Additional Material

Tips vs. Holes: ×10 Higher Scattering in FIB-made Plasmonic Nanoscale Arrays for Spectral Imaging

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Appendix A Surface-Averaged Electromagnetic Enhancement

In the Supporting Information (SI) the maximum values of the electromagnetic intensity enhancement and the SERS enhancement were calculated for a prolate spheroid. In this section the average values over the surface are computed following [Etchegoin-Leru] and [Bohren-Hoffman] and compared to the maximum values.

The surface average is computed by integrating the local field intensity over the surface. The electric field is found by solving Laplace's equation for the electric potential in ellipsoidal coordianates. Appropriate boundary condition must be imposed at the surface of the structure along with the constraint that at large distances the influence of the structure decays and the field approaches that of the incident field, of magnitude E_0 along the *z*-axis. A solution is most conveniently found based on the unperturbed potential, describing the incident field alone, using the method of variation of parameters: $\varphi = C(\vec{r})\varphi_0(\vec{r})$. The symmetry may be exploited to write $C(\vec{r})$ as a function of the noncompact coordinate – the generalization of the radial coordinate – alone. This gives a differential equation for which may be solved by integration. For the prolate (and oblate) spheroids, the integral may be computed analytically.

Local Field

Sphere

For the sphere the electric field on the outer surface can be expressed as

$$\vec{E}_{\text{out}} = E_0 \frac{3\epsilon_M \hat{z} + 3(\epsilon(\lambda) - \epsilon_M)(\hat{z}\cdot\hat{\rho})\hat{\rho}}{\epsilon(\lambda) + 2\epsilon_M} = E_0 \frac{3\epsilon_M(\hat{z} - (\hat{z}\cdot\hat{\rho})\hat{\rho}) + 3\epsilon(\lambda)(\hat{z}\cdot\hat{\rho})\hat{\rho}}{\epsilon(\lambda) + 2\epsilon_M} \quad (1)$$

where $\hat{\rho}$ is the radial unit vector, and in spherical coordinates

$$\hat{z}\cdot\hat{\rho} = \cos\theta = \frac{z}{R}. \quad (2)$$

In the right-hand expression, the field has been decomposed into two components, one normal to the surface and one parallel.

Prolate Spheroid

For the prolate spheroid expression (1) for the electric field outside the surface becomes

$$\vec{E}_{\text{out}} = E_0 \frac{3\epsilon_M \hat{z} + 3(\epsilon(\lambda) - \epsilon_M)(\hat{z}\cdot\hat{n})\hat{n}}{3L_z\epsilon(\lambda) + (3 - 3L_z)\epsilon_M} = E_0 \frac{3\epsilon_M(\hat{z} - (\hat{z}\cdot\hat{n})\hat{n}) + 3\epsilon(\lambda)(\hat{z}\cdot\hat{n})\hat{n}}{3L_z\epsilon(\lambda) + (3 - 3L_z)\epsilon_M} \quad (3)$$

where the unit normal vector $\hat{n}$ is found by normalizing the gradient of the surface potential function in **Error! Reference source not found.**:

$$\hat{n} = \frac{\left(\frac{x}{a^2}, \frac{y}{a^2}, \frac{z}{c^2}\right)}{\sqrt{\frac{r^2}{a^4} + \frac{z^2}{c^4}}} \quad (4)$$

and $r = \sqrt{x^2 + y^2}$ is the in-plane radius. From (4) it follows that

$$|\hat{z}\cdot\hat{n}|^2 = \frac{z^2}{c^4\left(\frac{r^2}{a^4} + \frac{z^2}{c^4}\right)} = \frac{\frac{a^2}{c^2}\frac{z^2}{c^2}}{\left(1 - \left(1 - \frac{a^2}{c^2}\right)\frac{z^2}{c^2}\right)}. \quad (5)$$

The local intensity enhancements follow from the expression for the fields upon computing the square of the magnitude of the field. The maximum value for the enhancement occurs at the 'poles' where the *z*-axis is normal to the surface, $|\hat{z}\cdot\hat{n}| = 1$.

At resonance the dielectric function satisfies $\epsilon(\lambda_*) = -2\epsilon_M + i\epsilon''(\lambda_*)$ for the sphere, and $\epsilon(\lambda_*) = -\left(\frac{1}{L_z} - 1\right)\epsilon_M + i\epsilon''(\lambda_*)$ for the spheroid. Substituting the appropriate expression into (1) and (3) and squaring gives the local intensity enhancement on-resonance for the sphere and the spheroid respectively. Evaluating at the poles gives leads to the expressions for the maximum enhancement on-resonance which was presented in Section XXX and is repeated here for convenience:

Sphere:

$$M_{\text{max,res}} \equiv \frac{E^2}{{E_0}^2} = \left|\frac{3\epsilon(\lambda_*)}{\epsilon''(\lambda_*)}\right|^2 = 9\left\{\left(\frac{2\epsilon_M}{\epsilon''(\lambda_*)}\right)^2 + 1\right\}. \quad (6)$$

Prolate spheroid:

$$M_{\text{max,res}} = \left|\frac{3\epsilon(\lambda_*)}{3L_z\epsilon''(\lambda_*)}\right|^2 = \frac{9}{(3L_z)^2}\left\{\left(\frac{1}{L_z}-1\right)^2\left(\frac{\epsilon_M}{\epsilon''(\lambda_*)}\right)^2+1\right\}. \tag{7}$$

Average Intensity Enhancement, on-resonance

The average of the intensity enhancement over the surface of the sphere will clearly be smaller than the maximum. To compute one must integrate the local intensity enhancement over the surface and divide by the surface area. Both are computed by using the appropriate coordinates, spherical polar coordinates or ellipsoidal coordinates.

Sphere

For the sphere the following expression is obtained for the average intensity enhancement, on-resonance:

$$\begin{aligned}\langle M_{\text{Sphere}}\rangle &= \frac{|3\epsilon_M|^2(1-\langle|\hat{z}\cdot\hat{\rho}|^2\rangle)+|3\epsilon(\lambda)|^2\langle|\hat{z}\cdot\hat{\rho}|^2\rangle}{|\epsilon''(\lambda_*)|^2}\\ &= \frac{|3\epsilon_M|^2+(|3\epsilon(\lambda)|^2-|3\epsilon_M|^2)\langle|\hat{z}\cdot\hat{\rho}|^2\rangle}{|\epsilon''(\lambda_*)|^2}.\end{aligned} \tag{8}$$

Using $\langle|\hat{z}\cdot\hat{\rho}|^2\rangle = \langle\cos^2\theta\rangle = \frac{1}{3}$ and substituting the resonance condition for $\epsilon(\lambda)$ in the numerator leads to

$$\langle M_{\text{Sphere}}\rangle = 9\left\{\left(\frac{\epsilon_M}{\epsilon''(\lambda_*)}\right)^2+\left[(2^2-1)\left(\frac{\epsilon_M}{\epsilon''(\lambda_*)}\right)^2+1\right]\frac{1}{3}\right\} = 9\left\{2\left(\frac{\epsilon_M}{\epsilon''(\lambda_*)}\right)^2+\frac{1}{3}\right\}. \tag{9}$$

The average enhancement is thus mildly reduced relative to the maximum enhancement. For the gold sphere in air the average intensity enhancement amounts to $\langle M\rangle_{\text{Sph}} = 4.125$ a decrease by factor of 0.37 relative to maximum value for the enhancement found above (section XXX) $M_{\text{max,Sph}} = 11.3$.

Prolate Spheroid

For the prolate spheroid the expression for the average intensity enhancement on-resonance is obtained similarly:

$$\begin{aligned}\langle M_{\text{Prolate}}\rangle &= \frac{|3\epsilon_M|^2(1-\langle|\hat{z}\cdot\hat{n}|^2\rangle)+|3\epsilon(\lambda)|^2\langle|\hat{z}\cdot\hat{n}|^2\rangle}{|3L_z\epsilon''(\lambda_*)|^2}\\ &= \frac{|3\epsilon_M|^2+(|3\epsilon(\lambda)|^2-|3\epsilon_M|^2)\langle|\hat{z}\cdot\hat{n}|^2\rangle}{|3L_z\epsilon''(\lambda_*)|^2}.\end{aligned} \tag{10}$$

Inserting the resonance condition into the numerator as well gives

$$\langle M_{\text{prolate}}\rangle = \frac{9}{(3L_z)^2}\left\{\left(\frac{\epsilon_M}{\epsilon''(\lambda_*)}\right)^2+\left[\frac{1}{L_z}\left(\frac{1}{L_z}-2\right)\left(\frac{\epsilon_M}{\epsilon''(\lambda_*)}\right)^2+1\right]\langle|\hat{z}\cdot\hat{n}|^2\rangle\right\}. \tag{11}$$

By performing the appropriate integral, $\langle|\hat{z}\cdot\hat{n}|^2\rangle$ can be expressed in terms of the eccentricity, e, of the cross section. Using $e = \sqrt{1-\frac{1}{\mathrm{AR}^2}}$ to relate the eccentricity and the aspect ratio the relation obtained is

$$\langle|\hat{z}\cdot\hat{n}|^2\rangle = \frac{1-e^2}{e^2}\frac{\frac{1}{e\sqrt{1-e^2}}\sin^{-1}e - 1}{\frac{1}{e\sqrt{1-e^2}}\sin^{-1}e+1} = \frac{1}{\mathrm{AR}^2-1}\frac{\frac{\mathrm{AR}^2}{\sqrt{\mathrm{AR}^2-1}}\sin^{-1}\left(\frac{\sqrt{\mathrm{AR}^2-1}}{\mathrm{AR}}\right)-1}{\frac{\mathrm{AR}^2}{\sqrt{\mathrm{AR}^2-1}}\sin^{-1}\left(\frac{\sqrt{\mathrm{AR}^2-1}}{\mathrm{AR}}\right)+1}, \tag{12}$$

which asymptotes at high aspect ratio to

$$\langle|\hat{z}\cdot\hat{n}|^2\rangle \approx \frac{1}{\mathrm{AR}^2} + o\left(\frac{1}{\mathrm{AR}^2}\right). \tag{13}$$

Inserting **Error! Reference source not found.** , $\frac{1}{L_z} \approx \mathrm{AR}\left(\frac{\mathrm{AR}}{\ln(\mathrm{AR})}\right)$, from Section XXX above, then leads to

$$\langle M\rangle \approx \mathrm{AR}^2\left\{\left(\frac{\mathrm{AR}}{\ln(\mathrm{AR})}\right)^2 + \left(\frac{\mathrm{AR}}{\ln(\mathrm{AR})}\right)^4\right\}\left(\frac{\epsilon_M}{\epsilon''(\lambda_*)}\right)^2. \tag{14}$$

The average enhancement is thus reduced by $\frac{1}{\mathrm{AR}^2}$ relative to the maximum value: it scales as $\mathrm{AR}^2\left(\frac{\mathrm{AR}}{\ln(\mathrm{AR})}\right)^4$ rather than $\mathrm{AR}^4\left(\frac{\mathrm{AR}}{\ln(\mathrm{AR})}\right)^4$.

For a gold particle in air with aspect ratio AR = 2 the average intensity enhancement is found to be $\langle M\rangle_{Prolate} = 10.6$ a nearly twenty-fold reduction relative to the maximum value computed in section XXX, $M_{max,Prol} = 198$. The gain in enhancement of a prolate spheroid relative to a sphere is also reduced when using the average values: $\frac{\langle M\rangle_{Prolate}}{\langle M\rangle_{Sph}} = 2.58$, significantly less than the value found (section XXX) for the ratio of the maximum values, $\frac{M_{Prolate}}{M_{Sphere}} \approx 18$.

Average SERS Enhancement, On-resonance

In the E^4 approximation the SERS enhancement is found as the square of the intensity enhancement. To find the average SERS enhancement one must integrate the square of the local intensity enhancement – ie the fourth power of the local field – over the surface.

Sphere

For the sphere this can be written on-resonance as:

$$\langle EF_{\mathrm{SERS}}\rangle = \langle M^2\rangle = \frac{\langle(|3\epsilon_M|^2(1-|\hat{z}\cdot\hat{n}|^2) + |3\epsilon(\lambda)|^2|\hat{z}\cdot\hat{n}|^2)^2\rangle}{|\epsilon''(\lambda_*)|^4}. \tag{15}$$

Expanding gives

$$\langle EF_{\mathrm{SERS}}\rangle = \frac{|3\epsilon_M|^4(1-2\langle|\hat{z}\cdot\hat{n}|^2\rangle + \langle|\hat{z}\cdot\hat{n}|^4\rangle) + 2|3\epsilon(\lambda)|^2|3\epsilon_M|^2\{\langle|\hat{z}\cdot\hat{n}|^2\rangle - \langle|\hat{z}\cdot\hat{n}|^4\rangle\} + |3\epsilon(\lambda)|^4\langle|\hat{z}\cdot\hat{n}|^4\rangle}{|\epsilon''(\lambda_*)|^4}. \tag{16}$$

Inserting $\langle|\hat{z}\cdot\hat{n}|^2\rangle = \langle\cos^2\theta\rangle = \frac{1}{3}$ and $\langle|\hat{z}\cdot\hat{n}|^4\rangle = \langle\cos^4\theta\rangle = \frac{1}{5}$ together with the resonance condition for the sphere, now leads to

$$\langle EF_{\text{SERS}}\rangle = \frac{27}{5}\left\{3 + 28\left(\frac{\epsilon_M}{\epsilon''(\lambda_*)}\right)^2 + 72\left(\frac{\epsilon_M}{\epsilon''(\lambda_*)}\right)^4\right\}. \tag{17}$$

For the gold sphere in air this gives $\langle EF_{\text{SERS,Sph}}\rangle = 27.2$ for the average value, significantly less than the maximum value $EF_{\text{SERS,Sph,max}} = 127$ found above (section XXX).

<u>Prolate Spheroid</u>

For the prolate spheroid the expression generalizing (15) is:

$$\langle EF_{\text{SERS}}\rangle = \langle M^2\rangle = \frac{\langle(|3\epsilon_M|^2 + (|3\epsilon(\lambda)|^2 - |3\epsilon_M|^2)|\hat{z}\cdot\hat{n}|^2)^2\rangle}{|3L_z\epsilon''(\lambda_*)|^4} \tag{18}$$

Expanding as before one obtains

$$\langle EF_{\text{SERS}}\rangle = \frac{1}{|L_z|^4}\frac{|\epsilon_M|^4 + 2|\epsilon_M|^2(|\epsilon(\lambda)|^2 - |\epsilon_M|^2)\langle|\hat{z}\cdot\hat{n}|^2\rangle + (|\epsilon(\lambda)|^2 - |\epsilon_M|^2)^2\langle|\hat{z}\cdot\hat{n}|^4\rangle}{|\epsilon''(\lambda_*)|^4}. \tag{19}$$

On resonance $\left|\frac{\epsilon(\lambda)}{\epsilon''(\lambda_*)}\right|^2 = \left[\left(\frac{1}{L_z} - 1\right)^2\left(\frac{\epsilon_M}{\epsilon''(\lambda_*)}\right)^2 + 1\right]$ as usual, so

$$\begin{aligned}\langle EF_{\text{SERS}}\rangle_{\text{Prolate}} = \frac{1}{|L_z|^4}\Bigg\{&\left(\frac{\epsilon_M}{\epsilon''(\lambda_*)}\right)^4 \\ &+ 2\left(\frac{\epsilon_M}{\epsilon''(\lambda_*)}\right)^2\left[\frac{1}{L_z}\left(\frac{1}{L_z} - 2\right)\left(\frac{\epsilon_M}{\epsilon''(\lambda_*)}\right)^2 + 1\right]\langle|\hat{z}\cdot\hat{n}|^2\rangle \\ &+ \left[\frac{1}{L_z}\left(\frac{1}{L_z} - 2\right)\left(\frac{\epsilon_M}{\epsilon''(\lambda_*)}\right)^2 + 1\right]^2\langle|\hat{z}\cdot\hat{n}|^4\rangle\Bigg\}.\end{aligned} \tag{20}$$

The dependence of $\langle|\hat{z}\cdot\hat{n}|^2\rangle$ on the aspect ratio is described by (12) above. For the fourth power one has [Etchegoin-Leru]

$$\langle|\hat{z}\cdot\hat{n}|^4\rangle = \frac{1-e^2}{e^4}\frac{3 - e^2 - 3\frac{\sqrt{1-e^2}}{e}\sin^{-1}e}{1 + \frac{1}{e\sqrt{1-e^2}}\sin^{-1}e} \tag{21}$$

As before the eccentricity equals $e = \sqrt{1 - \frac{1}{\text{AR}^2}}$ and thus

$$\langle|\hat{z}\cdot\hat{n}|^4\rangle = \frac{\text{AR}^2}{(\text{AR}^2-1)^2}\frac{2 + \frac{1}{\text{AR}^2} - \frac{3}{\sqrt{\text{AR}^2-1}}\sin^{-1}\left(\frac{\sqrt{\text{AR}^2-1}}{\text{AR}}\right)}{1 + \frac{\text{AR}^2}{\sqrt{\text{AR}^2-1}}\sin^{-1}\left(\frac{\sqrt{\text{AR}^2-1}}{\text{AR}}\right)} \tag{22}$$

For large aspect ratio this is asymptotic to

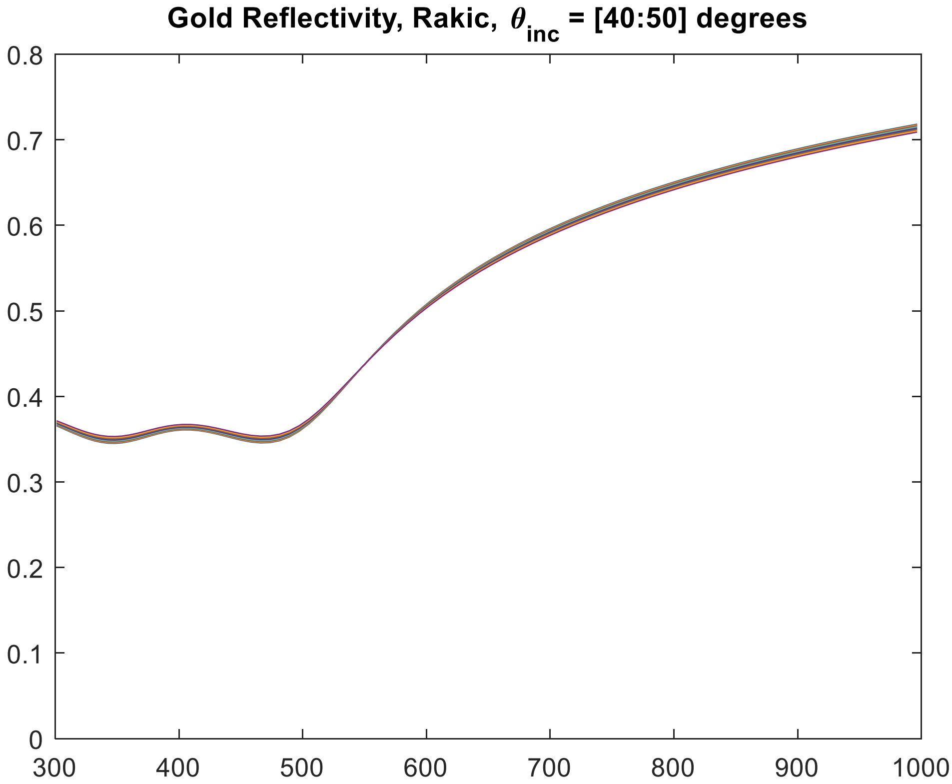
$$\langle|\hat{z}\cdot\hat{n}|^4\rangle \approx \frac{2}{\text{AR}^3\sin^{-1}(1)} = \frac{4}{\pi}\frac{1}{\text{AR}^3} \tag{23}$$

Inserting this and expressions (12) and Eq XXX for the asymptotic behavior of $\langle|\hat{z}\cdot\hat{n}|^2\rangle$ and $\frac{1}{L_z}$ respectively, into expression (20) for $\langle EF_{\mathrm{SERS}}\rangle$ shows the behavior of the latter at large aspect ratios to be

$$\langle EF_{\mathrm{SERS}}\rangle \approx \mathrm{AR}^5\left(\frac{\mathrm{AR}}{\ln(\mathrm{AR})}\right)^8 \frac{4}{\pi}\left(\frac{\epsilon_M}{\epsilon''(\lambda_*)}\right)^4. \qquad (24)$$

Comparing to the maximum SERS enhancement which scales as $\mathrm{AR}^8\left(\frac{\mathrm{AR}}{\ln(\mathrm{AR})}\right)^8$ (Eq XXX), it is interesting to note that while the intensity enhancement is reduced upon averaging over the surface by a factor of $\frac{1}{\mathrm{AR}^2}$, its square, the SERS enhancement, is reduced only by a factor of $\frac{1}{\mathrm{AR}^3}$.

For a gold particle in air with aspect ratio AR = 2 the average SERS enhancement is found to be $\langle EF_{\mathrm{SERS}}\rangle_{\mathrm{Prolate}} = 4844$ a reduction of more than eight-fold relative to the maximum value computed in section XXX, $EF_{\mathrm{SERS,Prol,max}} \cong 40{,}000$. The gain in enhancement of a prolate spheroid relative to a sphere, however is only moderately reduced when using the average values: $\frac{\langle EF_{\mathrm{SERS}}\rangle_{\mathrm{Prolate}}}{\langle EF_{\mathrm{SERS}}\rangle_{\mathrm{Sph}}} \approx 178$, smaller yet still on the same order as the ratio of the maximum values, $\frac{EF_{\mathrm{SERS,Prol,max}}}{EF_{\mathrm{SERS,Sph,max}}} \approx 310$, computed above in (section XXX) . This is consistent with what was noted for the scaling: the decrease in the average SERS enhancement is less than one might extrapolate from its definition as the square of the intensity enhancement.


Gold Reflectivity, Rakic, θ_{inc} = [40:50] degrees
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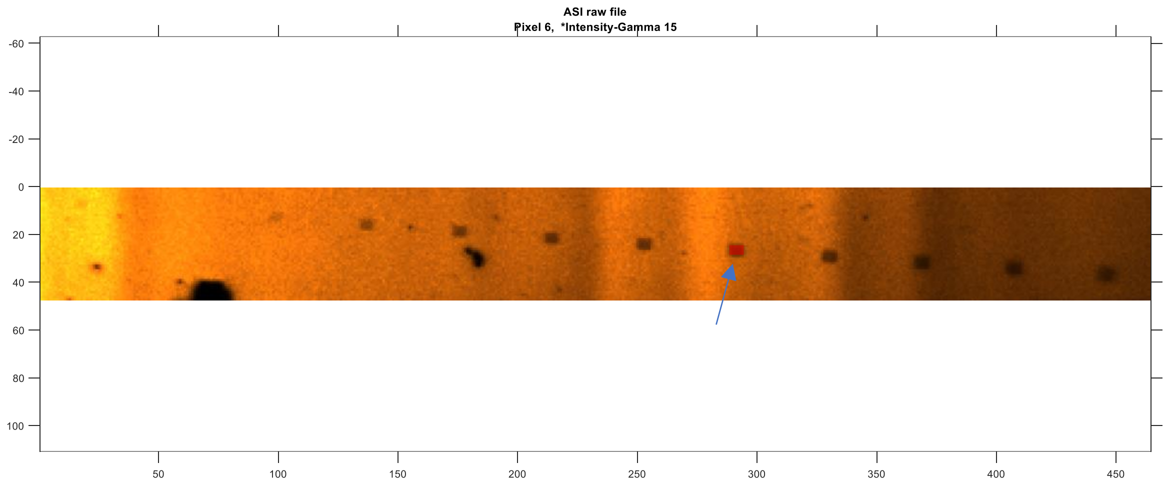
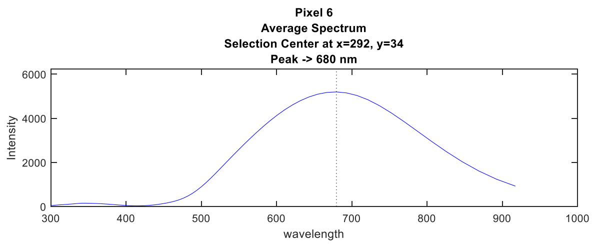
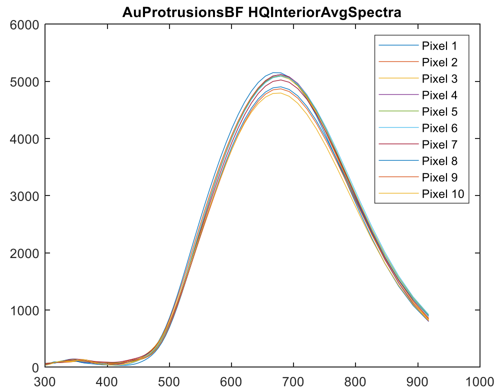
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
300
400
500
600
700
800
900
1000



(a)

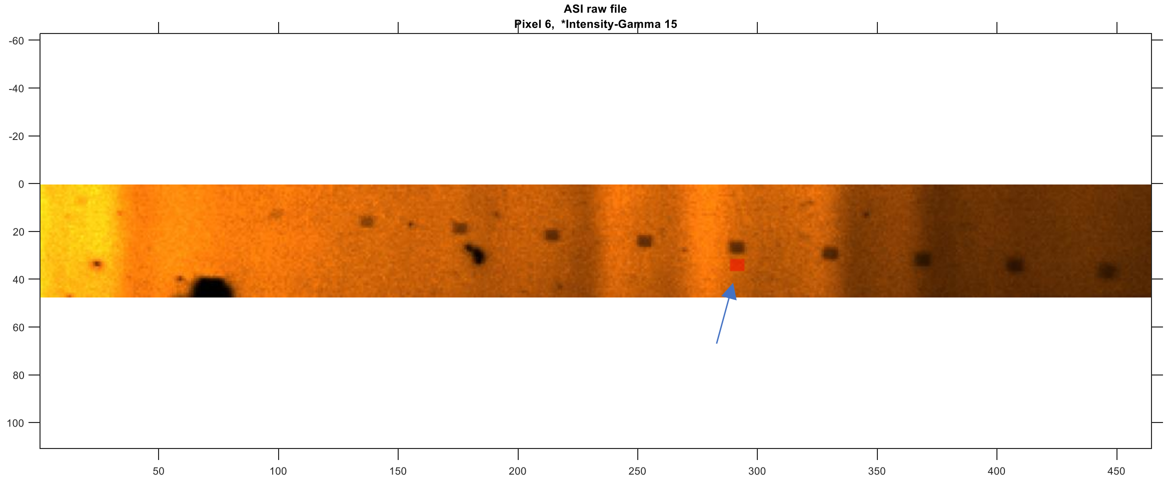


(b)



(c)

Figure 100



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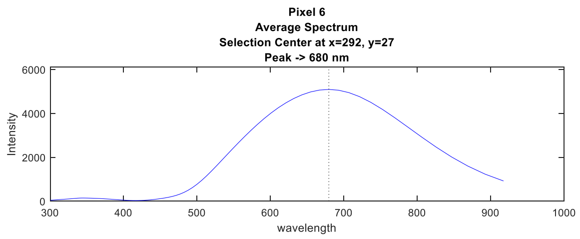

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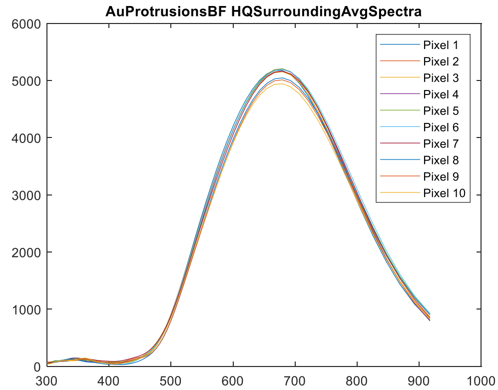


(c)

Figure 150

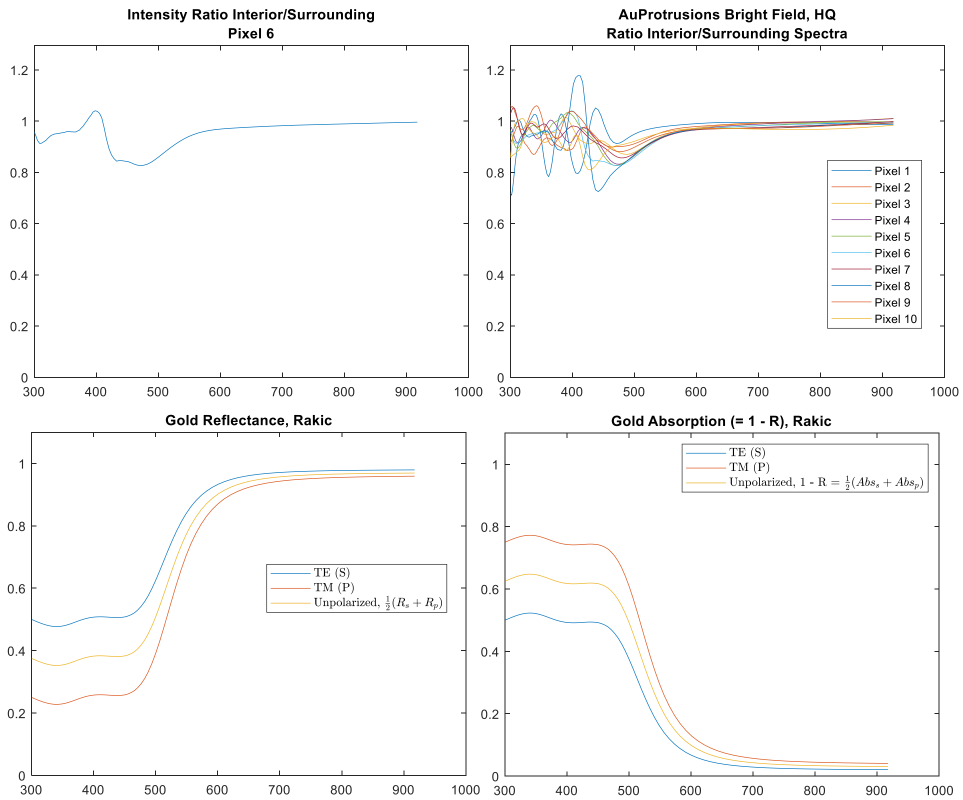
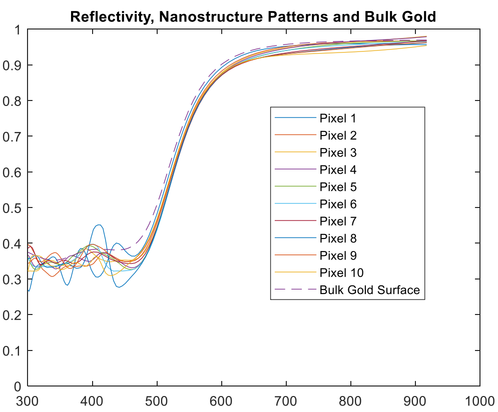
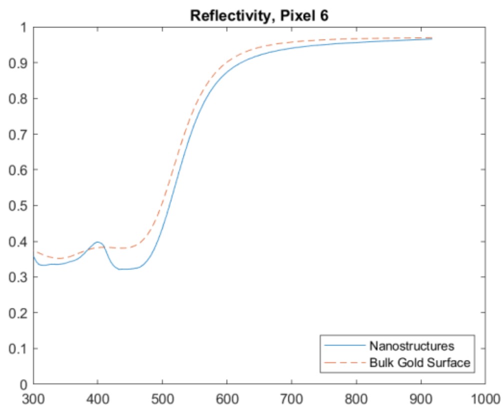

Intensity Ratio Interior/Surrounding
Pixel 6
AuProtrusions Bright Field, HQ
Ratio Interior/Surrounding Spectra
Pixel 1
Pixel 2
Pixel 3
Pixel 4
Pixel 5
Pixel 6
Pixel 7
Pixel 8
Pixel 9
Pixel 10
Gold Reflectance, Rakic
TE (S)
TM (P)
Unpolarized, $\frac{1}{2}(R_s + R_p)$
Gold Absorption (= 1 - R), Rakic
TE (S)
TM (P)
Unpolarized, 1 - R = $\frac{1}{2}(Abs_s + Abs_p)$

Figure 200


Reflectivity, Nanostructure Patterns and Bulk Gold
Pixel 1
Pixel 2
Pixel 3
Pixel 4
Pixel 5
Pixel 6
Pixel 7
Pixel 8
Pixel 9
Pixel 10
Bulk Gold Surface


Reflectivity, Pixel 6
Nanostructures
Bulk Gold Surface