

Supplementary Information

“Merely measuring the UV-Visible spectrum of gold nanoparticles can change their charge state”

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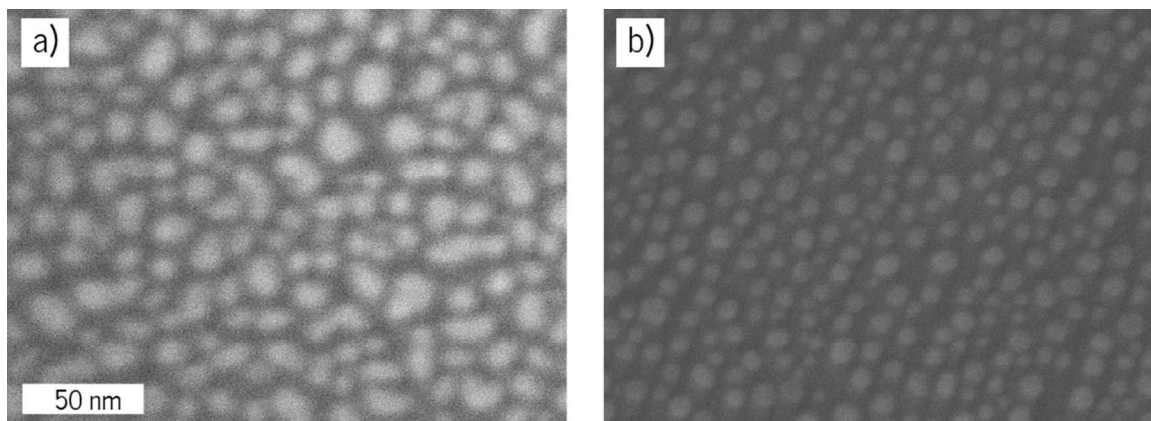


Figure S1. 2 nm mass thickness e-beam deposited gold a) before and b) after annealing at 500 °C in 5 slm N₂ yielding nanoparticles of approximately 5 nm radius.

The parameters in the Lorentzian sum were determined by least squares fitting of eq 1 to the

optical constants of bulk gold measured by Johnson and Christy and constraining ω_p and γ to 9.1 eV and 0.0757 eV, respectively, ε_∞ was determined to be 4.308 eV.¹

$$\varepsilon_1(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\omega\gamma} + \sum_j^N \frac{a_j}{\omega_{0j}^2 - \omega^2 - i\omega\Gamma_j} + \varepsilon_\infty \quad (1)$$

Excellent agreement between the fit and the measured optical constant values are shown in Fig S2, the Lorentzian parameters as determined by the least squares fit are shown in Table S2.

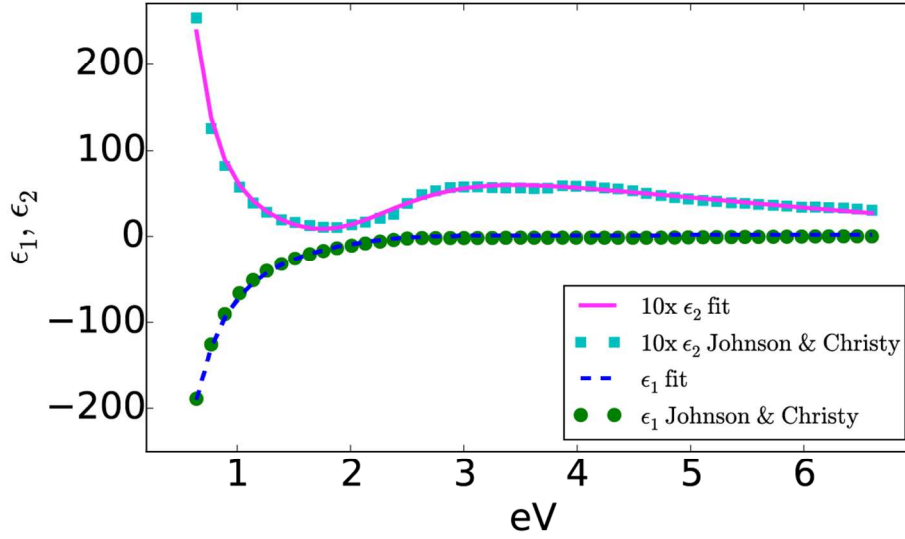


Figure S2. Least squares fitting of eq 1 to the optical constants measured by Johnson and Christy of bulk gold films.

Table S1. Values for the parameters in the summation term of eq 1 from least squares fitting of golds bulk optical constants.

j =	1	2	3
a_j (eV ²)	-21.74	71.37	75.52
ω_{0j} (eV)	-2.06	-5.65	3.33
Γ_j (eV)	1.92	5.83	4.03

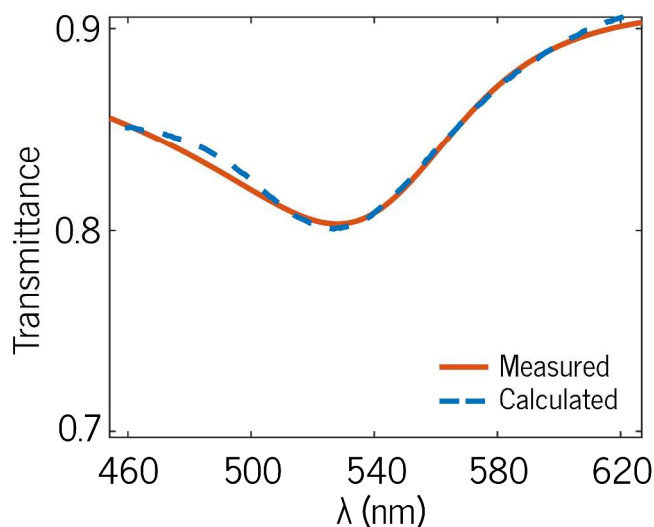


Figure S3. Transmission spectrum of gold nanoparticles of 5 nm radius deposited on quartz. The plasmon resonance has maximum absorbance at ~530 nm.

A Cary 500 UV-Vis-NIR was used for obtaining the transmission and reflection spectra. Below are side profiles below, the spectra were obtained in double beam mode as allowed by the software. Black plate and sample mount were used as the 0% and 100% transmittance baselines. For the reflectance measurement, 300 nm e-beam deposited silver was used as the 100 % reflectance reference and a black plate blocking the beam path was used at the 0% reflectance reference.

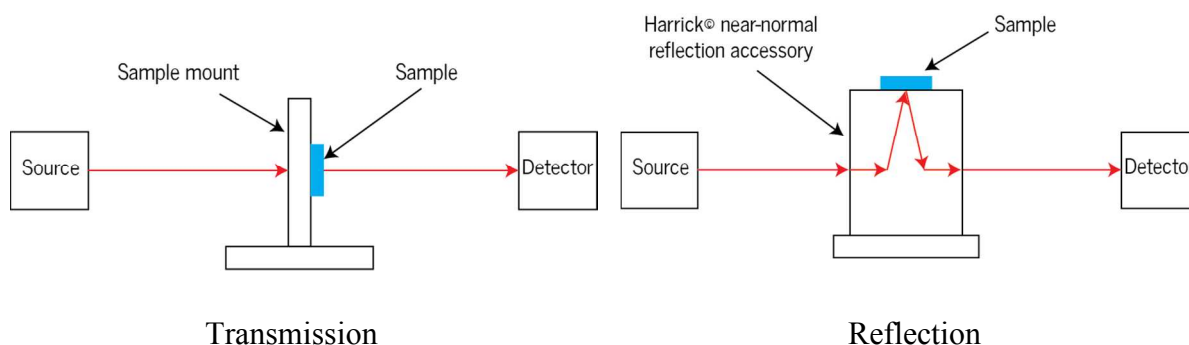


Figure S4. Schematic of the instrumental setup for obtaining transmission and reflection spectra using a Cary 500 UV-Vis-NIR

Below we include the extracted optical parameters for the gold nanoparticles for all samples with various metal-oxide shell thicknesses.

Table S2. Extracted optical parameters for the gold nanoparticles with metal-oxide shells before and after the deposition of either the silver or aluminum bulk layer.

oxide (nm)	Bare		Ag mirror		Bare		Al mirror		
	ω_p (eV)	γ (ev ⁻¹)	ω_p	γ	ω_p	γ	ω_p	γ	
Al ₂ O ₃	2	9	0.350	10.3	0.402	9	0.429	10.2	0.4
	5.5	9.43	0.356	9.51	0.345	9.38	0.472	9.5	0.4
	10	9.24	0.275	9.15	0.316	9.14	0.307	9.13	0.4
SiO ₂	1.5	8.99	0.381	10.6	0.200	9.1	0.300	10.4	0.300
	3.5	9	0.337	9.41	0.200	9.1	0.300	9.49	0.200
	7	9	0.331	9.1	0.200	9.1	0.300	9.2	0.204
TiO ₂	2	9	0.481	11.4	0.358	9.0	0.590	11.52	0.600
	4	9.1	0.446	9.8	0.453	9.1	0.523	9.8	0.441
	7	9.1	0.464	8.9	0.593	9.1	0.549	9.1	0.400

(1) Johnson, P. B.; Christy, R.-W. *Phys. Rev. B* **1972**, *6* (12), 4370.