Electronic Supplementary Information for

Nonmonotonous Shift of Quantum Plasmon Resonance and Plasmon-Enhanced Photocatalytic Activity of Gold Nanoparticles

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1. TEM images of large colloidal gold nanoparticles prepared at T_{etch} = 200 °C

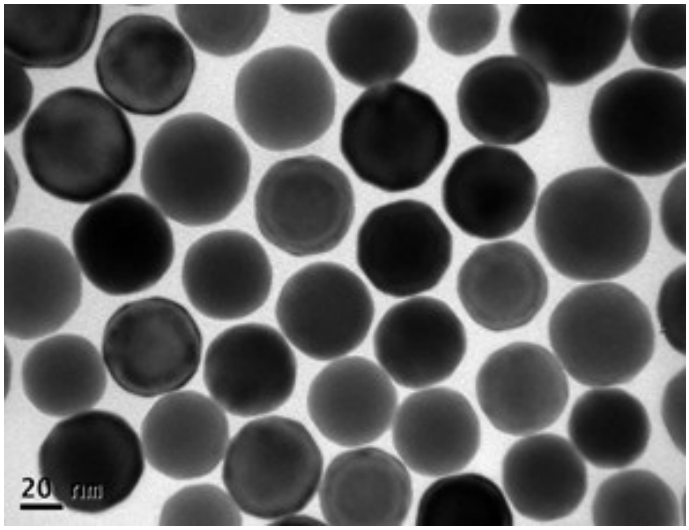

Figure S1. TEM image of large colloidal Au nanoparticles. The thermal etching temperature T_{etch} = 200 °C. The nanospheres of gold are obtained and the average diameter 2*R* is 44 ± 5 nm.

2. Extinction spectrum of gold nanoparticles with the longest SPR wavelength

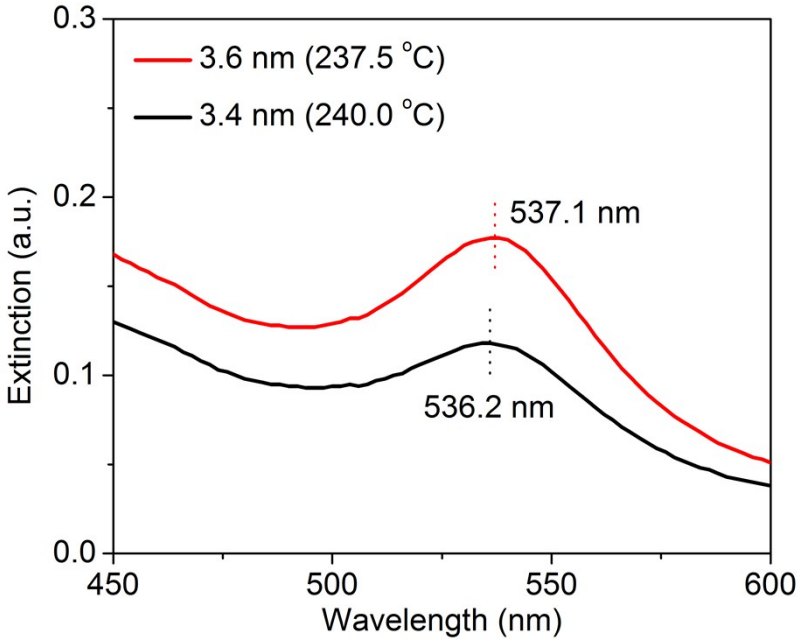

Figure S2. Extinction spectra of Au nanoparticles prepared at T_{etch} = 237.5 °C (2*R* = 3.6 nm) and T_{etch} = 240.0 °C (2*R* = 3.4 nm). The Au nanopaticles with 2*R* = 3.6 nm has the longest SPR wavelength of 537.1 nm.

3. Classical model and calculated SPR of gold nanoparticles

3.1 Fitting classical permittivity of bulk gold

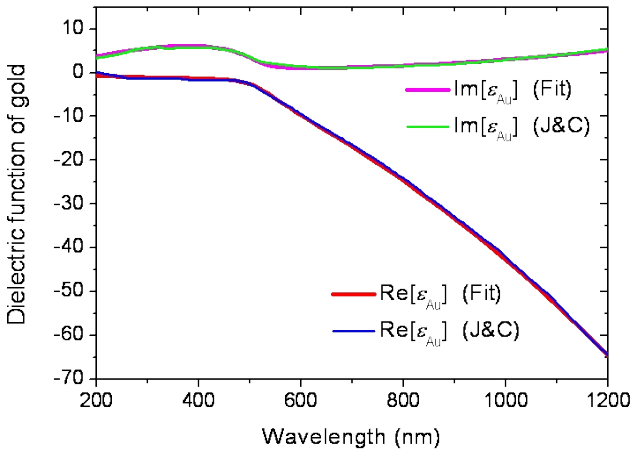

Figure S3. The real and imaginary components of permittivity of bulk gold. The empirical data is from the literature of Johnson and Christy. The theoretical calculations well coincide with the measurement results. $\varepsilon_\infty = 1$, $E_g = 2.386$ eV, $\omega_p^2 = 1.757\times10^{32}$ s^{-2}, $\gamma_{bulk} = 1.1\times10^{14}$ s^{-1}, $\gamma_{inter} = 1.885\times10^{14}$ s^{-1}, $v_F = 1.4\times10^6$ m/s.

3.2 SPR of gold nanoparticles calculated by classical model

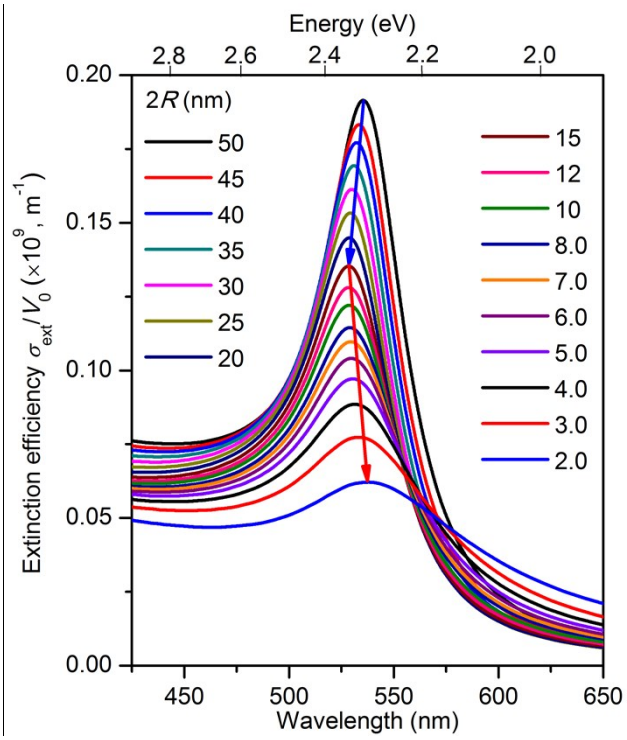

Figure S4. Calculated extinction efficiency (σ_{ext}/V_0) spectrum of Au nanoparticles with classical Mie model (the Drude dielectric function is not corrected by electron resonance transitions S_{if}). λ_{SPR} reaches the minimum at $2R \approx 15$ nm in classical regime and monotonously red-shifts in the quantum regime.

4. Quantum-corrected model and calculated SPR of gold and silver nanoparticles

4.1 Quantum-corrected permittivity of gold and silver nanoparticles

4.1.1 The largest principle quantum number on Fermi surface (n_F)

The discrete energy of electrons with principle and azimuthal quantum numbers (n,l) can be approximately expressed as,

$$E_{n,l} = \frac{\mathrm{h}^2\pi^2}{8MR^2}(2n + l + 2)^2 \tag{2}$$

The quantum number (n,l) at the Fermi surface satisfies,

$$2n + l = 2n_F \tag{3}$$

The total number N of occupied electrons ($2n_i + l_i \le 2n_F$) below the Fermi surface has a relationship,

$$N = \frac{8}{3}n_F^3 + 8n_F^2 + \frac{22}{3}n + 2 \tag{4}$$

Then the value of n_F has a dependent on radius of nanosphere,

$$\frac{8}{3}n_F^3 + 8n_F^2 + \frac{22}{3}n + 2 = \rho_e \times \frac{4\pi}{3}R^3 \ , \tag{5}$$

where ρ_e is electron density of plasmonic nanospheres.

4.1.2 Oscillator strength S_{if} of quantum transition ω_{if}

The transition frequency of the conduction electrons from the initial state (n_i, l_i) to the final state (n_f, l_f) is,

$$\omega_{if} = \frac{\mathrm{h}\pi^2}{8MR^2}(4n_i + 2\Delta n + 2l_i + \Delta l + 4)(2\Delta n + \Delta l)\,, \tag{6}$$

where $\Delta n = n_f - n_i$, $\Delta l = l_f - l_i$. The oscillator strength of quantum transition ω_{if} is defined as $S_{if} = 2M\omega_{if}\langle f \mid z \mid i\rangle^2 / \mathrm{h}N$, which has an analytic relationship after approximation [1],

$$\begin{aligned} S_{if} = S_{n,l,\Delta n,\Delta l} = {} & \delta_{\Delta l,-1}\frac{16l(2n + 2\Delta n + l + 1)^2(2n + l + 2)^2}{\pi^2 n_F^3(4n + 2\Delta n + 2l + 3)^3(2\Delta n - 1)^3} \\ & + \delta_{\Delta l,+1}\frac{16(l+1)(2n + 2\Delta n + l + 3)^2(2n + l + 2)^2}{\pi^2 n_F^3(4n + 2\Delta n + 2l + 5)^3(2\Delta n + 1)^3} \end{aligned}\ , \tag{7}$$

Equation (7) satisfies normalization when n_F is very large.

4.2 SPR of gold nanoparticles calculated by semi-classical model

The peak intensity, wavelength, and width of SPR of metal nanoparticles with diameter $R > R_{C,2}$ calculated by semi-classical model are all oscillate with $2R$ owing to

high-order quantum transitions of ω_{if} [2]. Both SPR wavelength and width at maximal SPR intensity are very close to the ones calculated by classic model for the large nanoparticles ($R > R_{C,1}$). Considering the ensemble heterogeneity effects (including inhomogeneous distributions of size, shape, and surface boundary) of the colloidal Au nanoparticles in this study, it is more reasonable to compare the experimental measured λ_{SPR} to the calculated ones with maximal SPR intensity.

4.3 SPR of silver nanoparticles calculated by semi-classical model

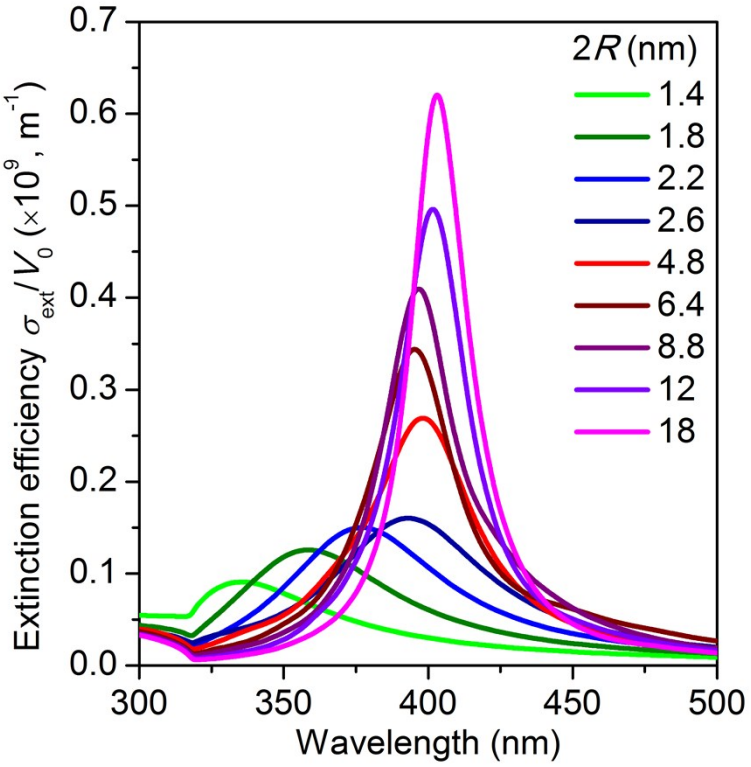

Figure S5. Extinction efficiency (σ_{ext}/V_0) spectrum of silver nanospheres with $2R$ = 18, 12, 8.8, 6.4, 4.8, 4.4, 2.6, 2.2, 1.8, and 1.4 nm. ε_∞ = 1, ω_p^2 = 1.78×10^{32} s^{-2}, E_g = 3.902 eV, γ_{bulk} = 1.1×10^{14} s^{-1}, γ_{inter} = 1.008×10^{13} s^{-1}, v_F = 1.39×10^6 m/s, A = 3/4. λ_{SPR} blue-shifts from 403.2 to 395.3 nm as $2R$ decreases from 18.0 to 6.4 nm, the slightly red-shifts to 398.4 nm as $2R$ reaches 4.8 nm, then dramatically blue-shifts to 334.7 nm as $2R$ further decreases to 1.4 nm.

5. Photodegradation of methylene blue with gold nanoparticles

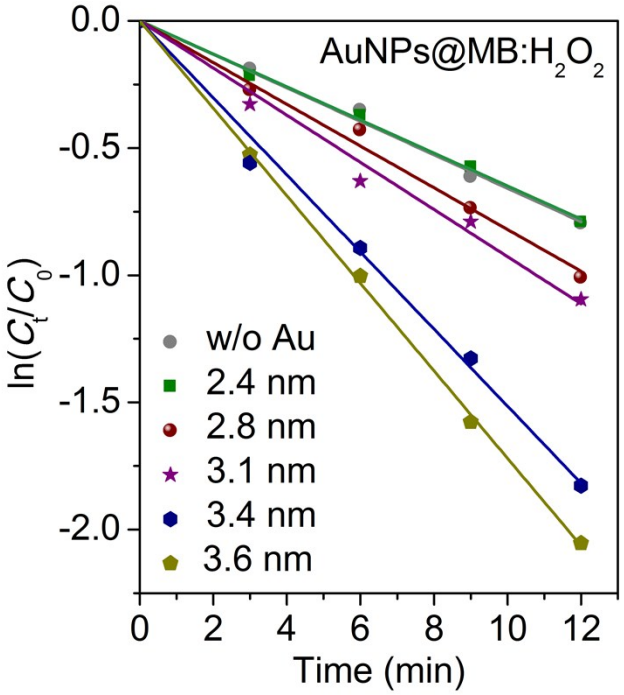

Figure S6. Linear dependences of $\ln(C/C_0) \sim t$ of MB:H_2O_2 with Au nanoparticles (AuNPs@MB:H_2O_2) ($2R$ = 2.4, 2.8, 3.1, 3.4, and 3.6 nm).

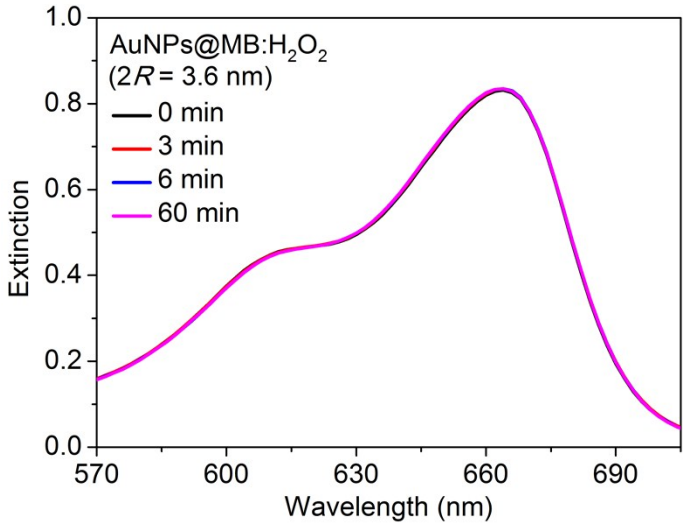

Figure S7. Extinction spectra of AuNPs@MB:H_2O_2 ($2R$ = 3.6 nm) recorded at the reaction time of 0, 3, 6, and 60 min without light illumination. Pure electron catalysis process is not observed in the degradation of MB:H_2O_2.

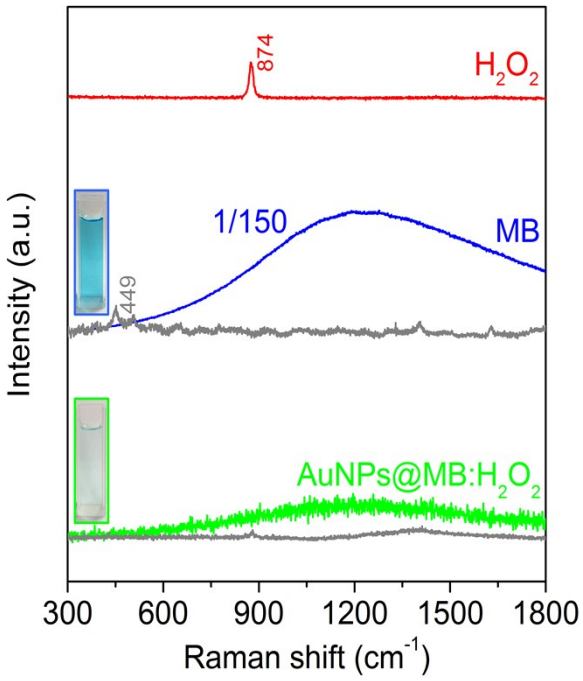

Figure S8. Raman scattering spectrum of H_2O_2, MB molecules, and AuNPs@MB:H_2O_2. The three color lines (red for H_2O_2, blue for MB, and green for AuNPs@MB:H_2O_2) are measured by using laser with a wavelength of 633 nm. MB molecules exhibits strong fluorescence around 1200 cm^{-1}, which is about 480 times stronger than that of AuNPs@MB:H_2O_2. The grey lines are measured by using laser with a wavelength of 785 nm. The inset shows the photos of MB and AuNPs@MB:H_2O_2 samples.

6. Photodegradation of 4-NP with gold nanoparticles

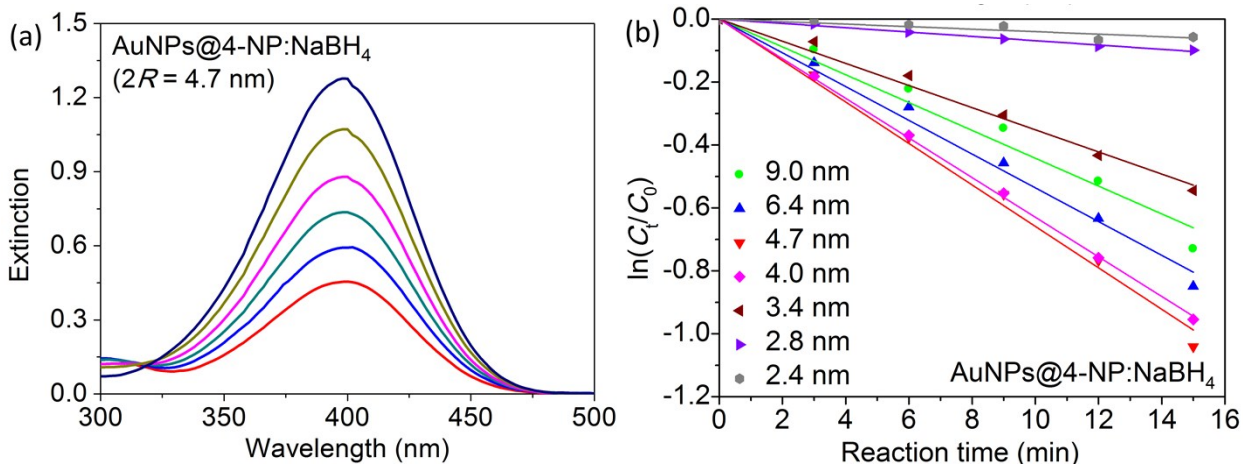

Figure S9. Size dependence of catalytic activity of Au nanoparticles in 4-NP:$NaBH_4$ (AuNPs@4-NP:$NaBH_4$). (a) Extinction spectra of AuNPs@4-NP:$NaBH_4$ (2R = 3.6 nm) recorded at the different time. (b) Normalized peak extinction intensity at 400 nm as a function of reaction time t. $\ln(C_t/C_0)$ is linearly dependent on t. Reaction rate K reaches the maximum at 4.7 nm.

References:

[1] Kraus, W. A. & Schatz, G. C. *J. Chem. Phys.* **79**, 6130 (1983).

[2] Scholl, J. A., Koh, A. L. & Dionne, J. A. *Nature* **483**, 421 (2012).