Gold Nanoparticle-Doped Silk Films as Biocompatible SERS

Substrates

Chengchen Guo, Genevieve N. Hall, John B. Addison, Jeffery L. Yarger*

Department of Chemistry and Biochemistry, Magnetic Resonance Research Center, Arizona State University, Tempe, Arizona, 85287-1604, USA

Supplementary Information

Theory of Surface Plasmon Resonance Simulation for AuNPs[1,2]

For the calculations, the Mie theory is used. The extinction cross-section σ_{ext} of a spherical particle with radius R embedded in a medium with refractive index n_m at a given wavelength is represented by

$$\sigma_{ext} = \frac{2\pi}{|k|^2}\sum(2L + 1)Re(a_L + b_L)$$

(1)

Here, $k = 2\pi n_m/\lambda$ is the wave vector, and $a_L(R, \lambda) \ and \ b_L(R, \lambda)$ are the scattering coefficients defined by equations 2a and 2b.

$$a_L = \frac{m^2\psi_L(mx)\psi_L^{'}(x) - \psi_L^{'}(mx)\psi_L(x)}{m^2\psi_L(mx)\eta_L^{'}(x) - \psi_L^{'}(mx)\eta_L(x)}$$

(2a)

$$b_L = \frac{\psi_L(mx)\psi_L^{'}(x) - \psi_L^{'}(mx)\psi_L(x)}{\psi_L(mx)\eta_L^{'}(x) - \psi_L^{'}(mx)\eta_L(x)}$$

(2b)

The size parameter $x = kR$ and $m = n/n_m$, where n is the complex refractive index of the particle and n_m is the real refractive index of the medium. $\eta_L(x)$ and $\psi_L(x)$ are Ricatti-Bessel functions. The first ten electric dipole terms ($L_{max} = 10$ in Eqns. 2a and 2b) were taken into consideration for better prediction.

For aqueous solution, the calculations were performed with water at 20 °C as the surrounding medium whose refractive index was assumed to be wavelength-independent (n_m=1.33). For AuNP-doped silk film, a wavelength-independent (n_m=1.54) refractive index of silk protein was assumed and applied in the calculations. [3,4] For the gold nanoparticles, the refractive index was modified from the refractive index of bulk gold based on the extended Drude model, which accounts for the influence of the reduced mean free path of the conduction electrons. The complex refractive index

for bulk gold was taken from the experimental work of Johnson and Christy[5], where the original data were fitted with a spline-fit to enable the calculation of Q_{ext} over a continuous range of λ.

The absorption spectra were obtained from the calculated value for the extinction efficiency via Eqn. 3.

$$A = \frac{\pi R^2 Q_{ext} d_0 N}{2.303}$$

(3)

d_0 is the path length of the spectrometer, usually 1 cm, and N is the number density of particles per unit volume.

Table S1. ^{13}C Chemical Shift Assignments for Solid-state NMR Spectra

Residue	Degummed silk	AuNP-silk nanocomposites	Lyophilized silkworm silk
Gly C$_\alpha$	43.3	43.6	44.1
Gly C=O	168 -175	168 -175	168 -175
Ala C$_\alpha$	49.7(β-sheet)	49.9 (β-sheet)	52.5 (α-helix) 49.9 (β-sheet)
Ala C$_\beta$	20.7(β-sheet) 16.6(α-helix)	20.8 (β-sheet) 16.6 (α-helix)	20.7 (β-sheet) 16.4 (α-helix)
Ala C=O	168 -175	168 -175	168 -175
Ser C$_\alpha$	55.3 (β-sheet)	55.2 (β-sheet)	58.9 - 64.9 (α-helix)
Ser C$_\beta$	64.5	64.7	58.9 - 64.9 (α-helix)
Ser C=O	168 -175	168 -175	168 -175
Tyr C$_\delta$	130.4	129.6	131.1
Tyr C$_\varepsilon$	116.0	116.6	115.7
Tyr C$_\zeta$	156.2	156.4	156.5
Tyr C=O	168 -175	168 -175	168 -175

Note: All chemical shifts were referenced to TMS and given in ppm.

Table S2. Summary of Experimental and Simulated Absorption Spectra of AuNPs

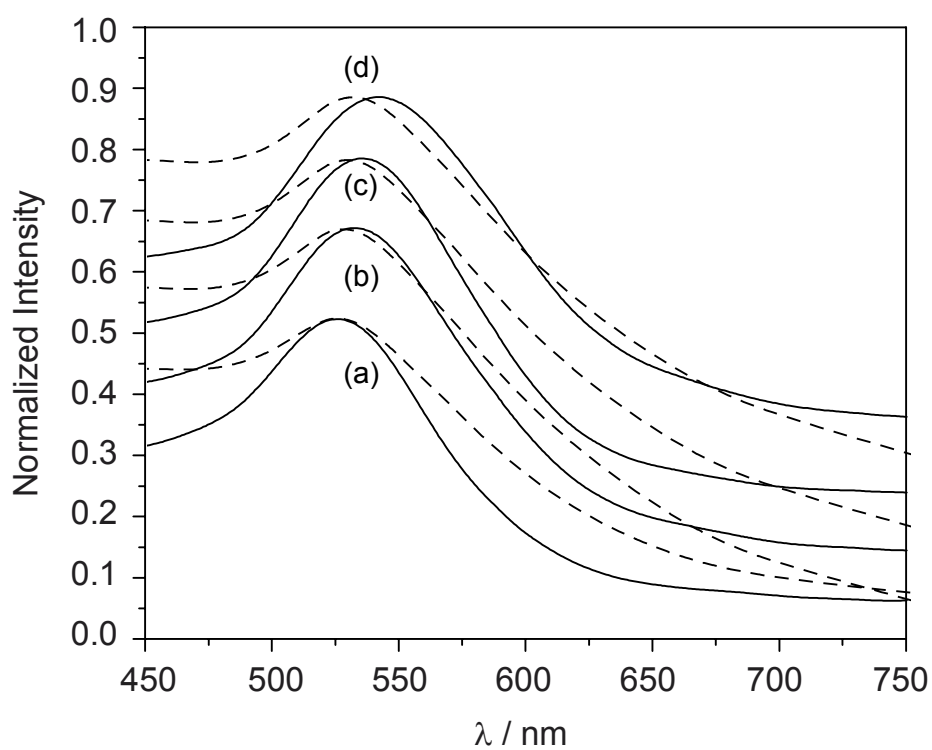| Sample	Diameter /nm	Experimental SPR peak /nm			Simulated SPR peak /nm		
		Aqueous	Silk film	Δλ	Aqueous	Silk film	Δλ
a	24.4	525	541	16	525	540	15
b	38.1	532	550	18	528	545	17
c	44.0	536	554	18	530	550	20
d	50.4	542	563	21	532	553	21

Figure S1. Experimental (solid lines) and simulated (dashed lines) absorption spectra of AuNPs in aqueous solutions with diameters of (a) 24.4 nm, (b) 38.1 nm, (c) 44.0 nm, and (d) 50.4 nm.
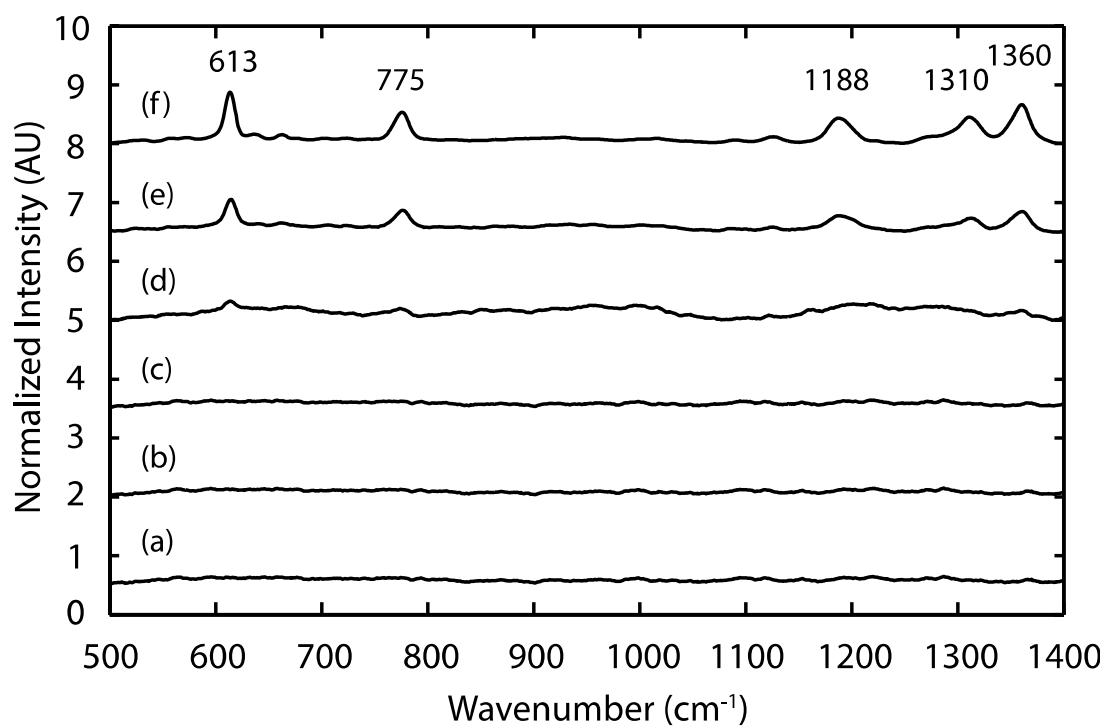
Figure S2. Raman spectra of bare silk films immersed in (a) 0.01 mM, (b) 0.10 mM, and (c) 1.0 mM solutions of rhodamine 6G. SERS spectra of AuNP-silk films immersed in (d) 0.01 mM, (e) 0.10 mM, and (f) 1.0 mM solutions of rhodamine 6G. All films were immersed in the appropriate solutions for ten minutes and then dried in air. SERS measurements were performed on a homemade Raman spectrometer with a 632.8 nm helium-neon excitation laser and a triple-grating monochromator (SpectraPro 300i, Action Research). The laser beam was focused onto the sample through a Mitutoyo M Plan Apo 50x objective with 0.42 N.A. Measuring power at the samples was 1 mW, and all spectra were collected in single scans with exposure times of 30 s.

Table S3. Vibrational assignments obtained from Raman spectra

Bulk 4-DMAP (cm^{-1})	4-DMAP on AuNP-silk film (cm^{-1})	Vibrational assignment
749	761	C-N-C wagging
949	949	Ring breathing CH$_3$ rocking
984	1016	Trigonal bending C-H out-plane bending
1063	1065	CH$_3$ rocking
1231	1228	C-H in-plane bending

References

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