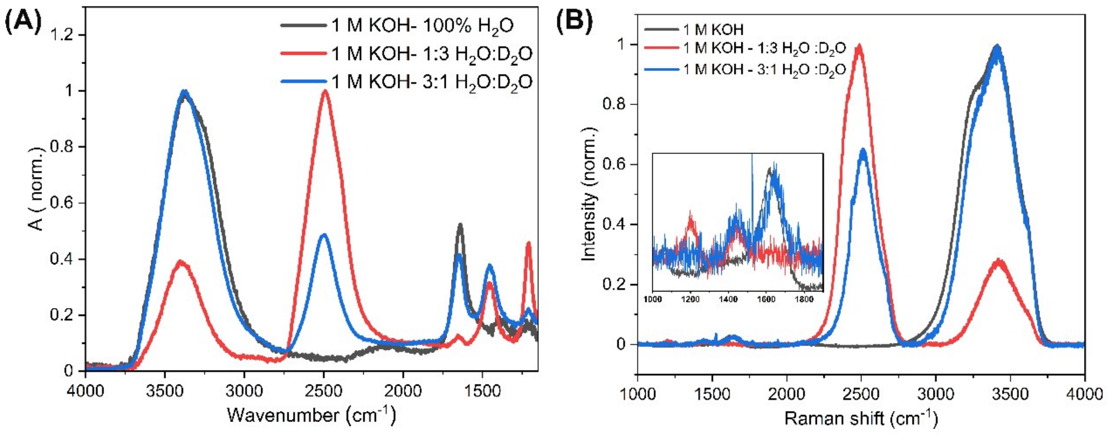

Figure S1 – Bulk ATR-IR (A) and Raman (B) spectra of water and isotopically diluted water.

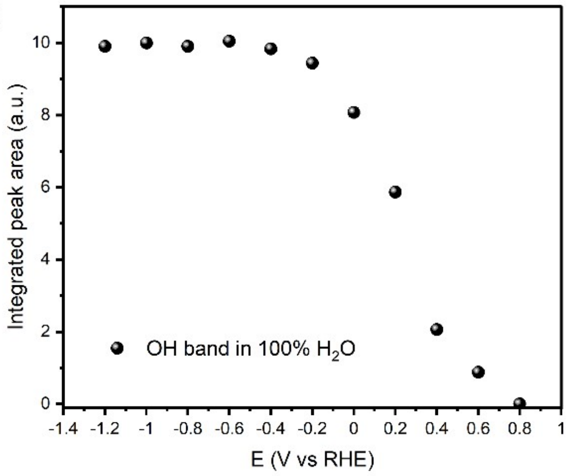

Figure S2- dependence of the integrated intensity of the ν_{OH} band with potential, from the ATR-SEIRA spectra of 1 M KOH solution (100% H_2O). The background spectrum was recorded at 0.8 V.

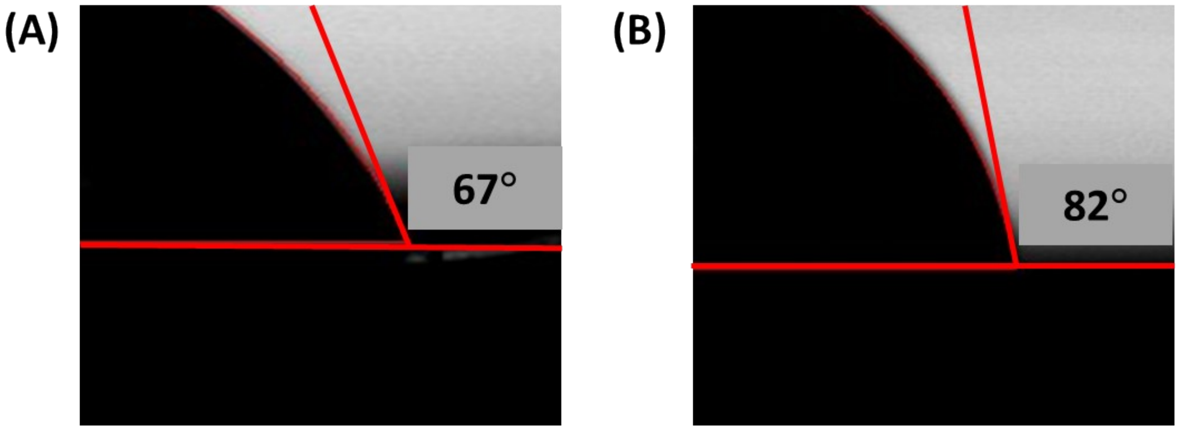

Figure S3- The contact angle on Au nanoparticle coated Au surface used for SERS of (A) H_2O (B) D_2O.

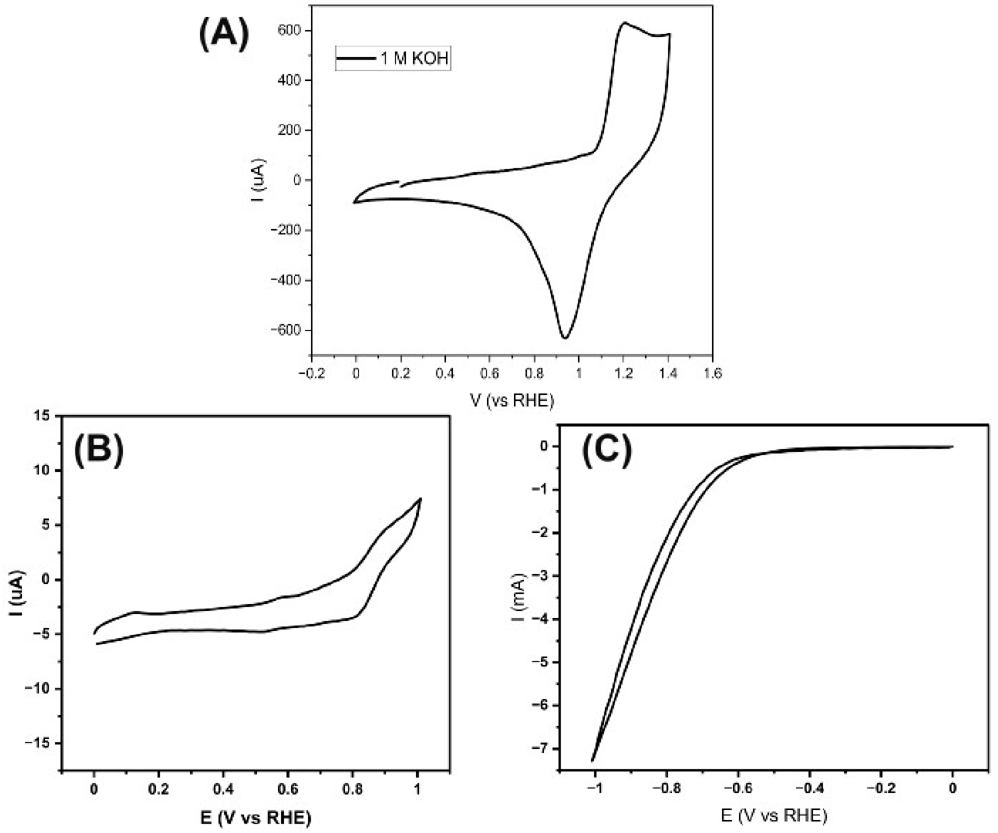

Figure S4- The cyclic voltammogram of Au deposited Si prism showing (A) gold oxidation and reduction (scan rate= 200 mV s^{-1}), (B) the dl layer (scan rate= 10 mV s^{-1}), and (C) the HER region (scan rate= 10 mV s^{-1}).

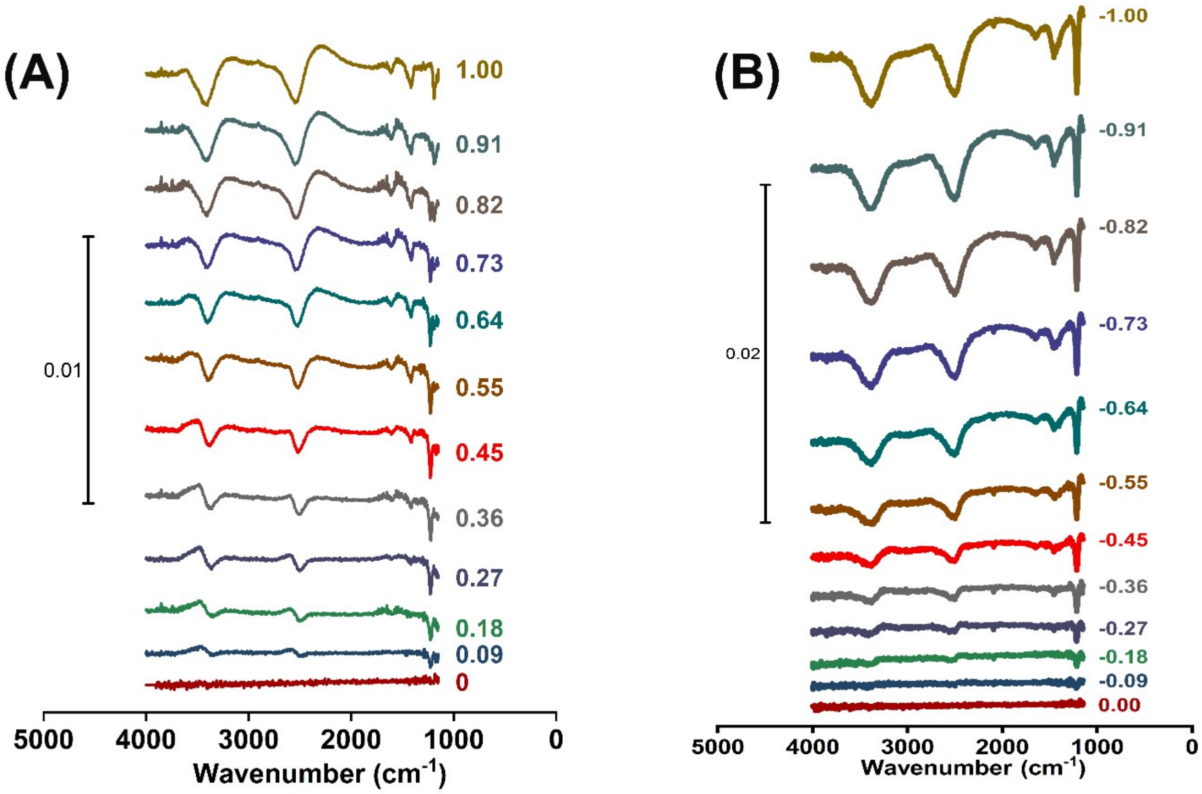

Figure S5- The ATR-SEIRAS data with applied bias for 1:3 H_2O:D_2O in the (A) dl region, and (B) HER region.

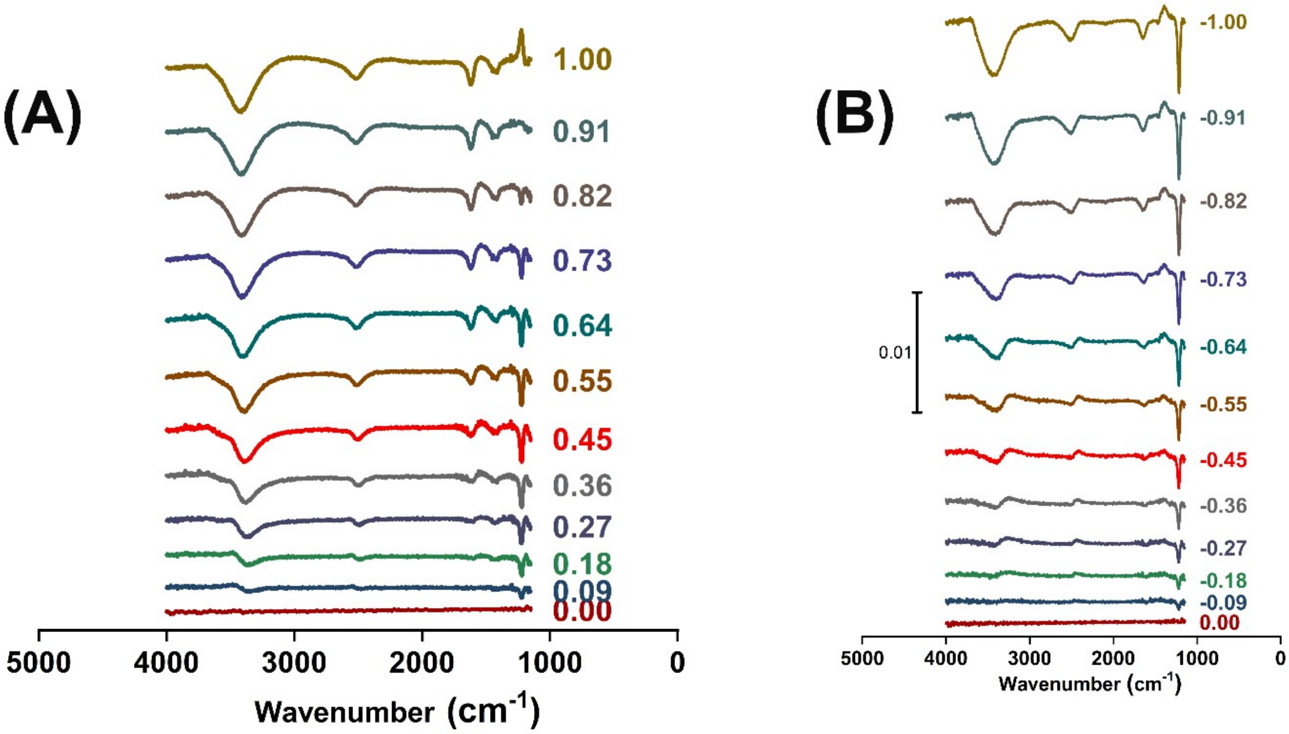

Figure S6- The ATR-SEIRAS data with applied bias for 3:1 H_2O:D_2O in the (A) dl region, and (B) HER region.

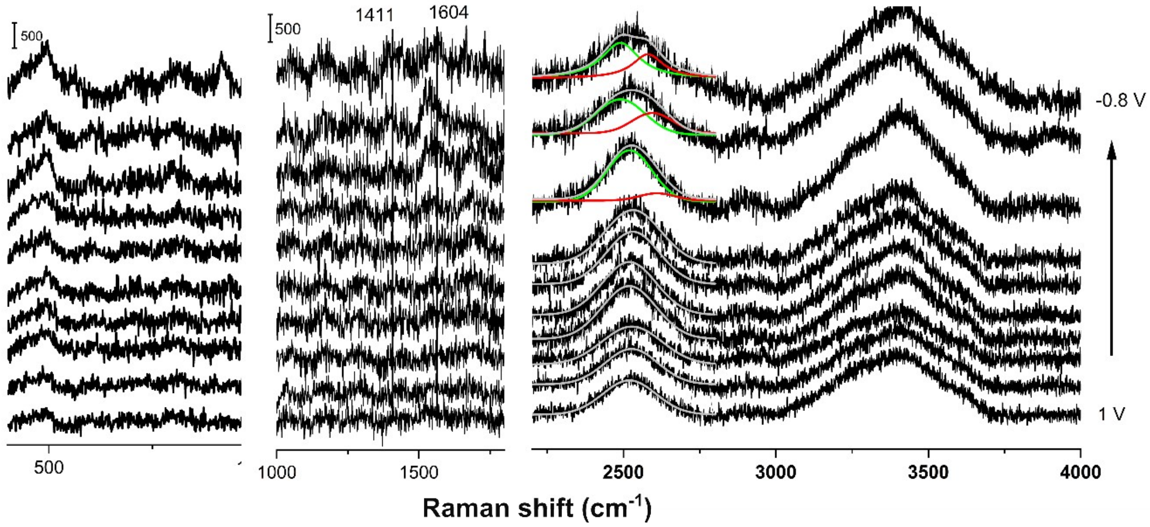

Figure S7- SERS data with applied bias for 3:1 H_2O:D_2O.

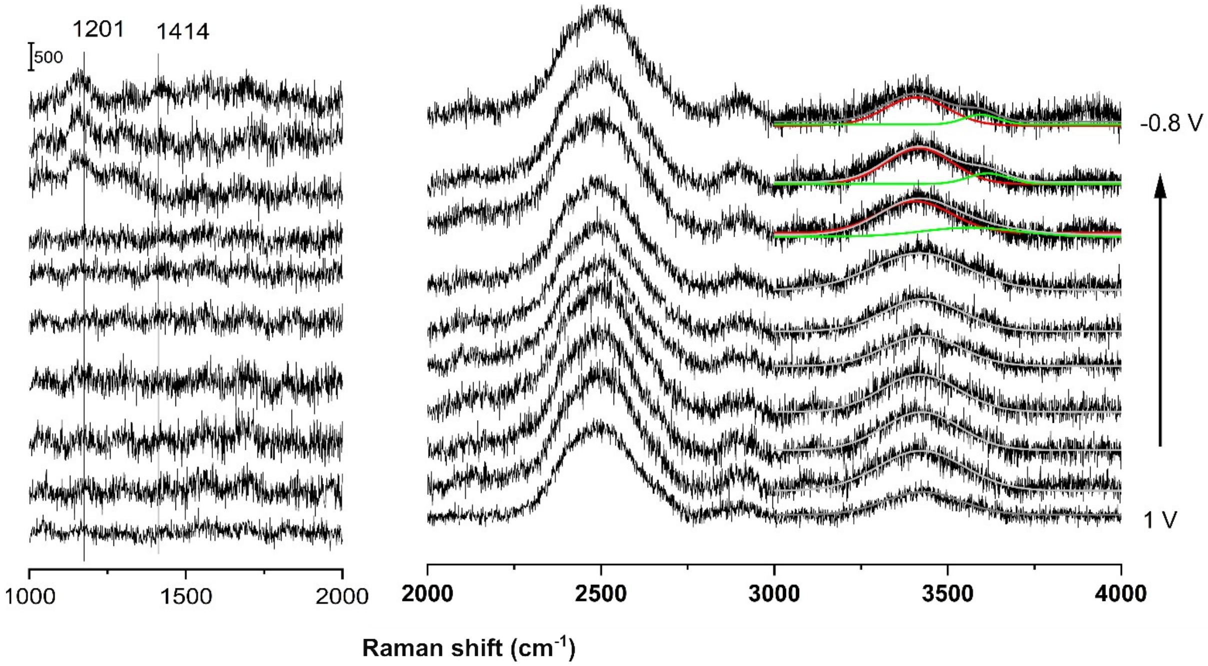

Figure S8- SERS data with applied bias for 1:3 H_2O:D_2O.

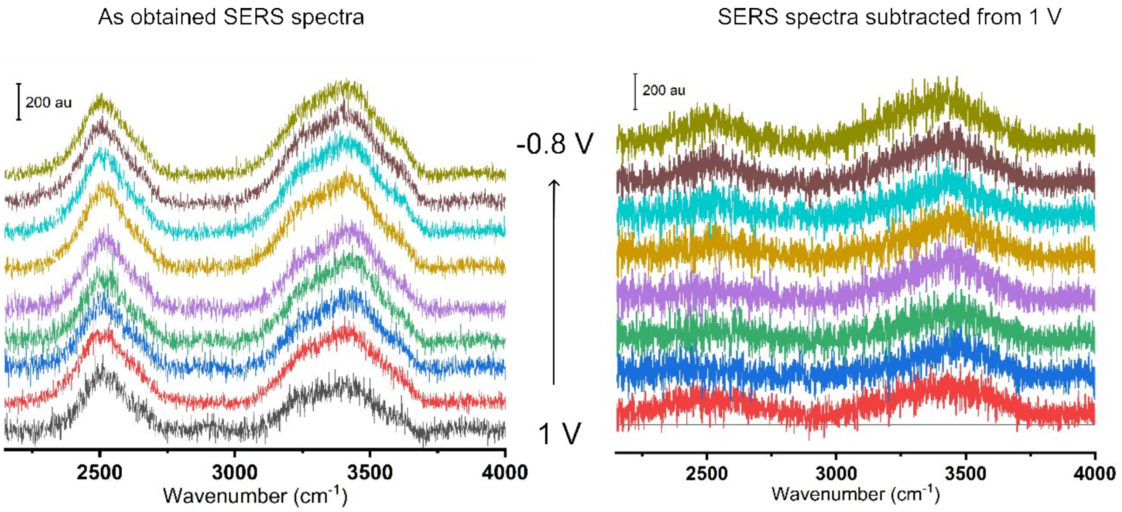

Figure S9 – The as obtained and subtracted from 1 V SERS spectra of 3:1 H_2O:D_2O system.

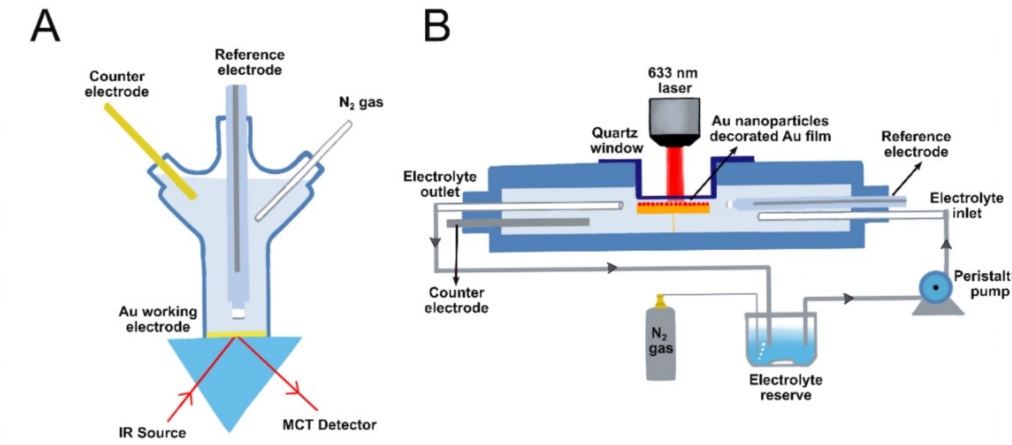

Figure S10: *Operando* ATR-SEIRAS (A) and SERS (B) cell set-ups used in our experiments.

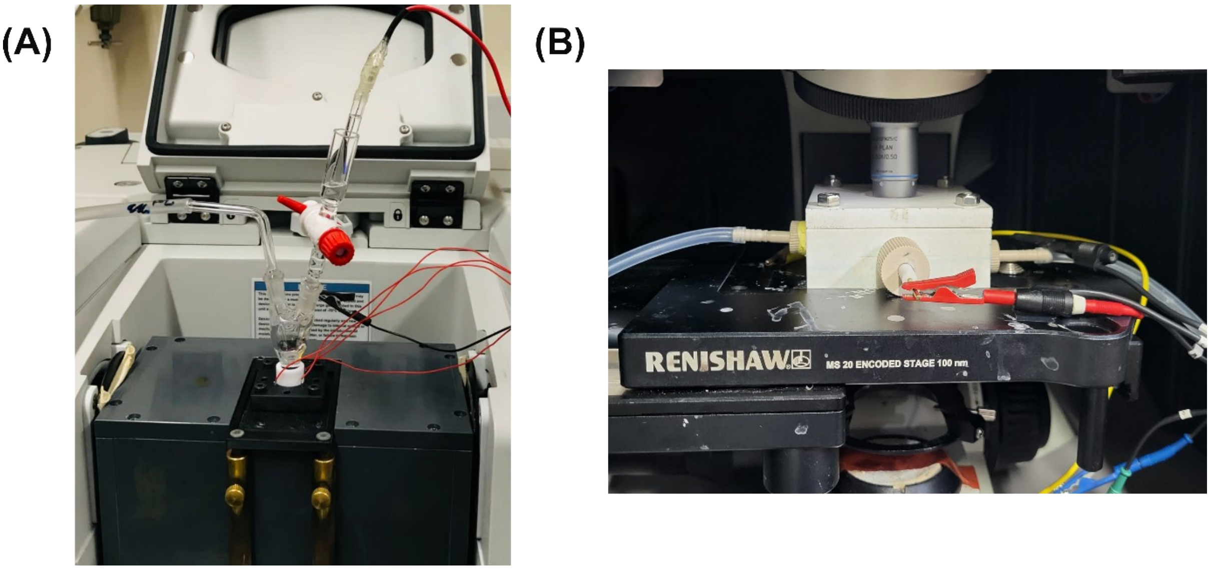

Figure S11- Images showing the home build in situ (A) ATR-SEIRAS cell, and (B) Raman cell.

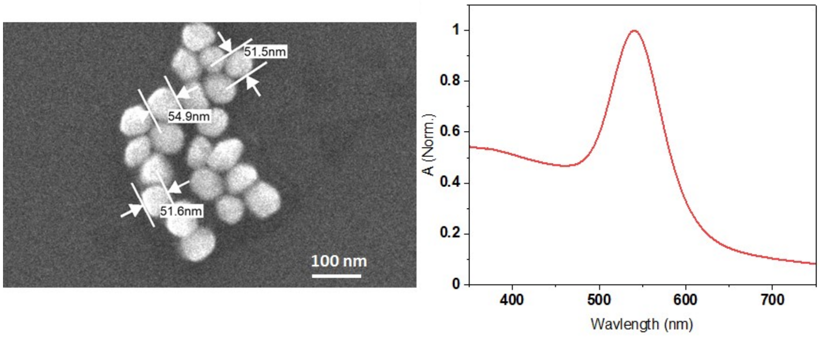

Figure S12 - SEM image showing the Au nanoparticle size ~50-55 nm, and a plasmon peak at 540 nm.

Reference

1. Sallam, Mai O., Guy AE Vandenbosch, Georges Gielen, and Ezzeldin A. Soliman. *Optics express,* 2014, 22.19, 22388-22402.