

Supporting Information

Additional Figures:

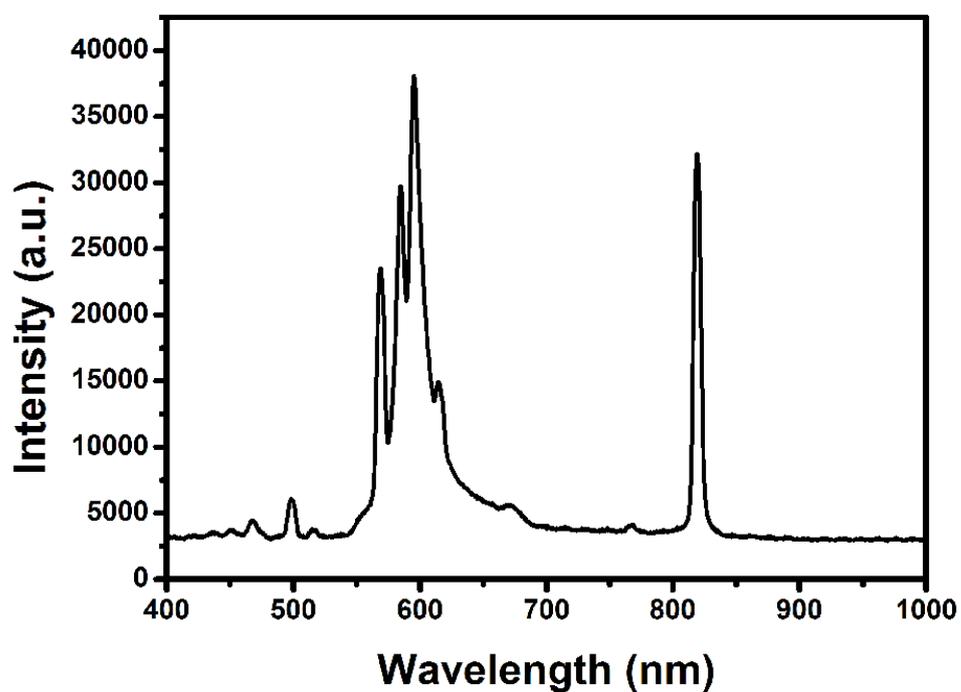


Figure S1. Emission spectra of sodium lamp.

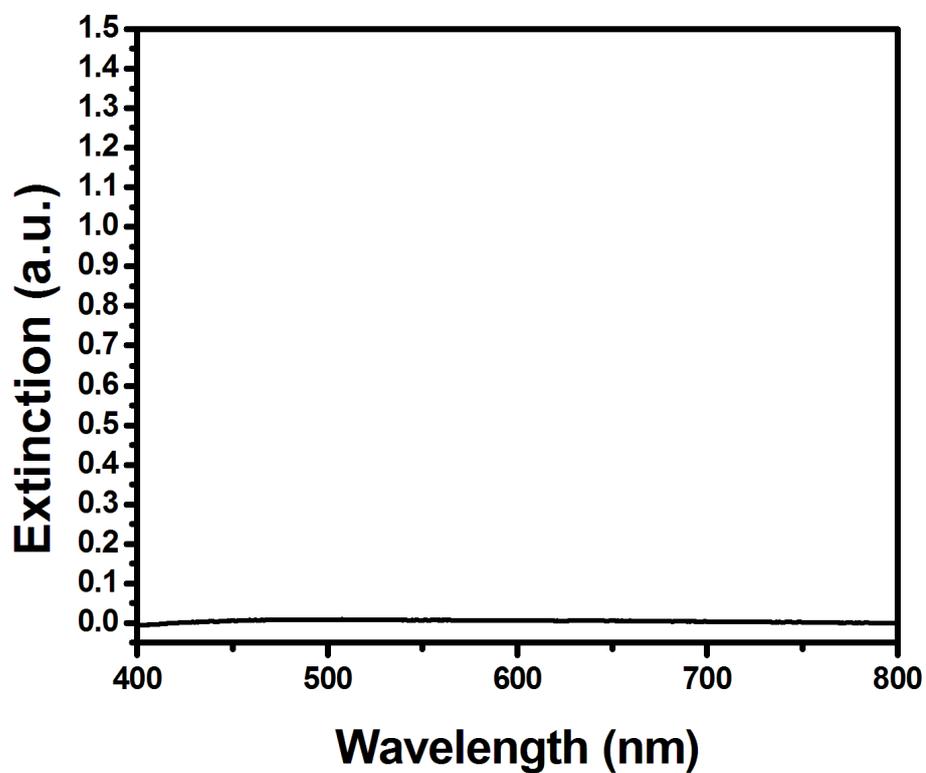


Figure S2. Final UV-Vis spectra of mixture solutions including Ag^+ ions, citrates, OH^- ions after irradiated 8 hours.

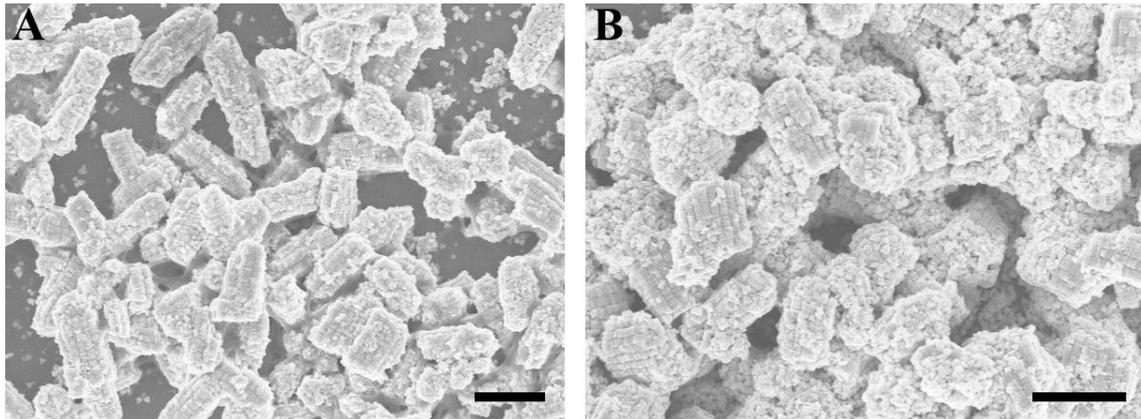


Figure S3. SEM images of self-assembly of triangular silver nanoprisms. Scale bars of A, B are 500 nm.

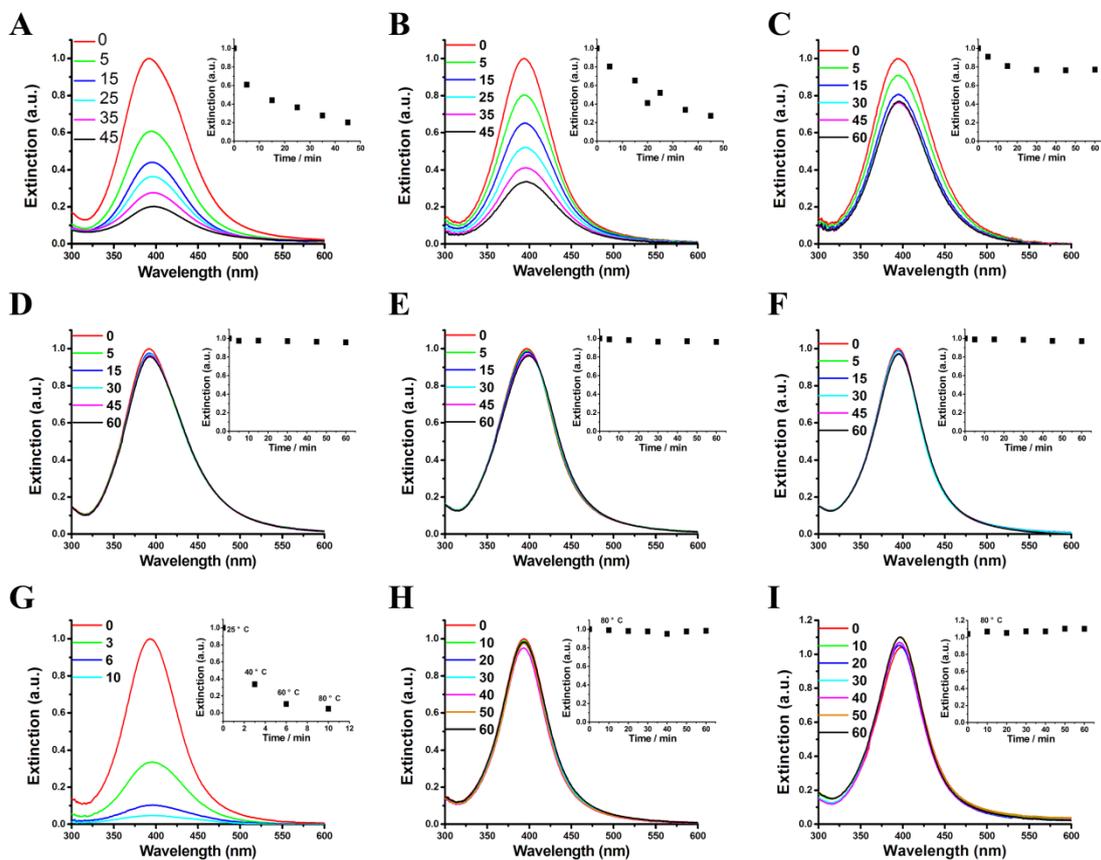


Figure S3. (A)~(F) Changes of UV-Vis spectra recorded immediately at room temperature after preparation of Ag NPs at different concentration of OH⁻: (A) without adding OH⁻ (B) 250 μL ,0.001 M OH⁻ ,(C) 250 μL , 0.005 M OH⁻ , (D) 250 μL , 0.025 M OH⁻ , (E) 250 μL ,0.1 M OH⁻ , (F) 250 μL ,0.125 M OH⁻ . (G)~(I) Changes of UV-Vis spectra when heated solution to 80 °C after preparation of Ag NPs at different concentration of OH⁻: (G) without adding OH⁻ , (H) 250 μL , 0.025 M OH⁻ , (I) 250 μL , 0.125 M OH⁻ .

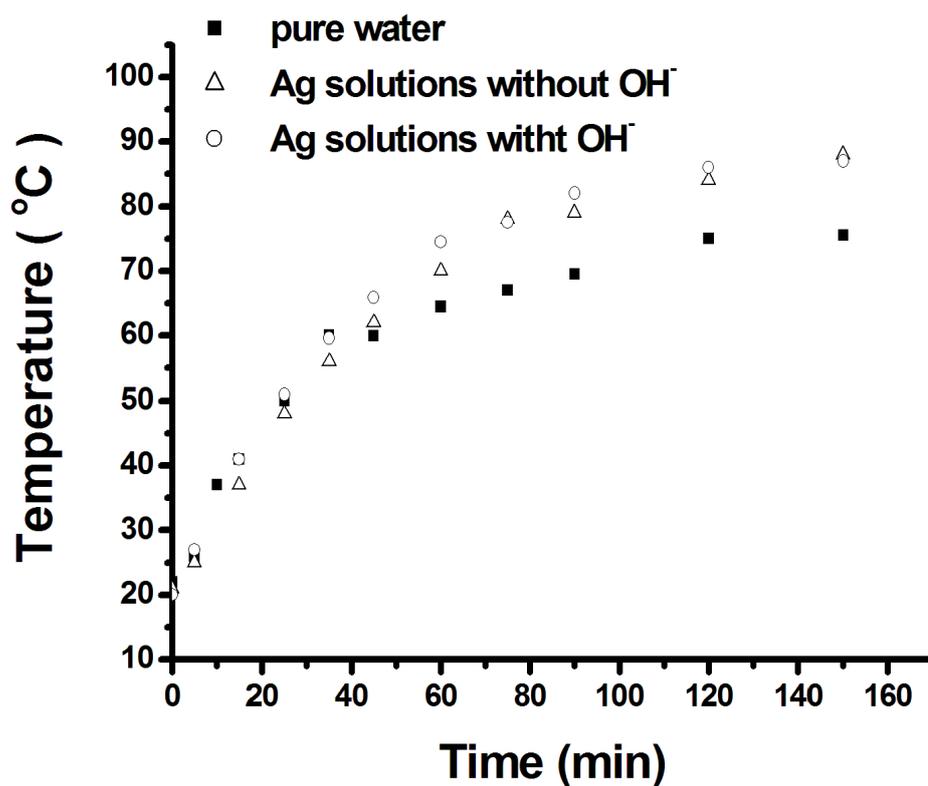


Figure S4. Temperature of solution (pure water, Ag solutions without and with OH⁻) monitored at different time when irradiation with sodium lamp. These data indicate that irradiation with sodium lamp will heat water. The temperature of Ag solution is higher than pure water, which may arise from the photothermal effects of noble metal nanoparticles.

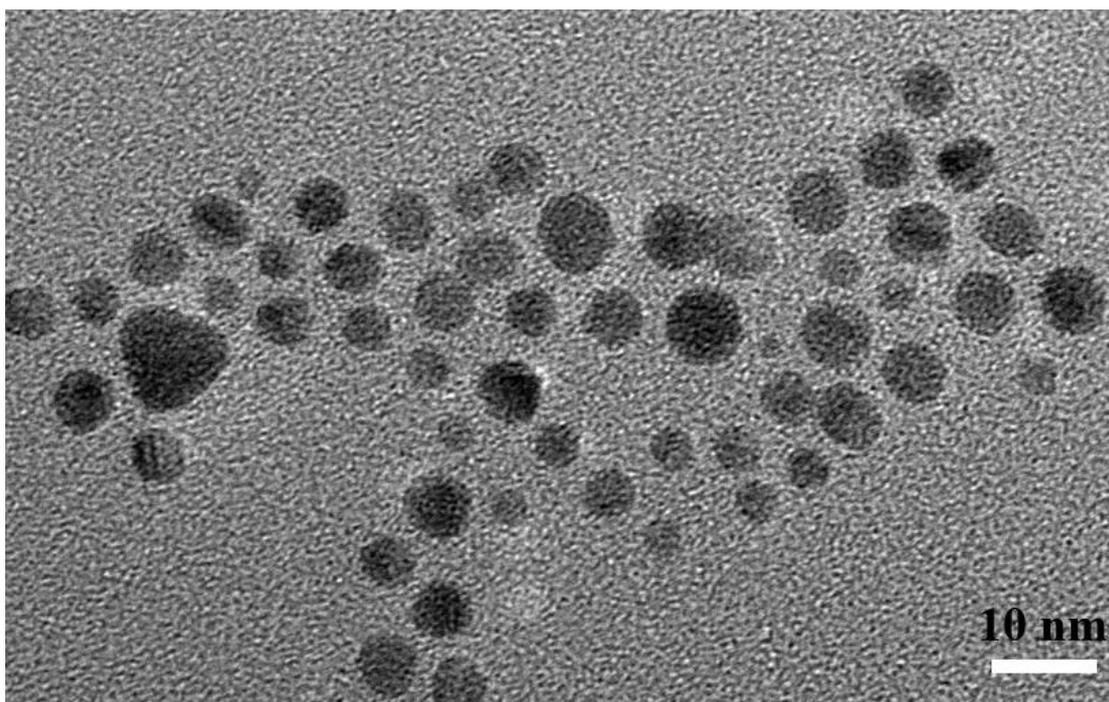


Figure S5. TEM images of synthesis silver nanoparticles without OH^- after irradiated 10 minutes.

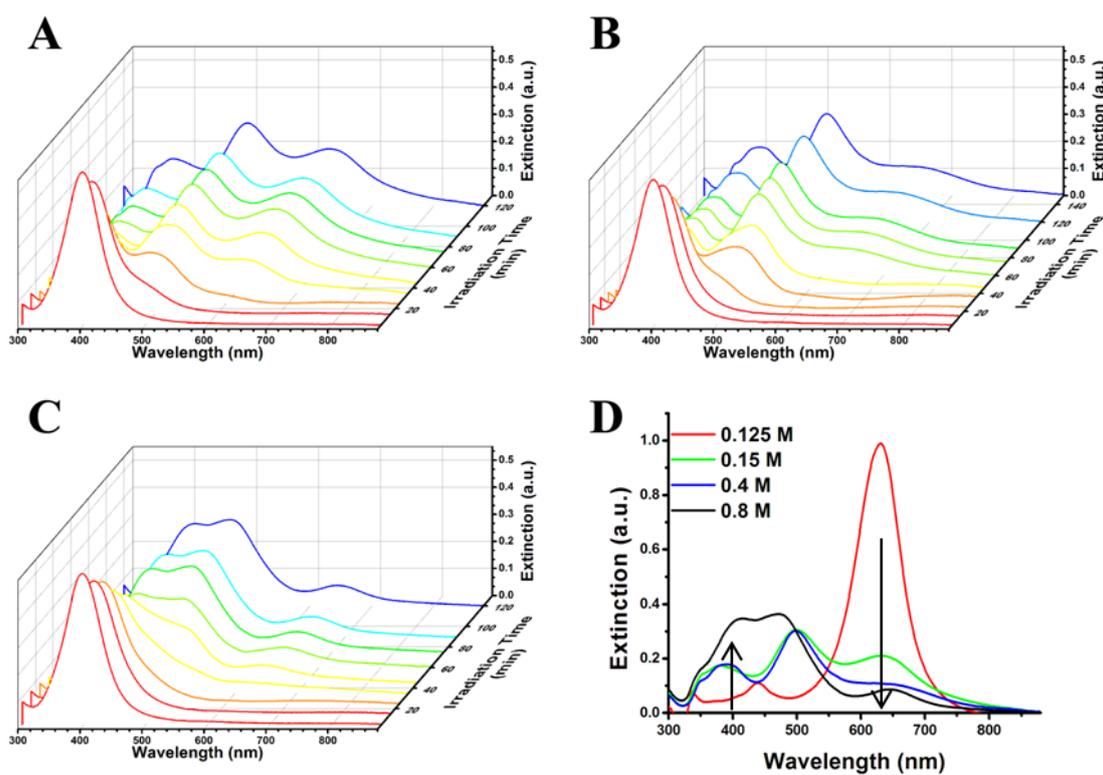


Figure S6. UV-Vis spectra of solutions obtained at different irradiation time when the silver nanoprisms synthesized in different high concentration of OH^- : (A) 0.15 M; (B) 0.4 M; (C) 0.8M; and (D) the final UV-Vis spectra of synthesis when adding different concentration of OH^- .

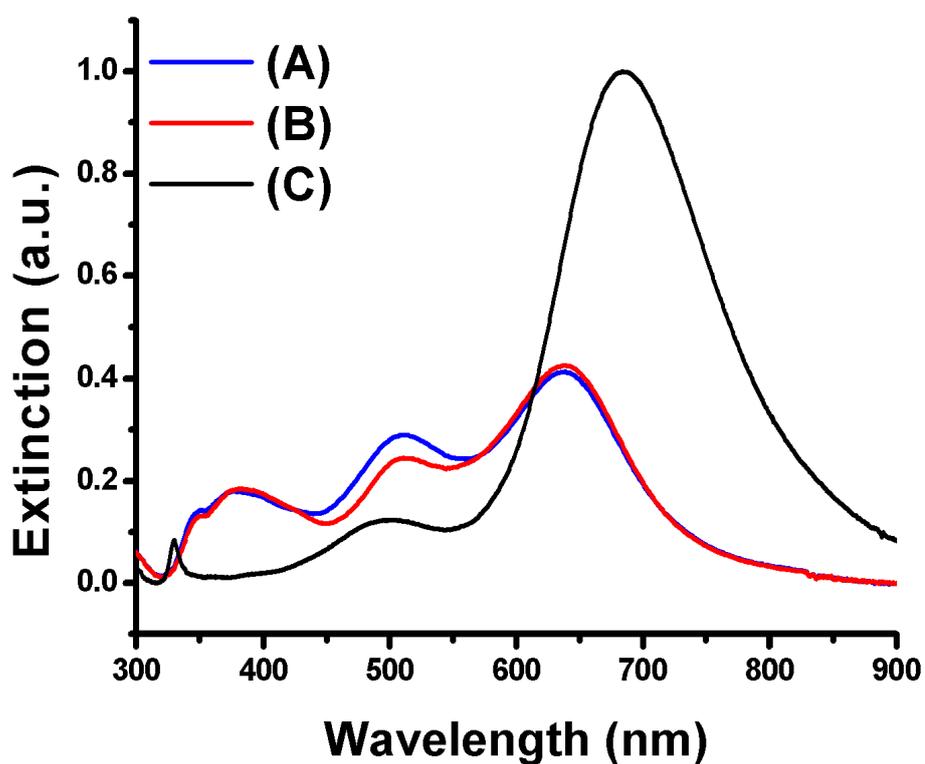


Figure S7. UV–Vis spectra of TSNPRs synthesized at different conditions: (A) stirring and adding OH⁻, but bubbling solution with oxygen-free argon gas before reaction, (B) without stirring and adding OH⁻, (C) without stirring and without adding OH⁻.

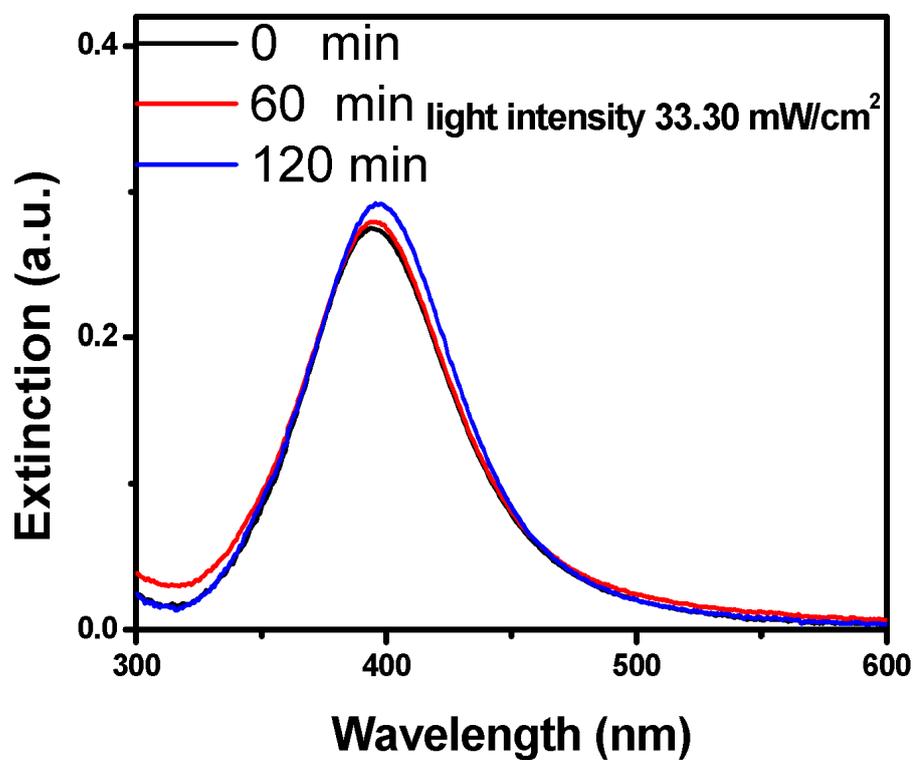


Figure S8. UV–Vis spectra change of reaction solutions irradiated with light intensity of 33.30 mW/cm².

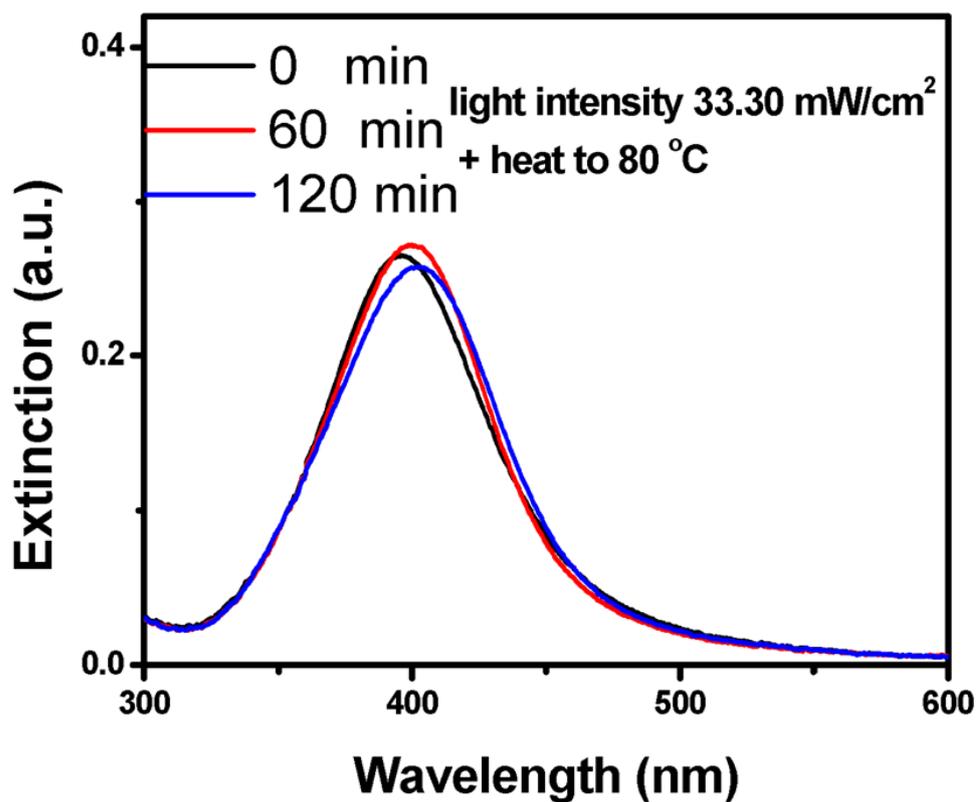


Figure S9. UV-Vis spectra change of reaction solutions irradiated with light intensity of 33.30 mW/cm^2 and meanwhile heated to $80 \text{ }^\circ\text{C}$.

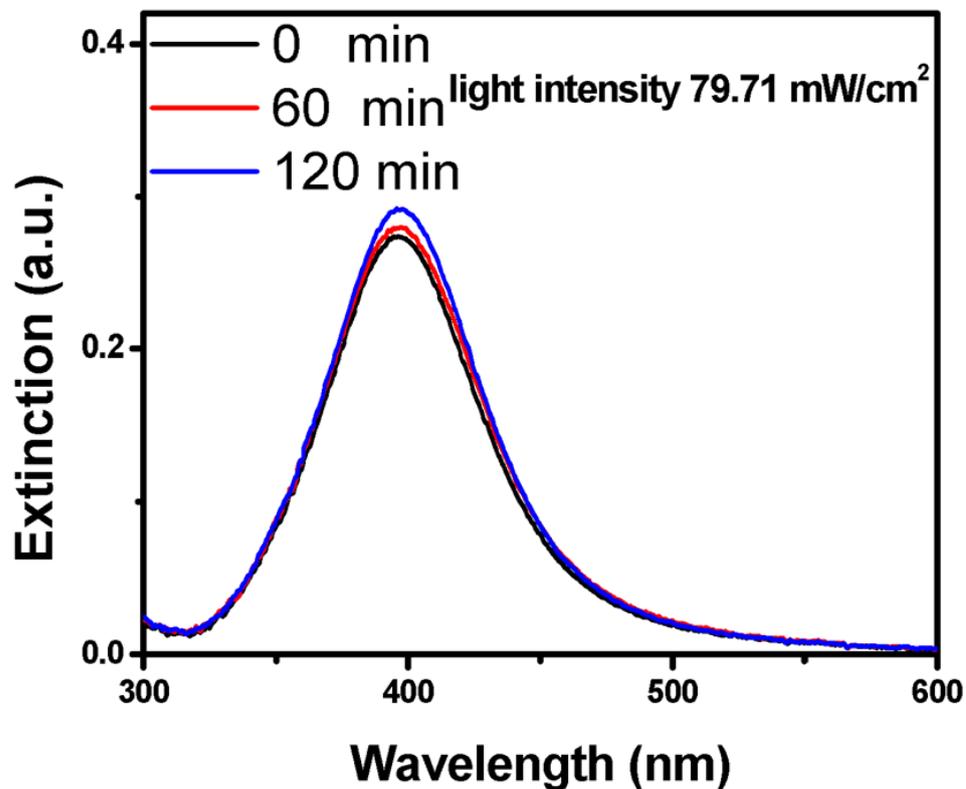


Figure S10. UV-Vis spectra change of reaction solutions irradiated with light intensity of 79.71 mW/cm^2 .

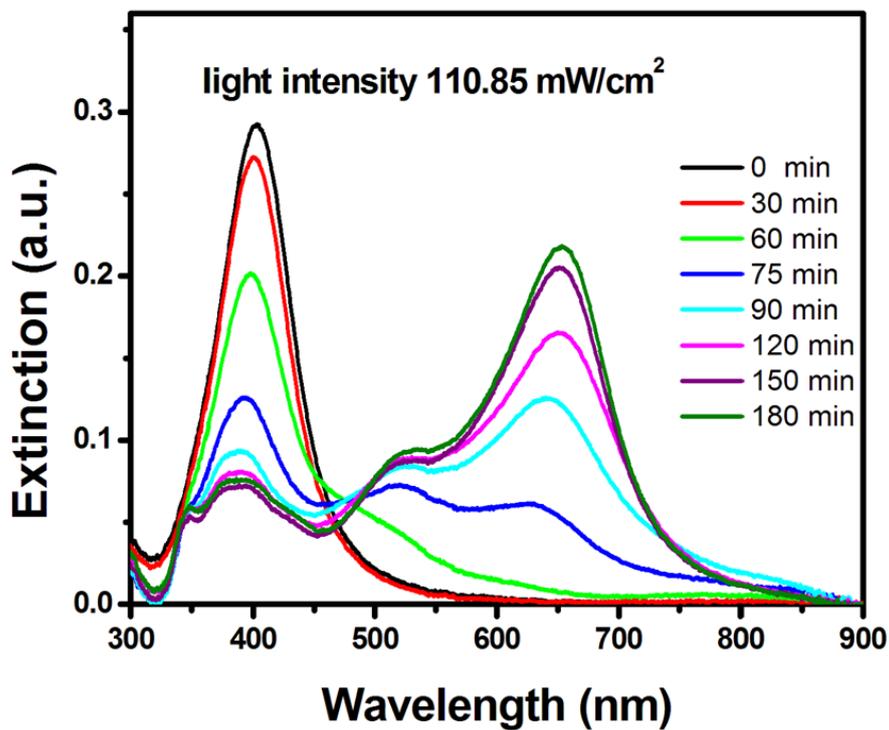


Figure S11. UV-Vis spectra change of reaction solutions irradiated with light intensity of 110.85 mW/cm^2 .

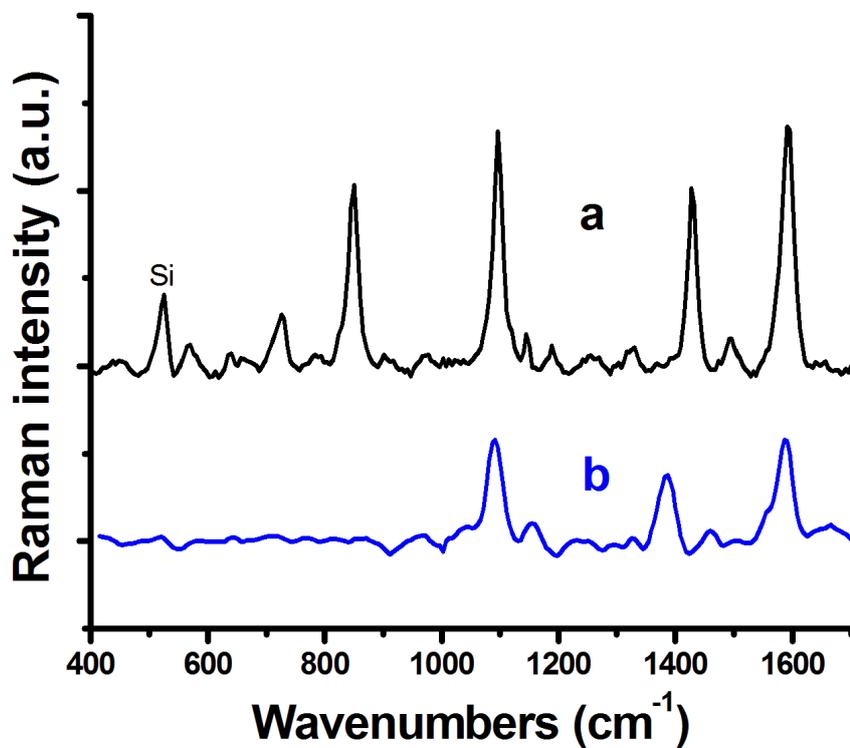


Figure S12. Raman spectra of (a) $3 \mu\text{L}$, 500 mM 4-MBA dried on the silicon wafer with diameters of 3 mm and (b) 500 mM 4-MBA in the solutions.

Calculations of EF were shown below:

$$EF = (I_{SERS} / I_{RS}) \times (N_{RS} / N_{SERS})$$

For the EF of silver nanoprisms solutions,

$$EF = \frac{I_{SERS}}{I_{Raman}} \times \frac{N_{Raman}}{N_{SERS}} = \frac{I_{SERS}}{I_{Raman}} \times \frac{C_{Raman} V_{Raman} N_A}{C_{SERS} V_{SERS} N_A} = \frac{I_{SERS}}{I_{Raman}} \times \frac{C_{Raman}}{C_{SERS}}$$

where C_{Raman} and C_{SERS} are the concentrations of 4-MBA in the normal Raman and SERS detections.

The volume of one silver nanoprism:

$$V_{SNPRs} = \frac{\sqrt{3}}{4} a^2 h$$

For good silver nanoprisms, $a=88$ nm, $h=24$ nm,

$$V_{SNPRs}(\text{good}) = 8.0478 \times 10^4 \text{ nm}^3,$$

$$\rho_{Ag} = 10.5 \text{ g cm}^{-3} = 10.5 \times 10^{-21} \text{ g nm}^{-3},$$

The weight of one good silver nanoprism:

$$W_{SNPRs}(\text{good}) = 10.5 \times 10^{-21} \times 8.0478 \times 10^4 \text{ g} = 8.45 \times 10^{-16} \text{ g},$$

Weight of the Ag in the growth solution:

$$W_{Ag} = 250 \times 10^{-6} \text{ L} \times 10 \times 10^{-3} \text{ mol/L} \times 107.87 \text{ g/mol} = 2.697 \times 10^{-4} \text{ g}$$

25 mL solution contains good SNPRs:

$$N_{SNPRs}(\text{good}) = \frac{2.697 \times 10^{-4}}{8.45 \times 10^{-16}} = 3.19 \times 10^{11}$$

1 mL solution contains good SNPRs:

$$N_{1ml}(\text{good}) = 1.276 \times 10^{10}$$

The concentration of good silver nanoprisms for SERS (2 mL solutions concentrated to 0.2 mL at last):

$$C_{SNPRs}(\text{good}) = \frac{1.276 \times 10^{10} \times 2 \text{ mol}}{6.02 \times 10^{23} \times 0.2 \times 10^{-3} \text{ L}} = 2.12 \times 10^{-10} \text{ M}$$

The surface of one silver nanoprism:

$$S_{SNPRs} = \frac{\sqrt{3}}{2} a^2 + 3ah$$

$$S_{SNPRs}(\text{good}) = 13042.5 \text{ nm}^2$$

We assumed that molecular footprint of 4-MBA molecules adsorbed as a monolayer was 0.54 nm^2 .

Concentration of 4-MBA molecules during SERS experiment for good silver nanoprisms:

$$C_{SERS}(\text{good SNPRs}) = \frac{13042.5}{0.54} \times 2.12 \times 10^{-10} \text{ M} = 5.12 \times 10^{-6} \text{ M}$$

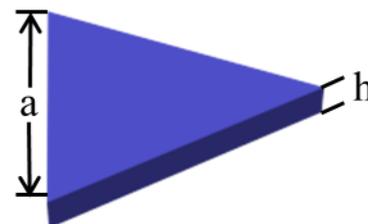
For SERS experiment of good SNPRs, accumulation time was 10 s, normal Raman detection, accumulation time was 1 s.

$$EF(\text{good SNPRs}) = \frac{123943/10}{38684} \times \frac{500 \times 10^{-3}}{5.12 \times 10^{-6}} = 3.12 \times 10^4$$

Similarly, for poor silver nanoprisms, $a=50$ nm, $h=10$ nm,

$$V_{SNPRs}(\text{poor}) = 1.0825 \times 10^4 \text{ nm}^3,$$

The weight of one poor silver nanoprism:



$$W_{SNPRs}(\text{poor}) = 10.5 \times 10^{-21} \times 1.0825 \times 10^4 \text{g} = 1.137 \times 10^{-16} \text{g},$$

25 mL solution contains poor SNPRs:

$$N_{SNPRs}(\text{poor}) = \frac{2.697 \times 10^{-4}}{1.137 \times 10^{-16}} = 2.37 \times 10^{12}$$

1 mL solution contains poor SNPRs:

$$N_{1ml}(\text{poor}) = 9.48 \times 10^{10}$$

The concentration of poor silver nanoprisms for SERS (2 mL solutions concentrated to 0.2 mL at last):

$$C_{SNPRs}(\text{poor}) = \frac{9.48 \times 10^{10} \times 2 \text{mol}}{6.02 \times 10^{23} \times 0.2 \times 10^{-3} \text{L}} = 1.575 \times 10^{-9} \text{M}$$

The surface of one silver nanoprism:

$$S_{SNPRs} = \frac{\sqrt{3}}{2} a^2 + 3ah$$

$$S_{SNPRs}(\text{poor}) = 3665.06 \text{ nm}^2$$

We assumed that molecular footprint of 4-MBA molecules adsorbed as a monolayer was 0.54 nm^2 .¹

Concentration of SERS experiment for good silver nanoprisms:

$$C_{SERS}(\text{poor SNPRs}) = \frac{3665.06}{0.54} \times 1.575 \times 10^{-9} \text{M} = 1.069 \times 10^{-5} \text{M}$$

For SERS experiment of poor SNPRs, accumulation time was 20 s, normal Raman detection, accumulation time was 1 s.¹

$$\text{EF}(\text{poor SNPRs}) = \frac{21009/20}{38684} \times \frac{500 \times 10^{-3}}{1.069 \times 10^{-5}} = 1.27 \times 10^3$$

For the EF of self-assembled structures, we estimated it in a quantitative way,²

$$\text{EF} = \frac{I_{SERS}}{I_{Raman}} \times \frac{N_{Raman}}{N_{SERS}} \approx \frac{I_{SERS}}{I_{Raman}} \times \frac{\sigma_s A}{\rho_s f A}$$

where σ_s is the area density of molecules on the substrates for normal Raman detection, A is focal area, the ρ_s is the surface density of molecules on the silver nanoprisms, f is occupied factor of self-assembled structures on the substrate. If these self-assembled structures occupied everywhere on the substrate in an extreme case ($f=1$), the area absorbed by 4-MBA on self-assembled structures approximate to 0.5 in the region a in Figure S13. Actually, region a has more self-assembled structures than region b due to “coffee ring” effect, resulting in region a has bigger EF than region b.

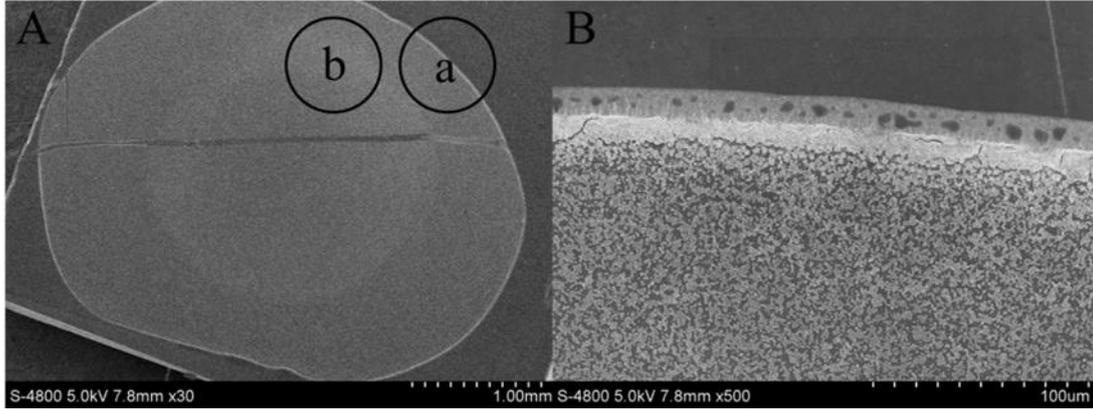


Figure S13. SEM images of self-assembly of triangular silver nanoprisms on the substrates

The area density of molecules on the substrates was estimated as follows:

3 μL 500 mM 4-MBA deposited on the silicon wafer, forming a shape of disk with radius ~ 1.5 mm. The Raman signal of silicon wafer (525 cm^{-1}) could be identified (FigureS12), which means that laser penetrated the normal Raman sample.

$$\sigma_s = \frac{3 \times 10^{-6} \times 500 \times 10^{-3} \times 6.02 \times 10^{23}}{3.14 \times 1.5 \times 10^{-3} \times 1.5 \times 10^{-3}} \text{ m}^{-2} = 1.278 \times 10^{23} \text{ m}^{-2}$$

We assumed that molecular footprint of 4-MBA molecules adsorbed as a monolayer was 0.54 nm^2 .¹

$$\rho_s = \frac{1}{0.54 \times 10^{-9} \times 10^{-9}} \text{ m}^{-2} = 1.852 \times 10^{18} \text{ m}^{-2}$$

The strongest Raman signal arose from the region a in Figure S13. In this region, we assume that the area of self-assembled structure occupied 50% of the detection area, so the occupied factor: $f=0.5$

For SERS experiment of self-assembled SNPRs, accumulation time was 0.1 s, normal Raman detection, accumulation time was 1 s.

$$\text{EF}(\text{self - assembled SNPRs}) = \frac{538662/0.1}{65722} \times \frac{1.278 \times 10^{23}}{0.5 \times 1.852 \times 10^{18}} = 1.13 \times 10^7$$

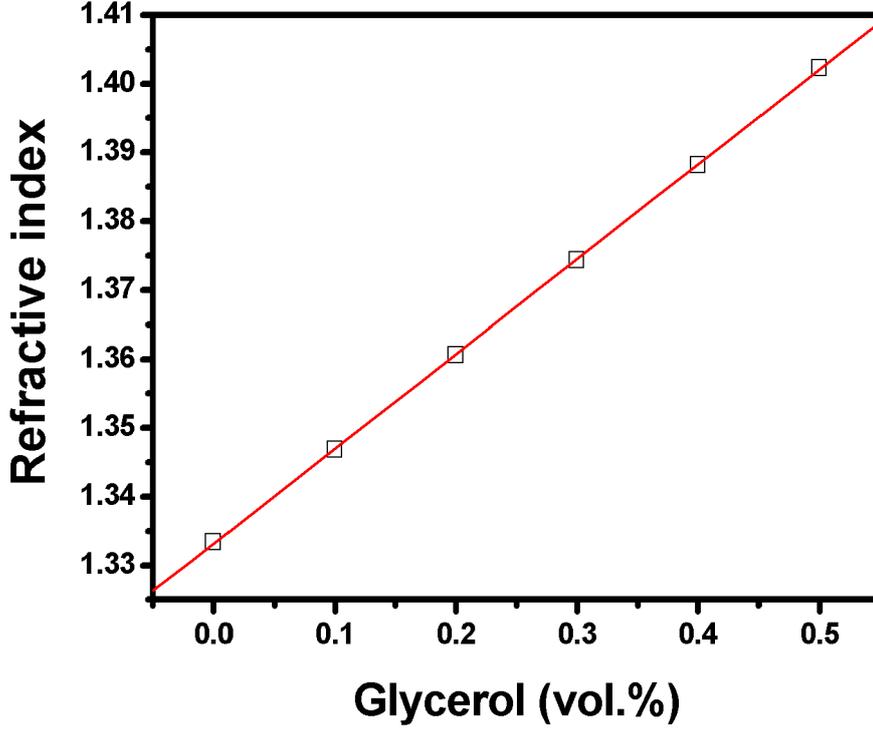


Figure S14. Dependence of the refractive index of water-glycerol solutions on the volume percentage of glycerol. The line is a linear fit. The refractive index of water-glycerol solutions could be calculated according to the Lorentz-Lorenz equation:³

$$\frac{n_{12}^2 - 1}{n_{12}^2 + 2} = \phi_1 \frac{n_1^2 - 1}{n_1^2 + 2} + \phi_2 \frac{n_2^2 - 1}{n_2^2 + 2}$$

where n_{12} is the refractive index of the liquid mixture, n_1 and n_2 are the indexes of water (1.3334) and glycerol (1.4746), respectively, and ϕ_1 and ϕ_2 are the volume fractions of the two components.

Derivation of Ag^+ ions release rate

The derivation process is similar to Zhang *et al.*⁴



$$[\text{H}^+] = \frac{10^{-14} \text{ (mol/L)}^2}{[\text{OH}^-]} \quad (3)$$

Silver nanoparticles were dissoluble in solution, and the oxidation reaction of silver nanoparticles could be treated by first-order reaction kinetics. According equation (1)~(3), similar to previous report,¹⁰ the release rate of Ag^+ ions can be expressed by the Arrhenius equation:

$$\begin{aligned} \gamma_{\text{Ag}^+} &= k C_{\text{AgNPs}} [\text{O}_2]^2 [\text{H}^+]^2 \\ &= f \exp\left(\frac{-E_a}{k_B T}\right) [\text{AgNPs}] [\text{O}_2]^2 [\text{H}^+]^2 \\ &= 10^{-28} \text{ (mol/L)}^4 f \exp\left(\frac{-E_a}{k_B T}\right) [\text{AgNPs}] [\text{O}_2]^2 [\text{OH}^-]^{-2} \end{aligned} \quad (4)$$

where k_B is the Boltzmann constant, T is temperature and E_a is the activation energy, $[\text{AgNPs}]$, $[\text{O}_2]$ and $[\text{OH}^-]$ are the molar concentration (mol/L) of silver nanoparticles (AgNPs), oxygen and OH^- , respectively. f is the frequency factor for the reaction, can be expressed as:

$$f = \pi r_{AB}^2 \left(\frac{8\pi k_B T}{\mu_{AB}} \right)^{1/2} N_A \quad (5)$$

$$r_{AB} = r_A + r_B \quad (6)$$

$$\mu_{AB} = \frac{m_A m_B}{m_A + m_B} \quad (7)$$

r_{AB} is the collision radius, and r_A and r_B represent the molecular radius of the reagents A and B, N_A is Avogadro's number, μ_{AB} is the reduced mass, m_A and m_B are the molecular weights of the reagents A and B. For this reaction, A is silver nanoparticles, B is oxygen or other molecules. So $r_A \gg r_B$, and $m_A \gg m_B$, equation (6) and (7) can be approximated as:

$$r_{AB} = r \quad (8)$$

where r is the radius of silver nanoparticles.

$$\mu_{AB} = m_A \quad (9)$$

where m_A is the molar weight of silver.

By inserting equation (8) and (9) into equation (5), we obtain:

$$f = \pi r^2 \left(\frac{8\pi k_B T}{m_A} \right)^{1/2} N_A \quad (10)$$

Then using the mass concentration ($[\text{Ag}]$) replaces the molar concentration of silver nanoparticles ($[\text{AgNPs}]$):

$$[\text{AgNPs}] = \frac{[\text{Ag}]}{N_A \rho \frac{4}{3} \pi r^3} \quad (11)$$

where ρ is the density of silver.

By inserting equation (10) and (11) into equation (4), we get:

$$\gamma_{\text{Ag}^+} = \frac{3}{4} \times 10^{-28} (\text{mol/L})^4 \left(\frac{8\pi k_B T}{m_A} \right)^{1/2} \rho^{-1} \exp\left(\frac{-E_a}{k_B T}\right) [\text{Ag}] r^{-1} [\text{O}_2]^{0.5} [\text{OH}^-]^{-2} \quad (12)$$

Reference:

1. Xia, X.; Zeng, J.; McDearmon, B.; Zheng, Y.; Li, Q.; Xia, Y., Silver Nanocrystals with Concave Surfaces and Their Optical and Surface-Enhanced Raman Scattering Properties. *Angewandte Chemie* 2011, *123* (52), 12750-12754.
2. Cathcart, N.; Kitaev, V., Monodisperse Hexagonal Silver Nanoprisms: Synthesis via Thiolate-Protected Cluster Precursors and Chiral, Ligand-Imprinted Self-Assembly. *ACS nano* 2011, *5*, 7411-7425.
3. Chen, H.; Kou, X.; Yang, Z.; Ni, W.; Wang, J., Shape- and size-dependent refractive index sensitivity of gold nanoparticles. *Langmuir* 2008, *24*, 5233-5237.
4. Zhang, W.; Yao, Y.; Sullivan, N.; Chen, Y., Modeling the primary size effects of citrate-coated silver nanoparticles on their ion release kinetics. *Environmental science & technology*, 2011, *45*, 4422-4428.