

Supporting Information

Synthesis of Porous Au-Ag Alloy Nanorods with Tunable Plasmonic Properties and Intrinsic Hotspots for Surface-Enhanced Raman Scattering

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S1. Experimental Details

S1.1 Reagents and chemicals

Hexadecyltrimethylammonium bromide (CTAB, >99%), hexadecyltrimethylammonium chloride (CTAC, >99%), sodium borohydride (NaBH_4 , 99%), hydrogen tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.9%), L-ascorbic acid (AA, 99.9%), hydrochloric acid (HCl , 36–38% in water), hydrofluoric acid (HF , $\geq 40\%$), $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution (25 wt% in water), Sodium Carbonate (Na_2CO_3 , 99%) were purchased from Aladdin Chemical Co., Ltd. Sodium oleate (NaOL , >95%) was purchased from TCI. Silver nitrate (AgNO_3 , 99.8%), diethylamine (DEA, 99%), and hydrogen peroxide (H_2O_2) were supplied by Sinopharm Chemical Reagent Co., Ltd. 4-nitrothiophenol ($\text{C}_6\text{H}_5\text{NO}_2\text{S}$, 4-NTP, 80 %) was purchased from Sigma-Aldrich. Tetraethoxysilane (TEOS, 99.9%) and absolute ethanol (EtOH) were purchased from Shanghai Chemicals. Ultrapure water obtained from a Direct-Q3 system with a resistivity of at least $18.2 \text{ M}\Omega \cdot \text{cm}$ was used in all experiments. All chemical reagents were used as received without further purification. Glassware and stir bars were cleaned in aqua regia and fully rinsed with ultrapure water.

S1.2 Synthesis of AuNRs

A seed solution was prepared by adding 0.6 mL of ice-cold solution NaBH_4 (10 mM) into 9.95 mL of a solution of 0.1 M CTAB and 0.05 mL HAuCl_4 (50 mM) solution under vigorous stirring at room temperature (27 °C) for 2 min. The resultant solution was left undisturbed for 3 h to ensure the complete decomposition of any NaBH_4 that remained in the reaction mixture. AuNRs were prepared using a seed-mediated growth method in a binary surfactant mixture composed of CTAB and NaOL according to a previously reported protocol with minor modifications¹. In a typical AuNRs synthesis, 9.0 g of CTAB and 1.234 g of NaOL were dissolved in 500 mL of warm water. The solution was then cooled to room temperature, and 4.8 mL of 20 mM AgNO_3 solution was added. The mixture was kept undisturbed at 30 °C for 15 min, after which 5 mL of

50 mM HAuCl₄ solution was added. After stirring for 90 min, 1.6 mL HCl (36-38 wt.% in water) was injected. After another 15 min of slow stirring, 800 μL of 0.1 M AA was added, and the solution was vigorously stirred for 30 s. Finally, 400 μL of a seed solution was injected into the growth solution, and then the solution was shaken for 30 s and left undisturbed in a 30 °C water bath for 12 h. The final product was separated and re-dispersed in 400 mL of CTAC solution (0.08 M) as the stock solution. Higher aspect ratio nanorods was prepared using the same parameters except the addition of 4.8 mL HCl (36-38 wt.% in water).

S1.3 Preparation of Au-Ag core-shell nanorods (Au@AgNRs)

Au@AgNRs were synthesized using a previously reported procedure with some modifications ². 1.6 mL of 20 mM AgNO₃ solution was added to 20 mL of colloidal Au nanorods solution. Then, the solution was mixed under magnetic stirring for 10 min, followed by the addition of 1.6 mL of 0.1M ascorbic acid. The reaction mixture was kept in a water bath at 65 °C for 8 h to ensure the complete Ag shell growth on the Au nanorods. This process led to the formation of Au-Ag core-shell nanocuboids, which were subsequently centrifuged and re-dispersed in 20 mL of CTAC solution (1.5 mM) to produce a silica coating.

S1.4 Characterization

Extinction spectra of the as synthesized nanoparticles were measured on ultraviolet visible-near infrared (UV-vis-NIR) spectrometer (UV-6300) in the range of 200–1100 nm. Transmission electronmicroscopy (TEM) images were conducted on a JEOL-1010 microscope operated at 80 kV. Scanning TEM (STEM) and High-resolution TEM (HRTEM) images and energy-dispersive X-ray (EDX) line-scanned elementmaps were acquired using a JEOL JEM-2100F microscope operated at 200 kV. ICP-MS measurements were performed on an Agilent 7700 system.

S1.5 Enhancement Factor (EF) calculation

The SERS enhancement factor (EF) is described as the intensity ratio between the SERS signal and that expected from regular non-SERS Raman scattering for a given analyte molecule, normalized by the special number of the probed molecule. The EF can be calculated by the following equation:

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

where I_{SERS} and I_{Normal} denote the intensities of 4-NTP at 1334 cm^{-1} Raman shift of the SERS and normal Raman spectra. N_{SERS} is the number of 4-NTP molecules adsorbed on the SERS substrate in the area being probed. N_{Normal} is the number of molecules within the excitation volume of the laser used in a regular Raman measurement. The SERS and normal Raman spectra were measured under the same condition (excitation: 785 nm, 30 mW; exposure time: 10 s).

In the Raman spectra experiment, 10 μl of 0.1M 4-NTP dissolved in ethanol was dropped on a round quartz substrate (diameter =6 mm). The diameter of the laser spot was approximately 2 μm . To determine N_{SERS} , a self-assembled monolayer of 4-NTP molecules (molecular footprint size 0.39 nm^2) was assumed to be closely packed on the surface of each nanoparticle ^{3,4}. The calculation of the desired value was therefore performed as the following:

$$\text{Area of the laser spot } (S_{laser}) = \pi \times (10^{-6} \text{ m})^2$$

$$\text{Area of all substrates } (S_{surface}) = \pi \times (3 \times 10^{-3} \text{ m})^2$$

$$\begin{aligned} N_{Normal} &= (\text{4-NTP concentration}) (\text{Volume of 4-NTP drop}) (\text{Avogado number}) (S_{laser} / \\ &S_{surface}) \\ &= (10^{-1}) \times (10^{-5}) \times (6.02 \times 10^{23}) \times (10^{-6})^2 / (3 \times 10^{-3})^2 \\ &= 6.69 \times 10^{10} \end{aligned}$$

$$N_{SERS} = S_{laser} / \text{4-NTP footprint}$$

$$= \pi \times (10^{-6})^2 / (0.39 \times 10^{-18})$$

$$= 8.05 \times 10^6$$

So, SERS enhancement factors (after etching in H_2O_2 and $\text{NH}_3 \cdot \text{H}_2\text{O}$)

$$\text{Au@AgNRs: } EF = (2754)/(279) \times (6.69 \times 10^{10}) / (8.05 \times 10^6) = 8.2 \times 10^4$$

$$\text{P-AuAgNR}_{741}: \text{EF} = (10450)/(279) \times (6.69 \times 10^{10}) / (8.05 \times 10^6) = 3.11 \times 10^5$$

$$\text{S-AuAgNR}: \text{EF} = (7508)/(279) \times (6.69 \times 10^{10}) / (8.05 \times 10^6) = 2.23 \times 10^5$$

$$\text{AuNRs}: \text{EF} = (1800)/(279) \times (6.69 \times 10^{10}) / (8.05 \times 10^6) = 5.36 \times 10^4$$

S2. Additional Figures

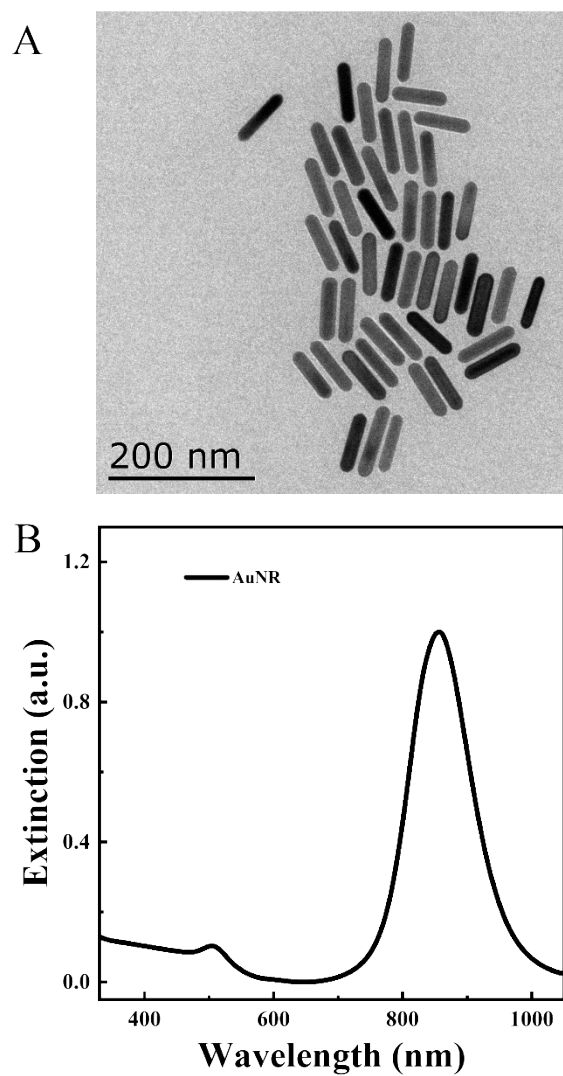


Fig. S1 TEM images of AuNRs (A) and corresponding experimental extinction spectrum (B).

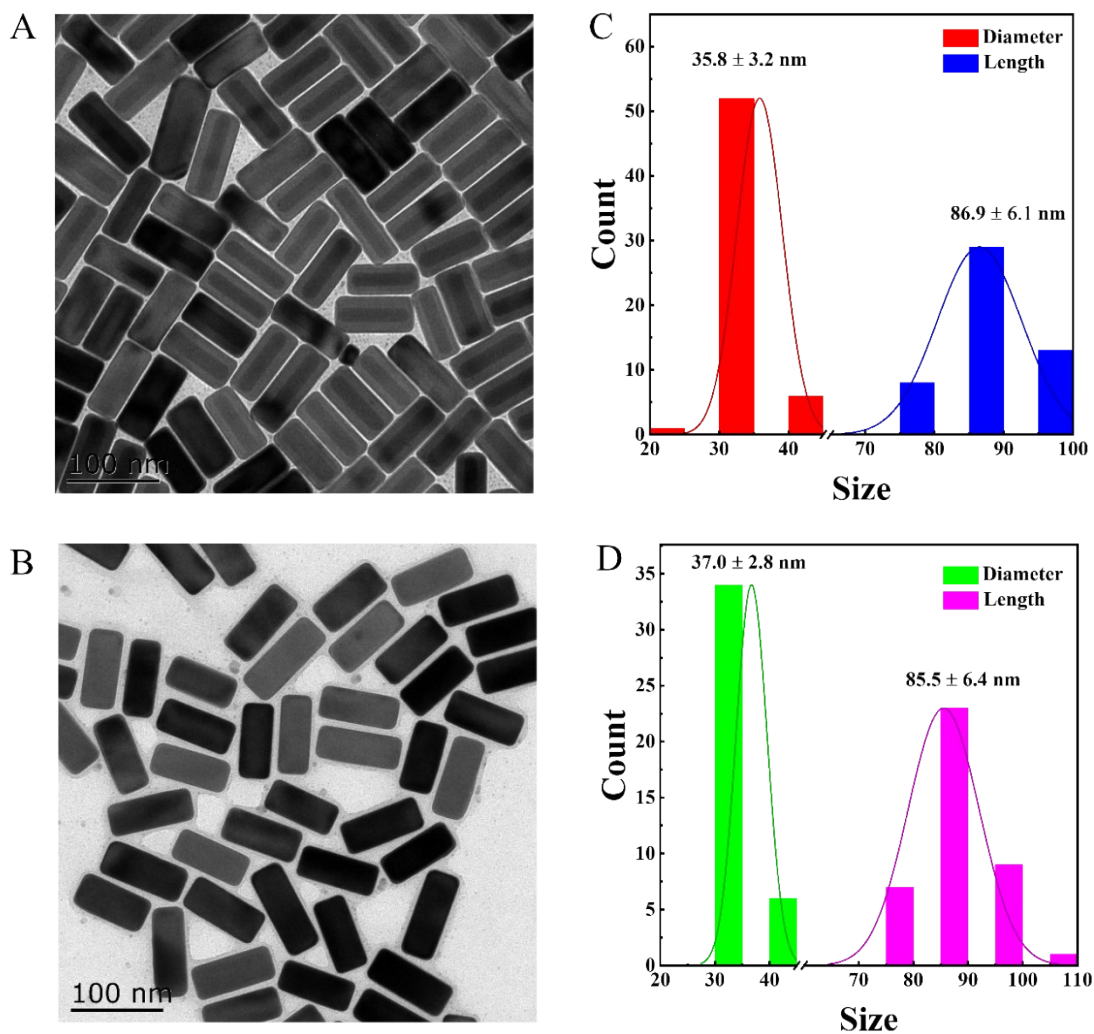


Fig. S2 TEM images of Au@AgNRs (A) and S-AuAgNRs (B). Histograms showing the distributions of the widths and lengths of the Au@AgNRs (C) and S-AuAgNRs (D).

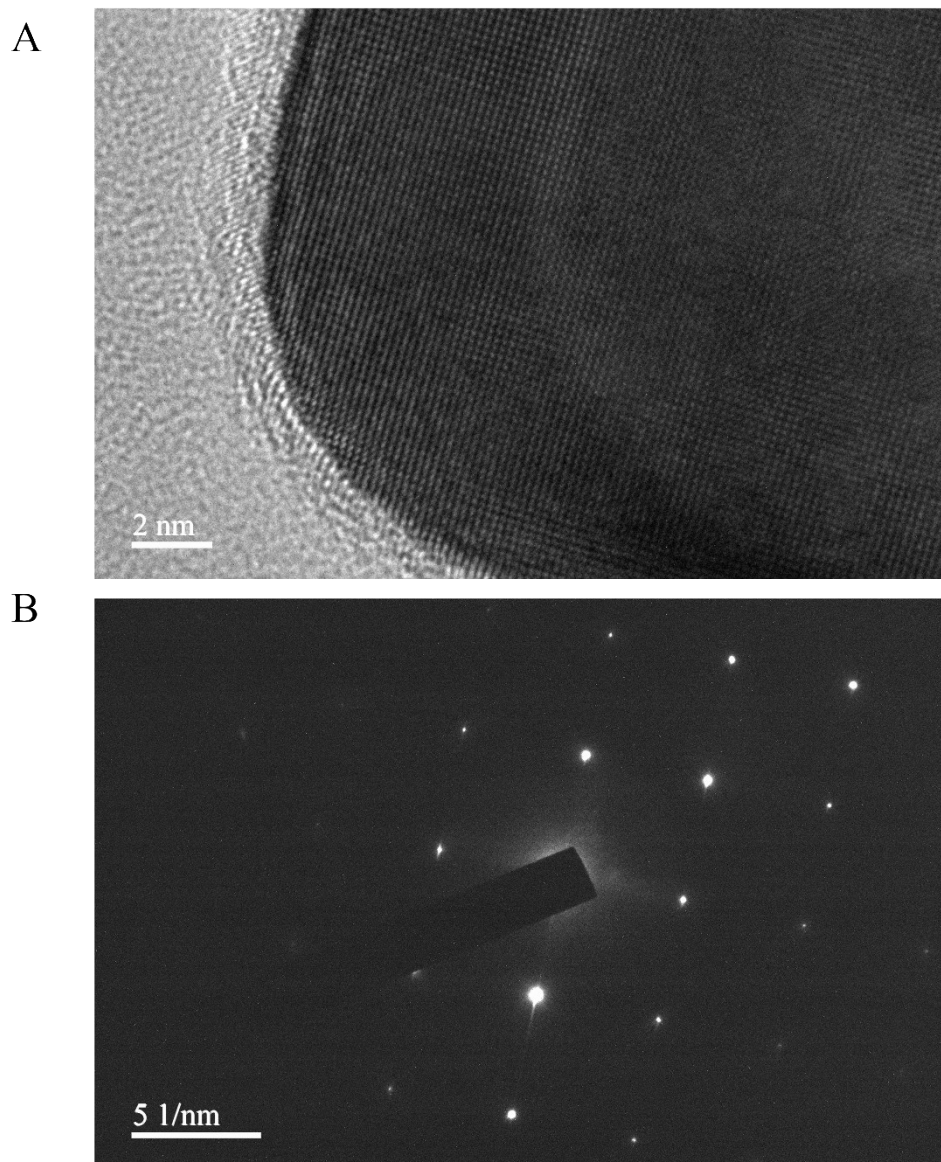


Fig. S3 HRTEM image of the S-AuAgNR (A). Electron diffraction pattern recorded on a whole S-AuAgNR basis (B).

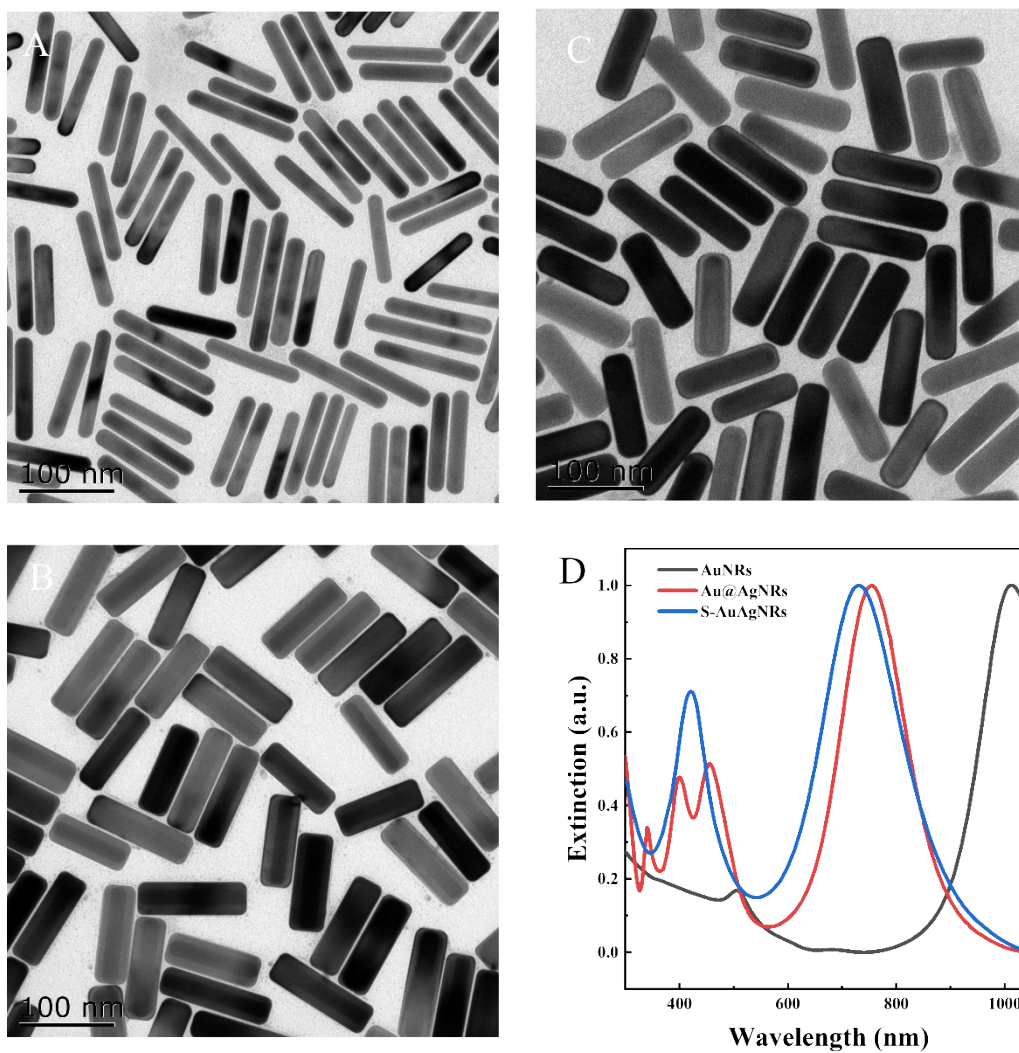


Fig. S4 TEM images of higher aspect ratio nanorods at different stages of a typical synthesis: AuNRs (A), Au@AgNRs (B), S-AuAgNRs (C) and the corresponding extinction spectra of the samples (D).

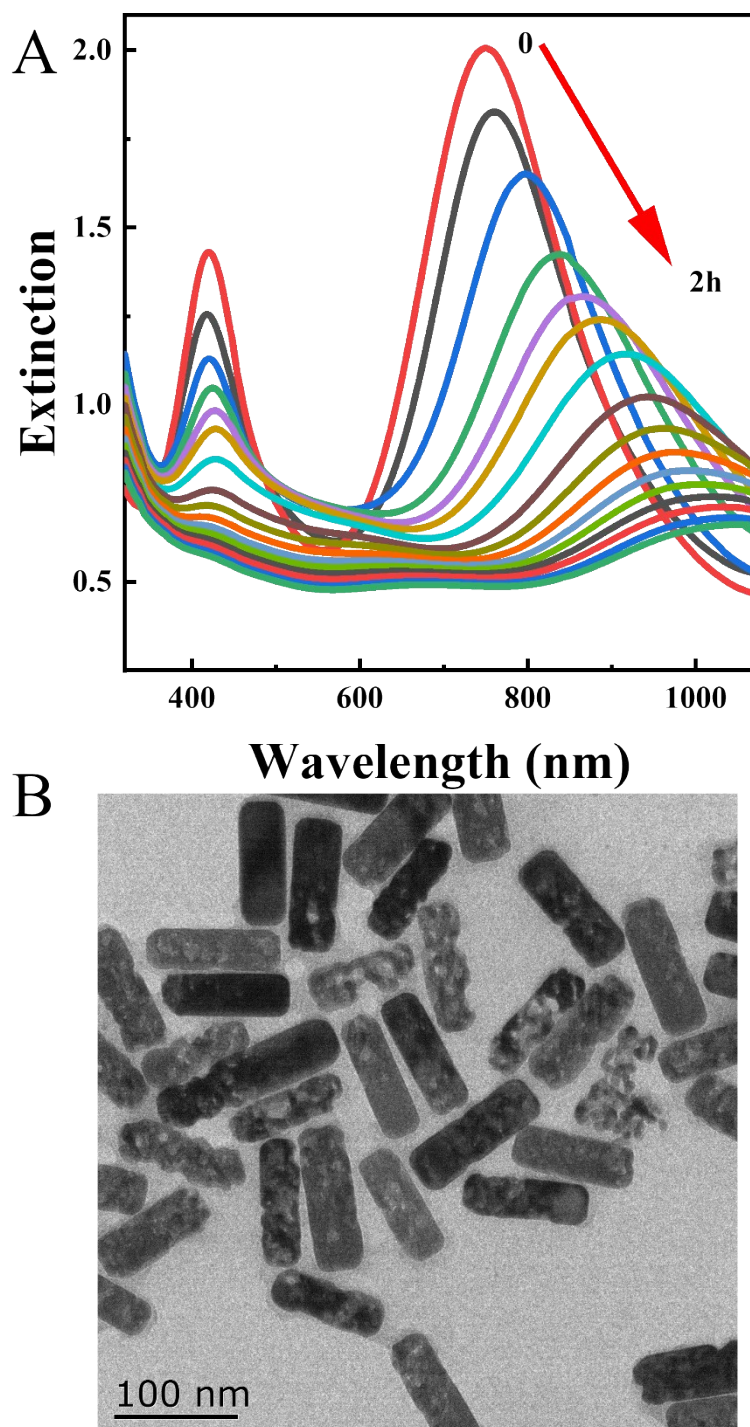


Fig. S5 (A) Extinction spectra of higher aspect ratio P-AuAgNRs as a function of dealloying time. (B) Representative TEM image of the P-AuAgNRs.

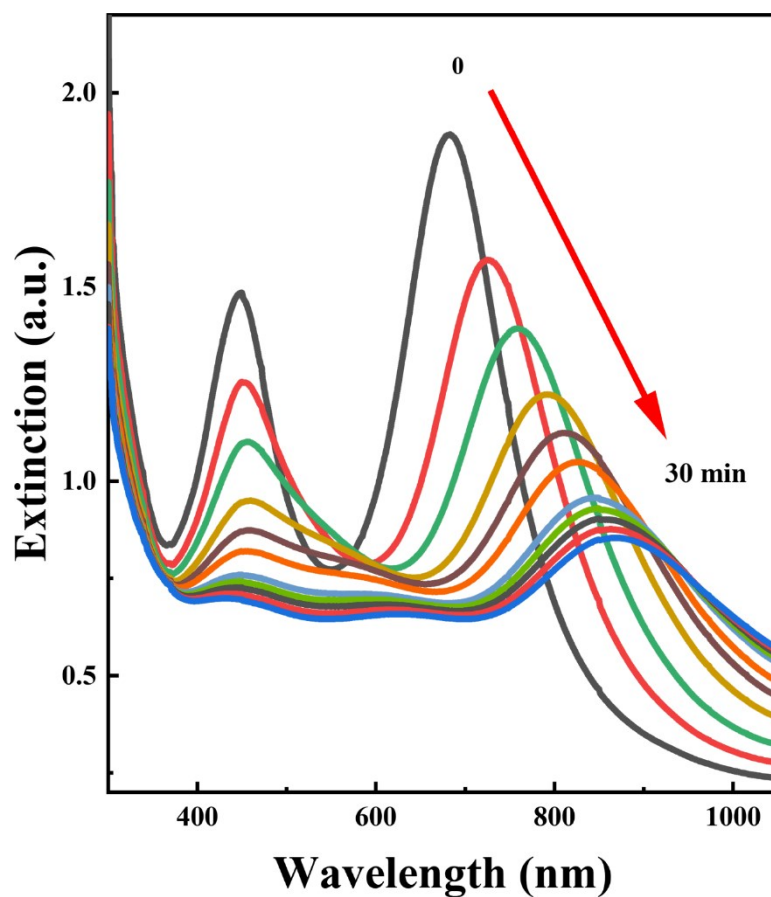


Fig. S6 Extinction spectra of P-AuAgNRs as a function of dealloying time. 0.15 mL of 0.025 M $\text{Fe}(\text{NO}_3)_3$ aqueous solution was mixed with 5 mL of the S-AuAgNRs suspension one time in the presence of 0.05 M CTAB.

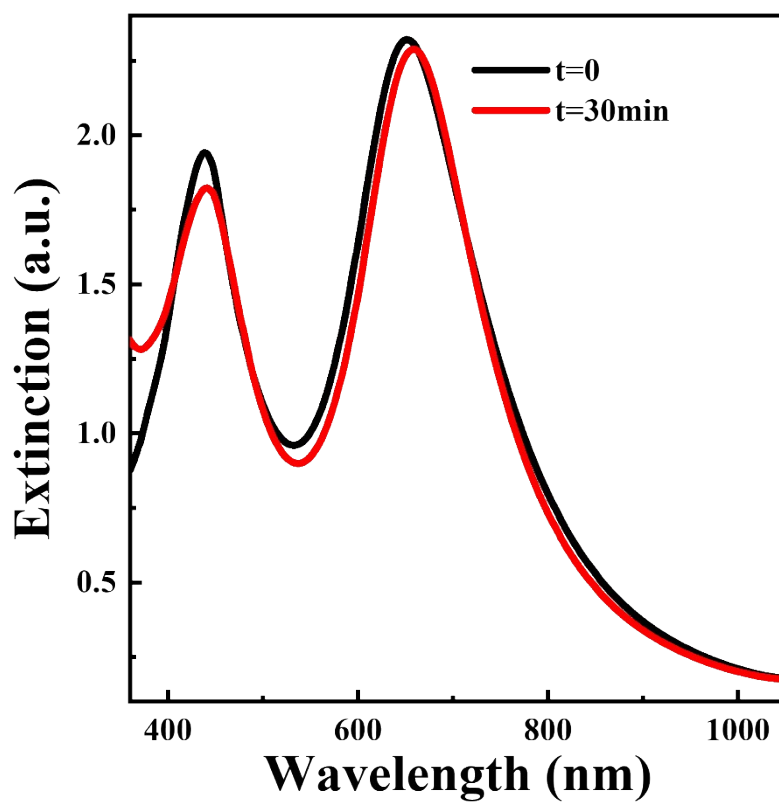


Fig. S7 Extinction spectra of S-AuAgNRs exposed to $\text{Fe}(\text{NO}_3)_3$ aqueous solution in the presence of CTAC.

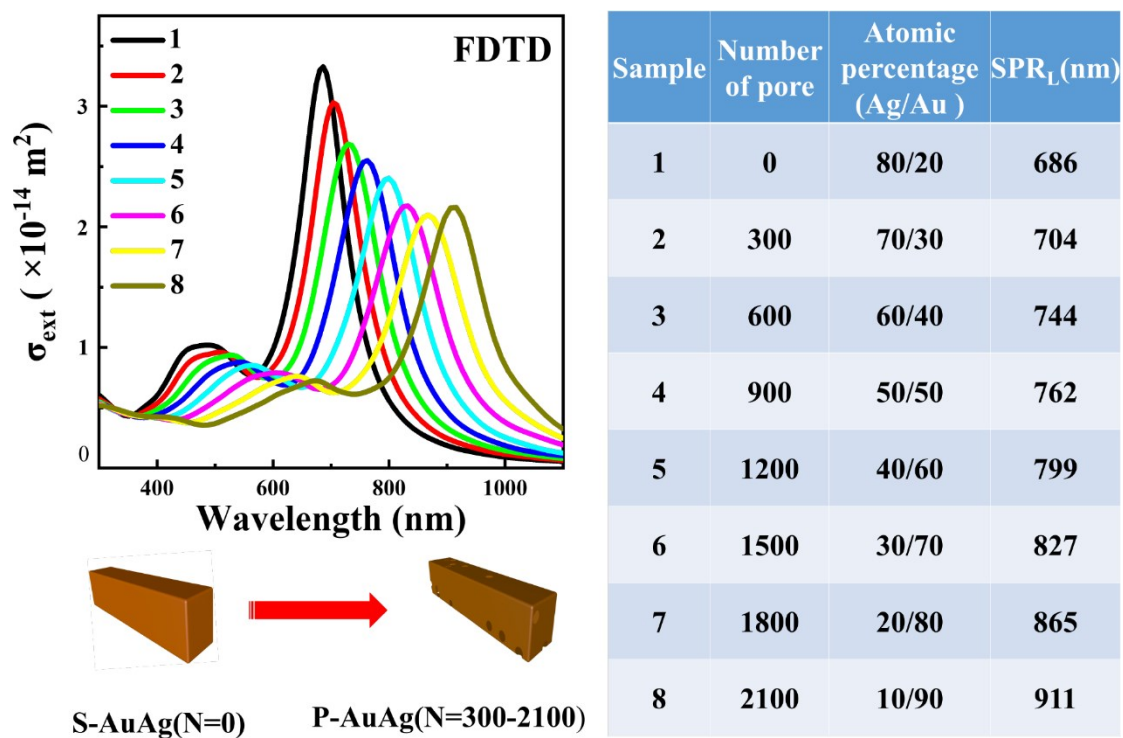


Fig. S8 FDTD-calculated extinction spectra of P-AuAgNRs. The geometric parameters are shown in the right panel.

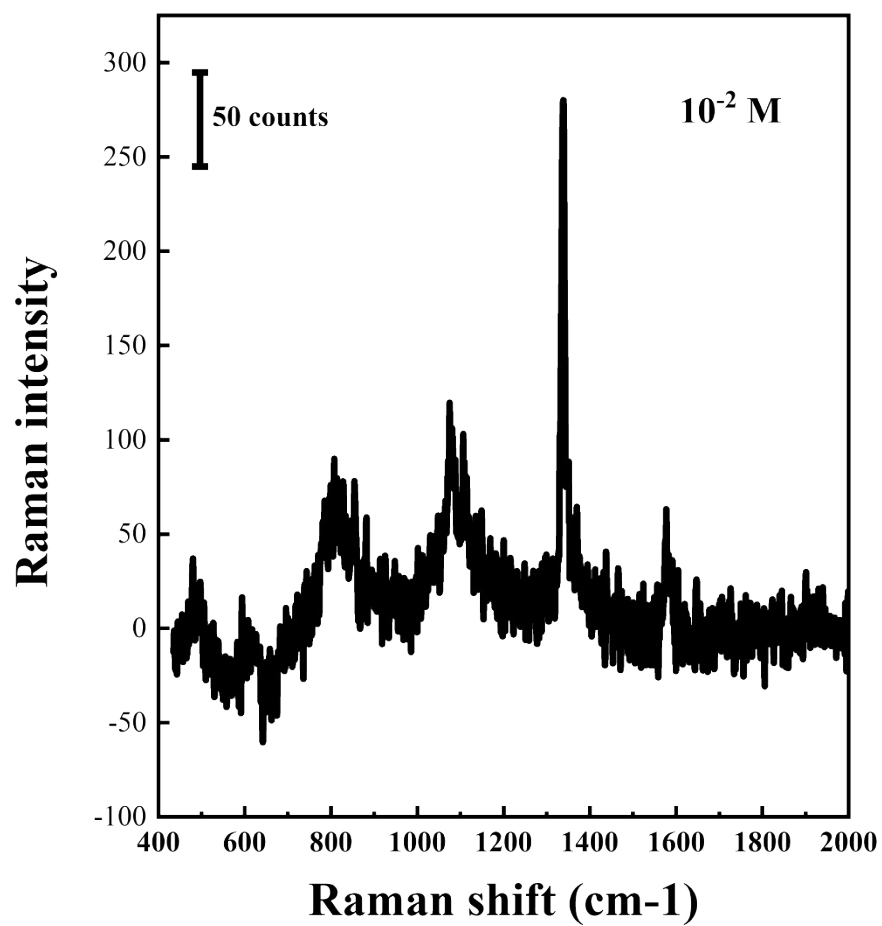


Fig. S9 Normal Raman signal of 10 μ l of 0.1 M 4-NTP solution dropped on the quartz substrate.

S3. References

- 1 X. C. Ye, C. Zheng, J. Chen, Y. Z. Gao and C. B. Murray, *Nano Lett.*, 2013, **13**, 765-771.
- 2 R. B. Jiang, H. J. Chen, L. Shao, Q. Li and J. F. Wang, *Adv. Mater.*, 2012, **24**, Op200-Op207.
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- 4 Q. F. Zhang, Y. D. Zhou, E. Villarreal, Y. Lin, S. L. Zou and H. Wang, *Nano Lett.*, 2015, **15**, 4161-4169.