Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for:

A Real-Time Monitoring for the Morphological Variations of Single Gold Nanorods

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1. Supplementary Methods

Calculation of the polarizability of nanoparticles

The reaction takes place in the inhomogeneous media and the solution is non-conducting medium. Then we use the analytic expressions for the Drude model with these considerations:

$$\varepsilon_r(\omega) = 1 + \alpha = 1 + \omega_p^2 \frac{1}{(\omega_0^2 - \omega^2) - i\gamma\omega} \quad (1)$$

And the bulk plasma frequency ω_p is far overweight the natural frequency ω_0, α is the polarizability, then (1) becomes the simple Drude model:

$$\varepsilon_r(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \quad (2)$$

Where $\varepsilon_r(\omega)$ is the complex permittivity, i is the unreliable figure, and Υ is the damping factor. Since restoring force $F = -m\omega_0^2 r$, we can easily infer the equation of electron forced vibration

$$mr'' = -eE - fr - gr' \quad (3)$$

Here, eE is the Electric field force, fr is quasi-elastic force, gr' is damping force. And we lead into two quantities, eigentone $\omega_0 = \sqrt{(f/m)}$, damping factor $\Upsilon = g/m$, to make the equation easy to settle, (3) becomes

$$r'' + \gamma r' + \omega_0^2 r = -\frac{eE_0 e^{-iwt}}{m} \quad (4)$$

We then can get the solution of equation (4)

$$r(t) = \frac{(-e)}{m} \frac{E_0 e^{-i\omega t}}{(\omega_0^2 - \omega^2) - i\gamma\omega} \quad (5)$$

From definition of electric dipole moment and polarization, we can get

$$p = qr \quad (6)$$

$$P = Np = -Ner \quad (7)$$

Put (5) into (7), it goes

$$P = \frac{Ne^2}{m} \frac{E_0 e^{-i\omega t}}{(\omega_0^2 - \omega^2) - i\gamma\omega} \quad (8)$$

Since $p = \varepsilon_0 \chi E$, then

$$\alpha = \omega_p^2 \frac{1}{\left(\omega_0^2 - \omega^2\right) - i\gamma\omega} \quad (9)$$

And we know that, $P_{x,y,z} = \frac{4\pi}{3}\varepsilon_0\varepsilon_m abc \frac{\varepsilon_{Au-\varepsilon_m}}{\varepsilon_{Au} + L_{x,y,z}\varepsilon_m}$ (10), then

$$\alpha_{x,y,z} = \frac{4\pi abc\left(\varepsilon_{Au} - \varepsilon_m\right)}{3\varepsilon_{Au} + 3L_{x,y,z}\varepsilon_m} \quad (11)$$

Where P is the dipole moment, x is the long axis, y and z is the short axis, ε_m is the dielectric constant of the medium, ε_0 is the dielectric constant of single nanorod. L_x and $L_{y,z}$ are the depolarization factor, [1,2] which defined as

$$L_x = \frac{1-e^2}{e^2}\left(-1 + \frac{1}{2e}\ln\left(\frac{1+e}{1-e}\right)\right) \quad (12)$$

$$L_{y,z} = \frac{1-L_x}{2} \quad (13)$$

The influence of aspect ratio due to transverse etching & plasmon shifts

Form the Clausius-Mossotti relation; we know that, the extinction cross section, C_{ext} is easily calculated as the sum of the absorption and scattering cross section via

$$C_{ext} = C_{abs} + C_{sca} \quad (14)$$

$$C_{sca} = \frac{k^4}{6\pi}\left|\alpha\right|^2 = \frac{8\pi}{27}k^4a^2b^2c^2\left|\frac{\varepsilon_{Au} - \varepsilon_m}{\varepsilon_{Au} + L_{x,y,z}\varepsilon_m}\right|^2 \quad (15a)$$

$$C_{abs} = k\,\mathrm{Im}[\alpha] = 4\pi kabc\,\mathrm{Im}\left|\frac{\varepsilon_{Au} - \varepsilon_m}{\varepsilon_{Au} + 2L_{x,y,z}}\right|^2 \quad (15b)$$

The nanoparticles we use here are indeed metallic. Implying that a is far less than λ, we can simply say that $C_{sca} \propto \lambda^4$, that is why we cannot see the particles in the camera like CCD, the background of scattering is too large to small objects. Form equation (15), we can also see that both absorption and scattering are enhanced when dipole excitation exist.

$$\lambda^4 = k'C_{ext} \quad (16)$$

$$\lambda_{sca}^4 = k'C_{sca} = K_{sca}a^2b^2c^2\left|\frac{\varepsilon_{Au} - \varepsilon_m}{\varepsilon_{Au} + L_{x,y,z}\varepsilon_m}\right|^2 \quad (17)$$

$$\lambda_{abs}^{4} = k'C_{abs} = K_{abs}abc\,\mathrm{Im}\left|\frac{\varepsilon_{Au}-\varepsilon_{m}}{\varepsilon_{Au}+2L_{x,y,z}}\right|^{2} \quad (18)$$

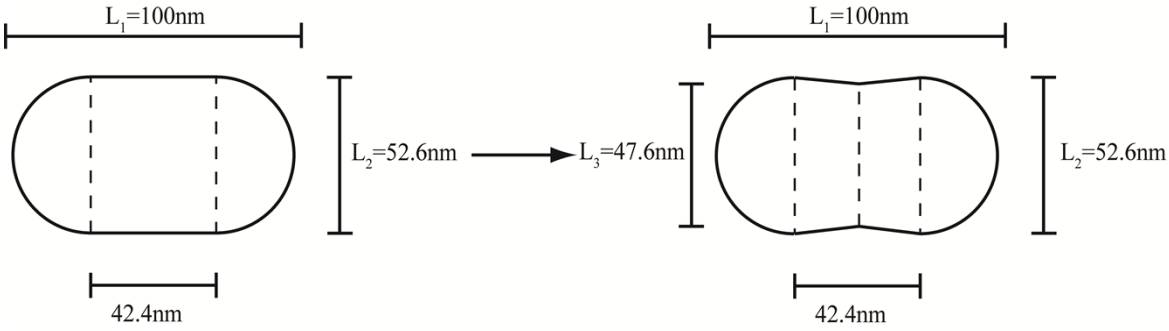
$$K_{sca} = \frac{8\pi}{27}k^{4}k' \quad (19)$$

$$K_{abs} = \frac{4\pi}{3}kk' \quad (20)$$

The λ_{sca} can be calculated as a function of x, y, z and ε_m. The nanoparticles here is gold nanorod, the width (y axis) and height (z axis) could use the same variable.

$$\lambda_{sca} = f\left(\mathrm{x}, y, \varepsilon_{m}\right) \quad (21)$$

If we want to calculate the Plasmon Shifts, we need to know the aspect ratio alters in the etching reaction. For the GNRs and dumbbell-like nanoparticles shown in Figure 2, the average size of nanorods is assumed to be two hemispheres and a cylinder. The reaction first takes place in the {110} surface, and then turns to {111} surface. In order to imitate the real process clearly, we use a model to describe the etching reaction. The cylinder is etched into two circular truncated cones and the ends of GNRs stay the same.



The average sizes of GNRs and dumbbell-like nanoparticles were 52.6×100 nm and 47.6×100 nm, respectively. And the average aspect ratio is 1.9 (before) and 2.1 (after) the etching reaction.

As we known, the plasmon resonance wavelength is dependent on the particle sharp factor.

$$\lambda = \lambda_{p}\sqrt{\varepsilon_{\infty}+\left(\frac{1-L}{L}\right)\varepsilon_{m}} \quad (22)$$

The LSPR wavelength changes in water (ε_m=1.769) was calculated when the original scattering peak (λ) is 650±5nm. ε_{∞} is the high frequency contribution to the metal dielectric function (12.2 for gold). With these data, the particle sharp factor can be got easily, L=0.125. The morphologic changes is related to the volume and aspect ratio. Then we can get

$$V_{NR} = \frac{1}{6}\pi L_2^3 + \pi\left(\frac{L_2}{2}\right)^2 (L_1 - L_2) \quad (23)$$

$$V_{ND} = \frac{1}{6}\pi L_2^3 + \frac{1}{12}\pi(L_1 - L_2)(L_2^2 + L_2 L_3 + L_3^2) \quad (24) \qquad (0 < L_3 \leq L_2)$$

$$e_1 = \frac{L_1}{L_2} \quad (25a)$$

$$e_2 = \frac{L_1}{L_3} \quad (25b)$$

The original GNRs had a maximum diameter (long axis, L_1) and a minimum diameter in the middle section (short axis, L_2), respectively. The GNRs have a minimum diameter in the middle section (L_3) after the transverse etching. The aspect ratio before the etching reaction (L_1:L_2) is e_1 and the aspect ratio after the etching reaction (L_1:L_3) is e_2. So it is easy to form the plasmon resonance wavelength shift by equation 22:

$$\Delta\lambda = -\frac{(e_2 - e_1)(e_1 + 2e_2)(e_1 - 1)}{2e_2^2(3e_1 - 1)}\lambda_p\sqrt{\varepsilon_\infty + \left(\frac{1 - L}{L}\right)\varepsilon_m} \quad (26)$$

λ_p is the bulk plasma wavelength for gold[3]. The wavelength changes, $\Delta\lambda$ = 27.89nm, show the similar result in the experiment. And if the calculation is based on the theory that the crystal face is still {110}, and the changes of GNRs is just come from a larger cylinder to a small one, the order of magnitude is quite different.

Appendix C. Stoichiometry and Reaction Rate[4]

$$AuCl_4^- + 3e^- = Au^0 + 4Cl^-,\ E_0 = +1.002V(NHE) \quad (27)$$

$$AuCl_2^- + e^- = Au^0 + 2Cl^-,\ E_0 = +1.154V(NHE) \quad (28)$$

$$AuCl_4^- + 2e^- = AuCl_2^- + 2Cl^-,\ E_0 = +0.926V(NHE) \quad (29)$$

It is obvious that conproportionation of $AuCl_4^-$ cannot be occurred favorably via reaction below

$$AuCl_4^- + 2Au^0 + 2Cl^- = 3AuCl_2^-,\ K_1 = 1.9 \times 10^{-8} \quad (30)$$

In the same way, we can get the redox reactions when Cl^- is taken place by Br^-, the conproportionation can be calculated as

$$AuBr_4^- + 2Au^0 + 2Br^- = 3AuBr_2^-,\ K_2 = 4.96 \times 10^{-6} \quad (31)$$

And CTAB is known as a cationic surfactant. The increase of CTAB concentration facilitates the formation of CTAB micelles, meanwhile, the bromide concentration from CTAB.

2. Supplementary Figures

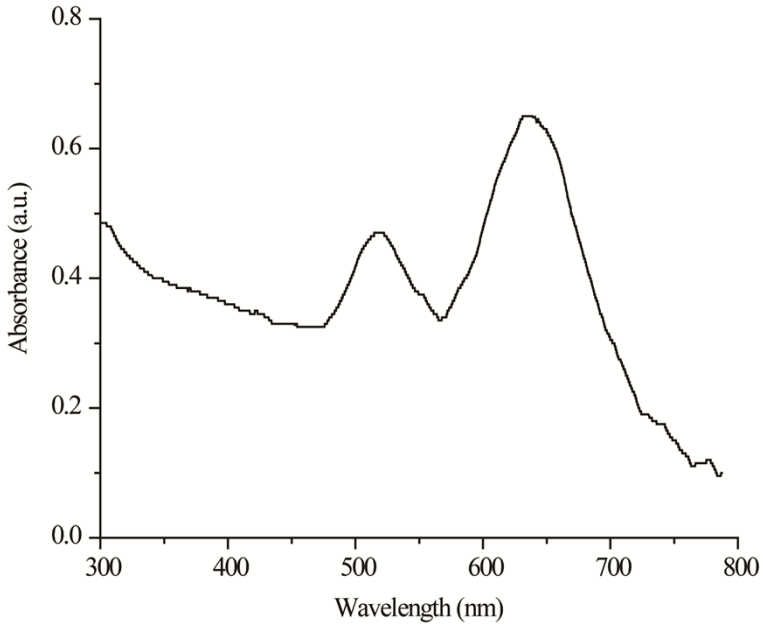


Fig. S1 UV-vis spectra of GNRs solution.

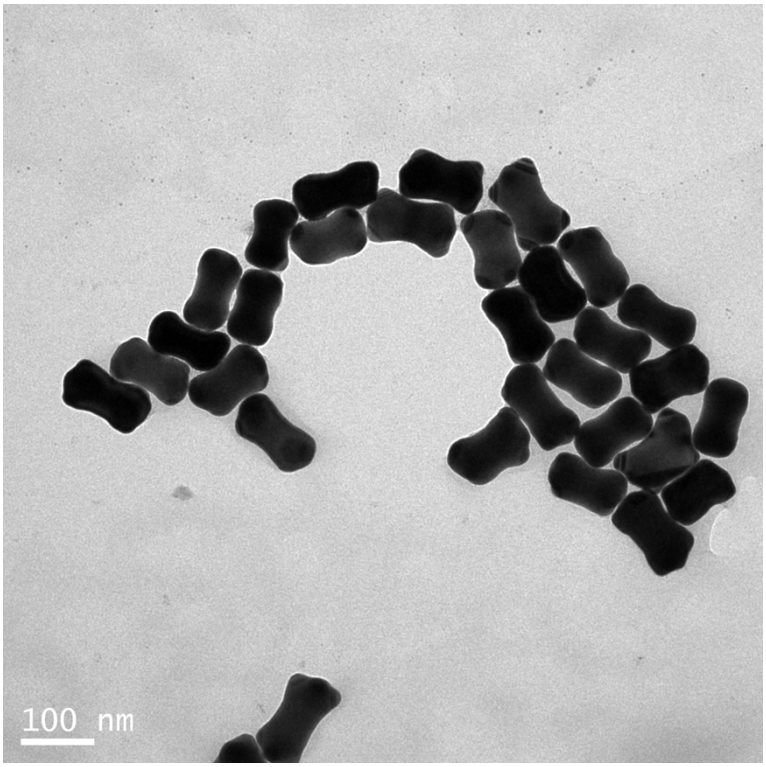


Fig. S2 TEM images recorded after reaction with cysteine then etching in micellar solution for 20 min.

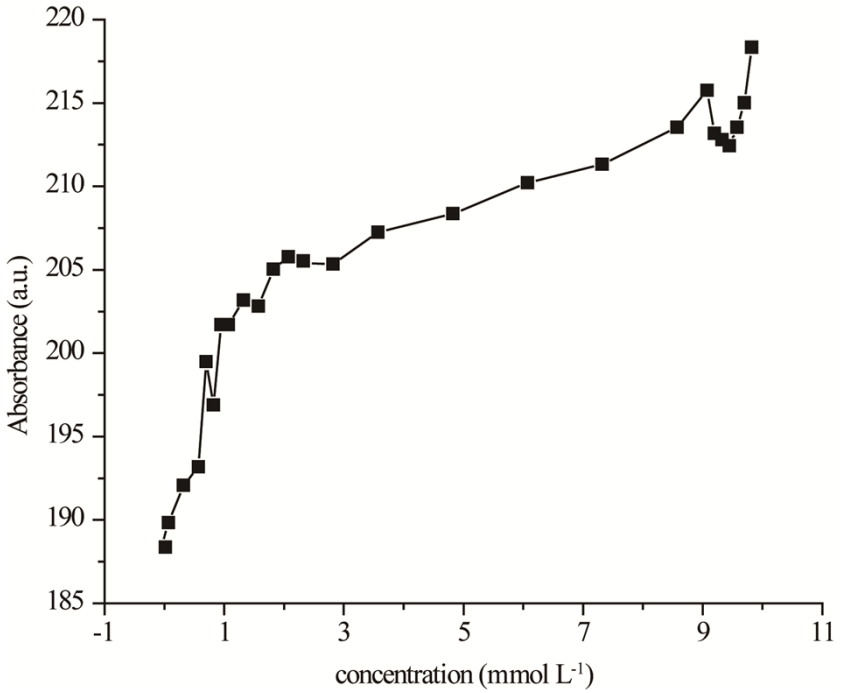


Fig. S3 Absorbance changes of the UV-spectrophotometry at varing CTAB concentrations.

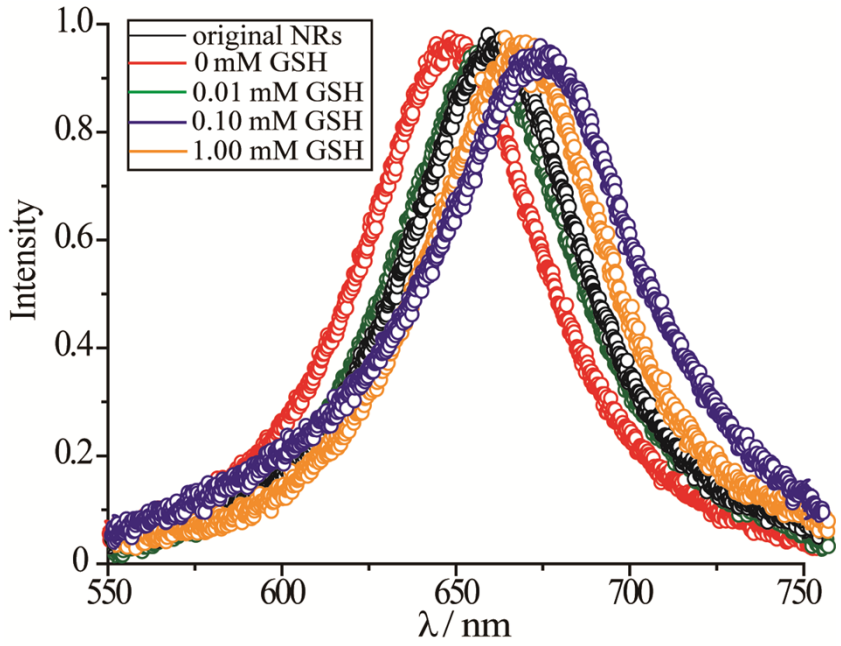


Fig. S4 The scattering peak shift of single gold nanoparticle before (-) and after addition glutathione solution at 0 mM (-), 0.01 mM (-), 0.1 mM (-), and 1 mM (-) after 40 min reaction in micellar solution.

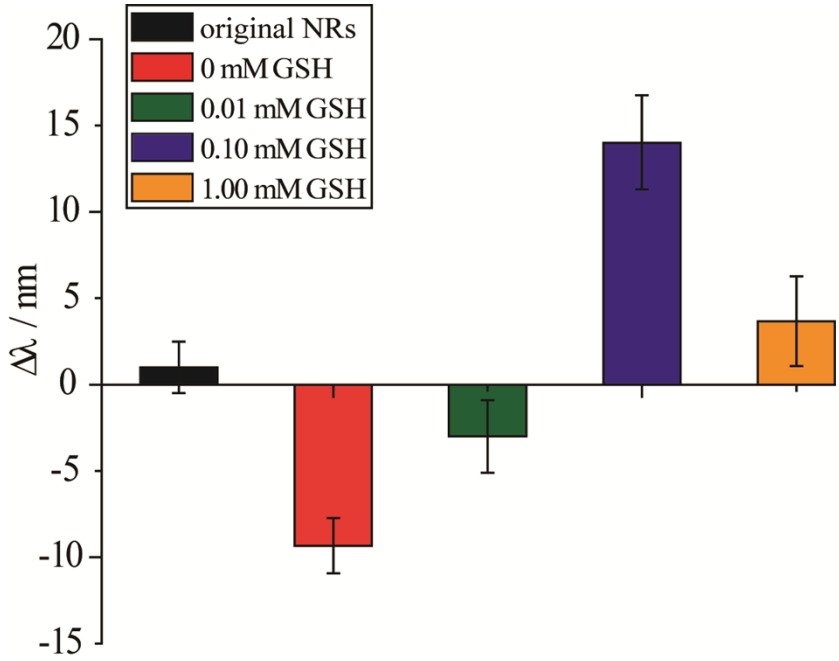


Fig. S5 The maximum scattering peak of gold nanoparticles before (-) and after addition glutathione solution at 0 mM (-), 0.01 mM (-), 0.1 mM (-), and 1 mM (-) after 40 min reaction in micellar solution.

3. References

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