Electronic Supplementary Material (ESI) for Nanoscale.
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Supplementary Information for:

Bidirectional Plasmonic Coloration with Gold Nanoparticles by Wavelength-Switched Photoredox

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Extinction spectrum of acetone

The extinction spectrum of acetone shows a band centered at 260 nm as shown in Fig. S1 in our experiment.

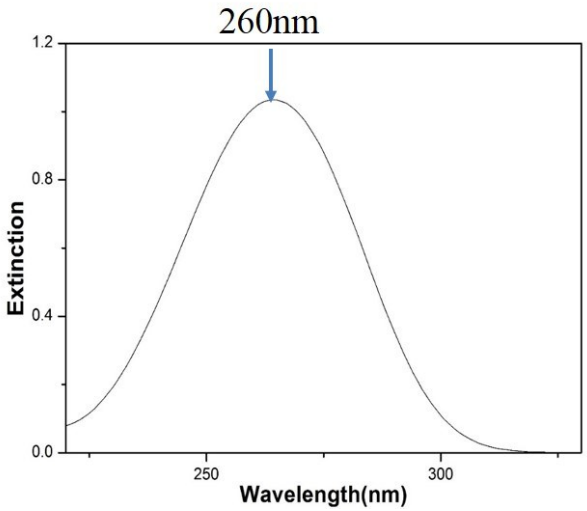

Figure. S1. The extinction spectrum of acetone.

Acetone effect in the photoreduction of gold nanorods

With the irradiation of 254 nm light for 5 h, the extinction spectra of growth solution (I) with acetone and without acetone have been shown in Figure. S2, respectively. Without acetone in the growth solution (I), we found the AuNRs can barely be formed by the light irradiation.

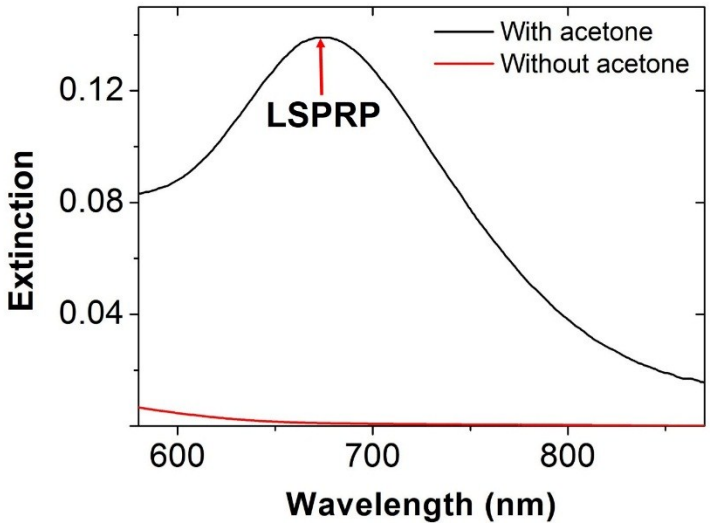

Figure. S2. Acetone effect in photoreduction of gold nanorods. Black curve (irradiation time of 5 h, in growth solution (I) with 65 μL acetone), red curve (irradiation time of 5 h, in growth solution (I) without acetone).

Relationship between the equivalent photoreduction rate (R_r) and the concentration of gold precursor

The relationship between the equivalent photoreduction rate (R_r) and the concentration of gold precursor ([Au^+]) has been investigated, as shown in Figure. S3. We found that the R_r have increased from 0.33 nm/min to 0.60 nm/min, with increasing the [Au^+] from 1.0 mM to 2.0 mM.

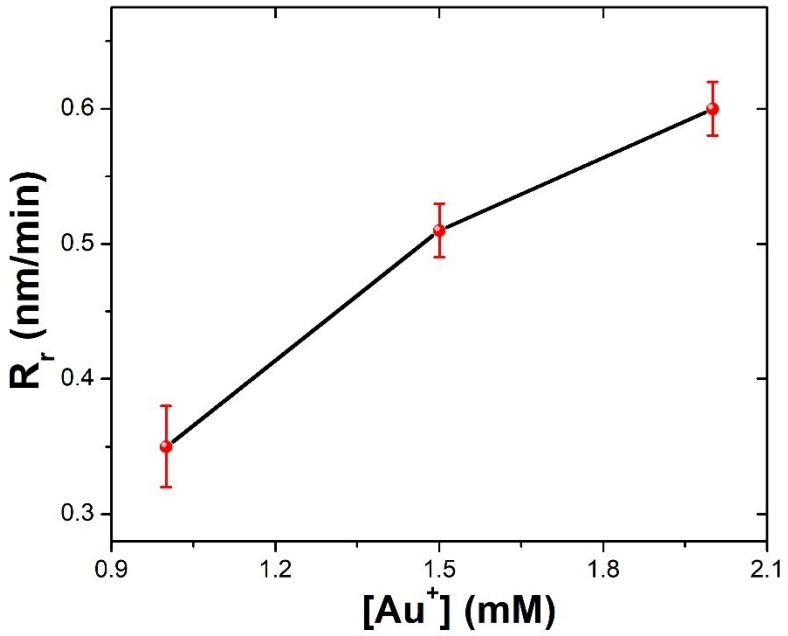

Figure. S3. Relationship between the equivalent photoreduction rate (R_r) and the concentration of gold precursor [Au^+] in the growth solution (I).

Varing $|R_o|$ corresponding to exposure light of different wavelengths

$|R_o|$ is obtained at approximately 0.03 nm/min with exposure to visible light (420 nm - 700 nm), which can be attributed to that hot electrons formed through intraband excitation by SPR is less reactive to oxidation. In contrast, combined intra-band and inter-band excitation of hot electrons upon exposure to Near-UV-Vis light (300 nm - 700 nm, λ_2) increased the $|R_o|$ by 31.6 times.

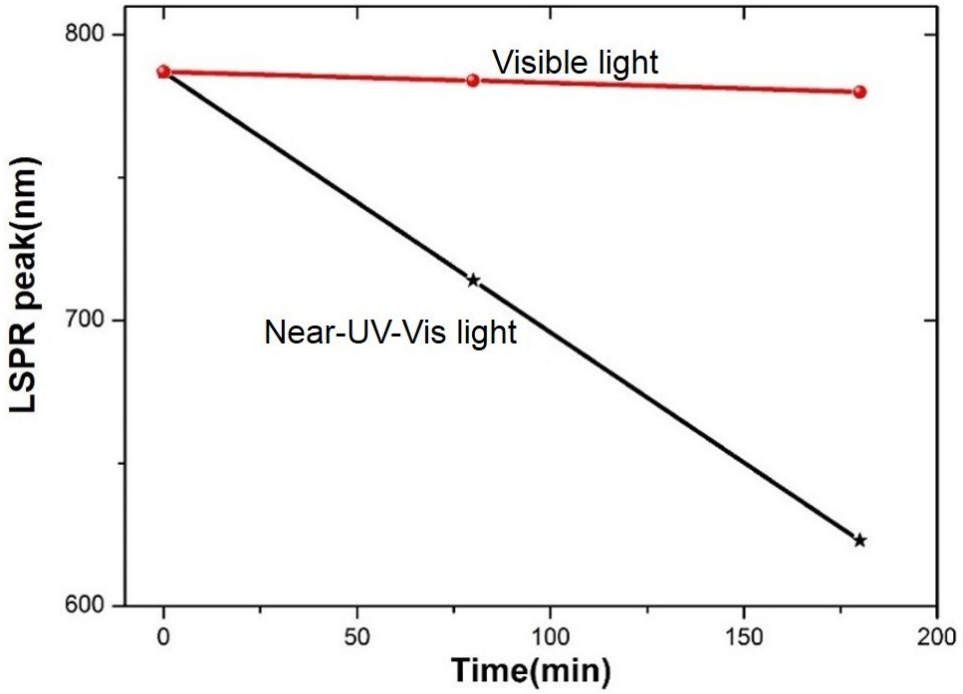

Figure. S4. Different $|R_o|$ corresponding to exposure to two wavelengths of light. Shown with red curve for visible light irradiation, and $|R_o|$ = 0.03 nm/min; and black curve for λ_2 irradiation, and $|R_o|$ = 0.79 nm/min.

Oxygen effect in the photooxidation process

Figure. S5 shows that the localized surface plasmon resonance peak (LSPRP) of AuNRs solutions has been tuned by the light irradiation for 75 min. Through bubbling nitrogen to the AuNRs solution for 15 min to remove the oxygen (O_2) in the AuNRs solution, the LSPRP blue shifts from 770 nm to 752 nm in the spectrum, the range of which is shorter than that for the sample without removing O_2 (from 770 nm to 710 nm). This means the oxygen dissolved in the AuNRs solution is capable of oxidizing the rods upon the light irradiation.

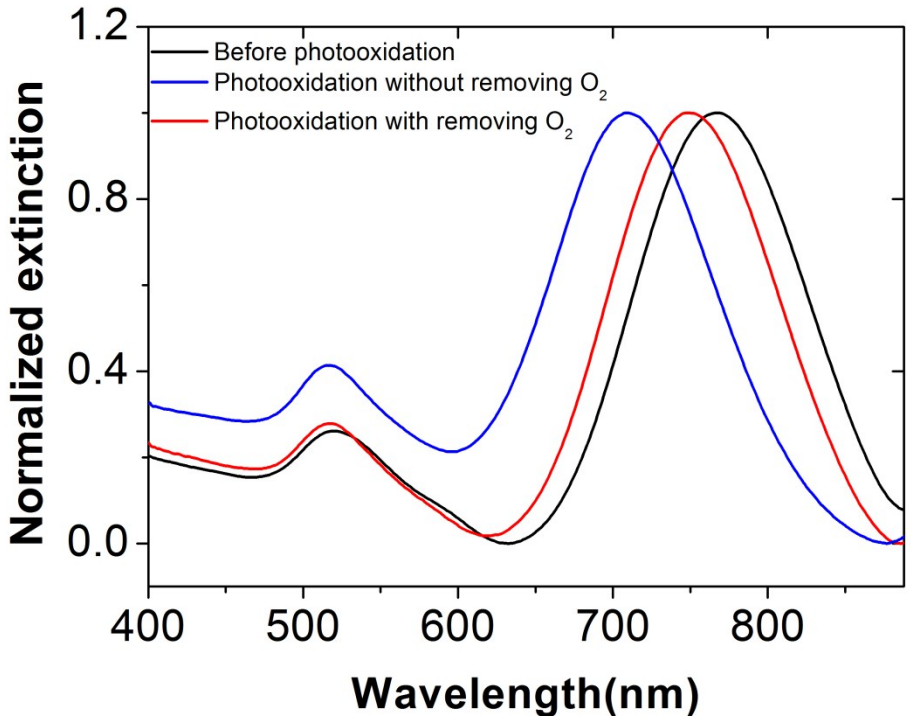

Figure. S5. Extinction spectra of AuNRs solutions before and after photooxidation. The LSPRP of AuNRs solution is at 770 nm before the light irradiation (Initial state, black curve). After light irradiation for 75 min, for the samples with (red curve) and without (blue curve) removing oxygen, the LSPRPs of AuNRs blue shift from 770 to 752 nm and from 770 nm to 710 nm, respectively.

Photograph of AuNRs in photooxidation

A digital photograph of the AuNRs samples was taken out with varying oxidation time for extinction spectra measurements in Figure. S6. The blue-shift of the LSPRP caused a continuous color change during photooxidation.

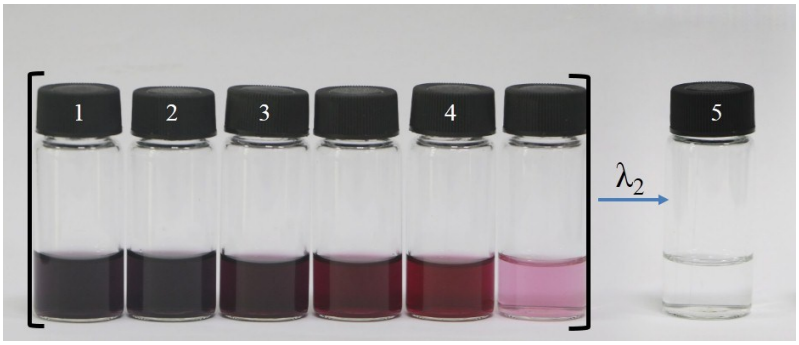

Figure. S6. The color changing with Near-UV-Vis light (λ_2)-steered photooxidation, from 1: Deep purple to 5: transparent with increasing oxidation time.

Extinction spectra of supernatant after photooxidation of AuNRs

From the extinction spectrum of the supernatant after photooxidation reaction, we can find a band stretch from 240 nm to 265 nm, symbolizing the presence of monovalent gold ions in the supernatant.

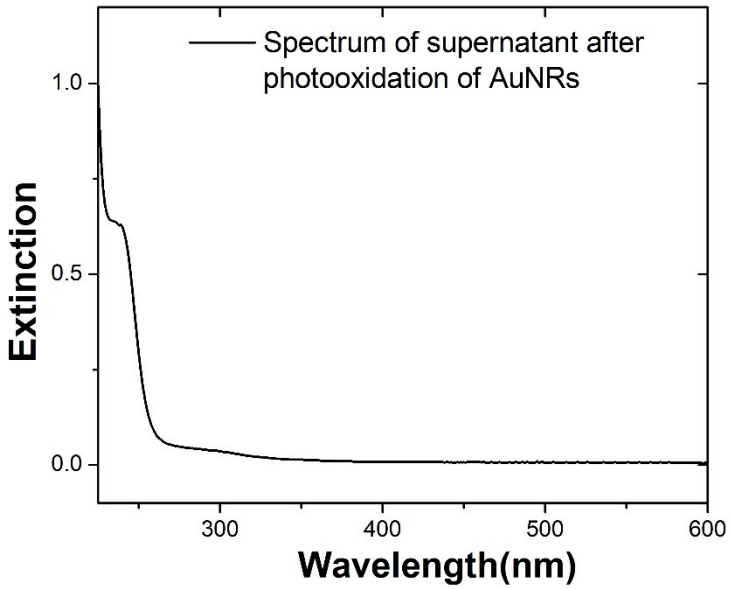

Figure. S7. The extinction spectra of the supernatant solution after the photooxidation of AuNRs.

Field intensity distribution maps on AuNRs

The simulations of the field intensity distribution on AuNRs were performed by using the finite-difference-time-domain (FDTD) method with perfectly matched layer boundary condition. The light source is a planar wave with the broadband wavelength ranging from 400 nm to 700 nm. And the incident light was linearly polarized. The override mesh cell size used in the simulation was $0.5 \times 0.5 \times 0.5$ nm^3. The aspect ratios of AuNRs used in the simulation were ranged from 2 to 4 and the width of the AuNRs is 10 nm. The enhancements of electric fields on the AuNRs tips ($|E/E_0|^2$, where E is the field intensity on the AuNRs tips and E_0 is the field intensity of the incident light) calculated at each LSPRR are 29, 19 and 12, respectively.

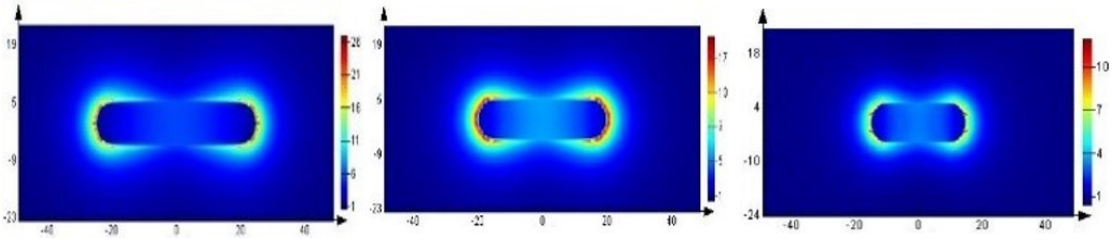

Figure. S8. Field intensity distribution maps of AuNRs corresponding to AR = 4 for the left, 3 for the middle and 2 for the right.

Calculation of LSPRP

According to Mie-Gans theory[2], the relation between the aspect ratio (AR) of the AuNRs and the LSPRP can be numerically calculated. The wavelength dependent extinction coefficient γ of randomly oriented gold nanoparticles in the dipole approximation can be expressed as: $\gamma = \frac{2\pi W}{3\lambda}\sum_i \frac{(1/P_i^2)\varepsilon_2}{(\varepsilon_1 + \frac{1-P_i}{P_i}\varepsilon_m)^2 + \varepsilon_2^2}$, where W is the function of number of particles and ε_m is the dielectric constant of the surrounding medium, λ is the wavelength of the interacting light, and $\varepsilon_1$and ε_2 are the real and complex part of the material dielectric function, respectively. P_i are the polarization factors for three axes a, b, c of the rod with c>a=b (c for long axial, a and b for the other two short axes), which can be defined as $P_c = \frac{1-e^2}{e^2}[\frac{1}{2e}\ln\left(\frac{1+e}{1-e}\right) - 1]$, $P_a = P_b = \frac{1-P_c}{2}$, $e = \sqrt{1-(\frac{1}{AR})^2}$, respectively. Accordingly, the AuNRs LSPRP can be obtained with respect to the aspect ratio increasing from 2 to 4 (Figure. S9) during wavelength-steered photoredox process.

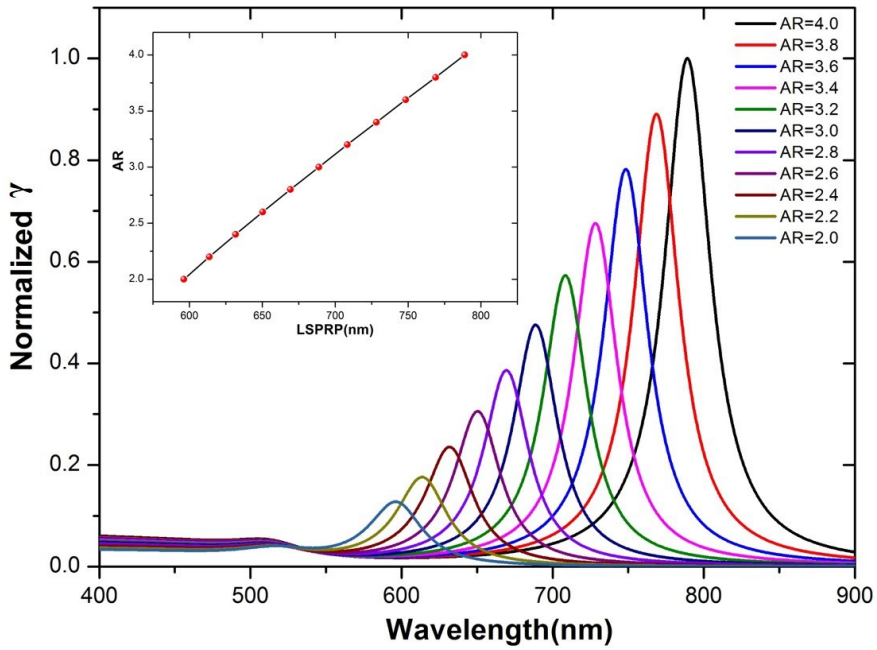

Figure. S9. The simulated results of the relation between the LSPRP and the aspect ratio (range from 2 to 4).

AuNRs solutions with different pH values after standing for 60 h

AuNRs solutions with three different pH values (pH = 6, pH = 3, pH = 1) were kept in the dark for 60 h. We can find that without light irradiation, the variance of pH values led to barely changes in the SPR properties of the AuNRs solution.

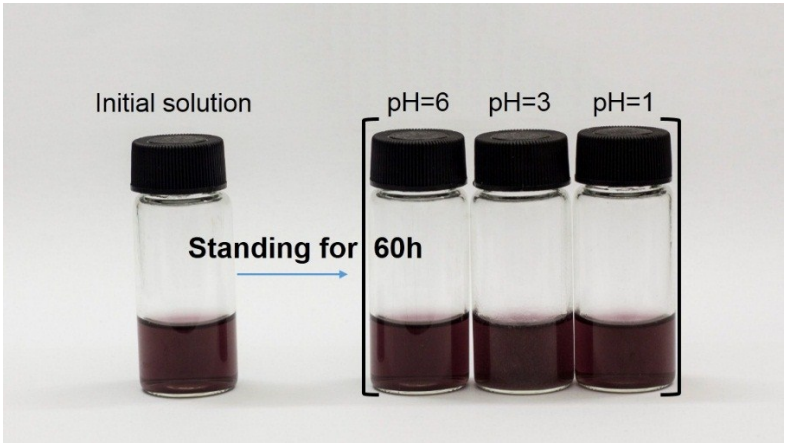

Figure. S10. The photograph of AuNRs solutions with different pH values before and after standing for 60 h.

Relationship between the equivalent photooxidation rate ($|R_o|$) and the density of AuNRs

The relationship between equivalent photooxidation rate $|R_o|$ and the optical density (OD) value of AuNRs solution has been investigated, as shown in Figure. S11. With increasing the OD value of AuNRs solution from 0.03 to 0.14, the $|R_o|$ is decreased from 1.03 nm/min to 0.67 nm/min, which can be ascribed to the descended efficiency of photo-shortening rods, considering more AuNRs are waiting for being reshaped for a given concentration of oxidants.

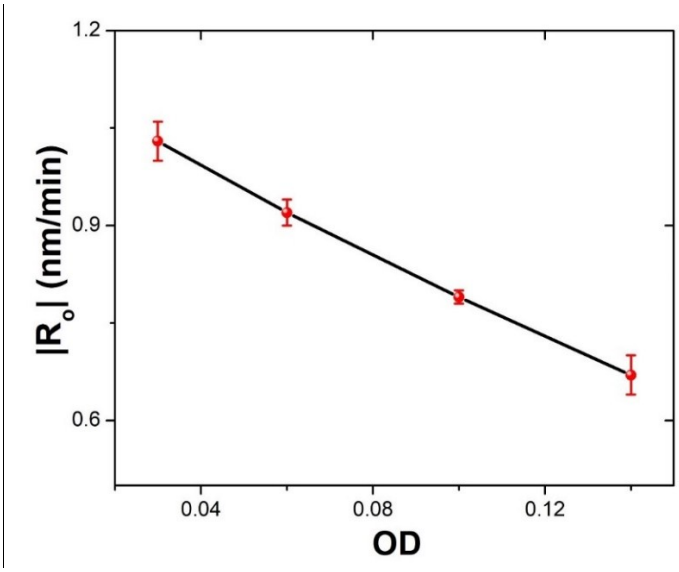

Figure. S11. Relationship between the equivalent photooxidation rate ($|R_o|$) and the optical density (OD) values of AuNRs.

Extinction spectra of AuNRs solution in the third cycle of LSPRP tuning

In the third cycle of LSPRP tuning, the LSPRP of AuNRs solution increased from 630 nm to 660 nm (photoreduced state, as shown in Figure. S12a) and returned to 630 nm (photooxidized state, as shown in Figure. S12b).

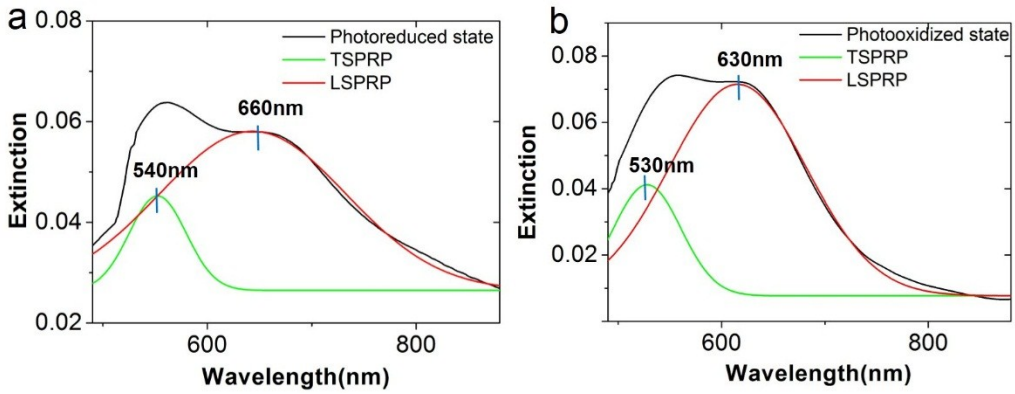

Figure. S12. Extinction spectra acquired corresponding to (a) the "photoreduced" state and (b) the "photooxidized" state of the AuNRs solution, respectively, in the third cycle of LSPRP tuning.

Extinction spectrum of AuNRs solutions before and after photooxidation for coloration tuning

The extinction spectrum of AuNRs solutions before and after photooxidation is shown in Figure. S13. From the spectrum, we can find the LSPRP is at ~780 nm (black curve). After light irradiation for 300 min, the LSPRP of AuNRs is absent.

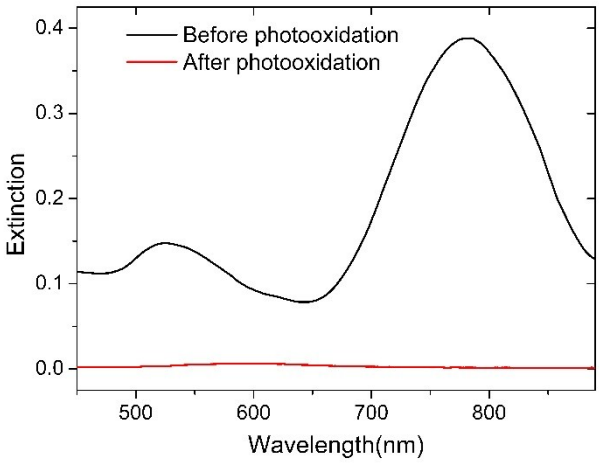

Fig. S13. Extinction spectrum of AuNRs solutions before and after photooxidation for coloration tuning. The LSPRP of AuNRs solution is at 787 nm before the light irradiation (black curve). After light irradiation for 300 min, the LSPRP of AuNRs is absent (red curve).

TEM image of AuNRs with LSPRP at 787nm

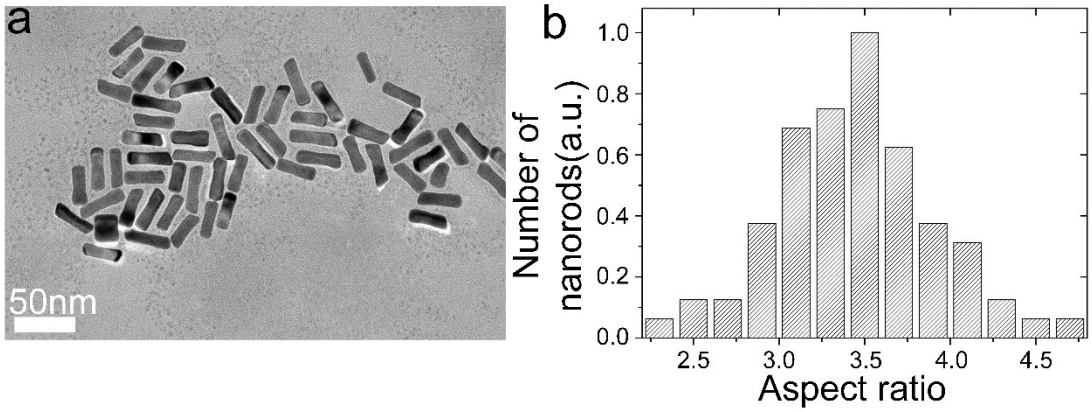

Fig. S14. The TEM image of AuNRs before photooxidation for coloration tuning and the corresponding distribution histogram. The mean length is 43.9 ± 6.5 nm with the average aspect ratio (AR) at 3.5 ± 0.5.

Photoreduction-based SPR tuning with solutions exposed to light of wavelength λ_1 for coloration experiments

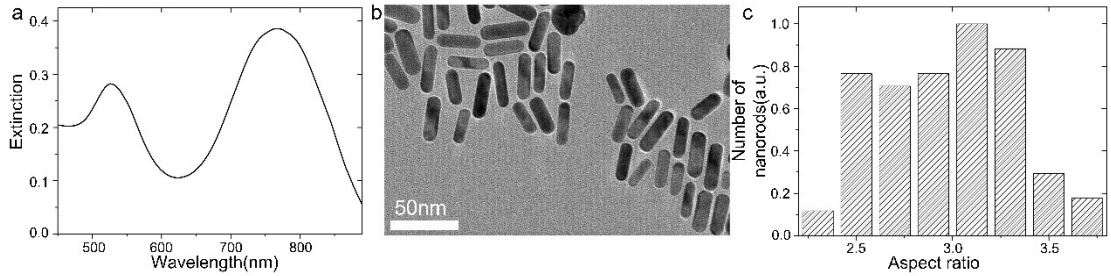

Fig. S15. Photoreduction-based coloration with solutions exposed to light of wavelength λ_1. (a) Extinction spectrum acquired after reduction. The LSPRP at 780 nm appears during reduction. (b) The corresponding TEM image of AuNRs taken after photoreduction. (c) is the distribution histogram of AuNRs corresponding to (b). The mean length (ML) of AuNRs for (b) is 29.1 ± 3.8 nm. The scale bar in (b) represents 50 nm.

Absorption spectra of growth solution (II) with varied molar ratios of AA to Au^{3+}

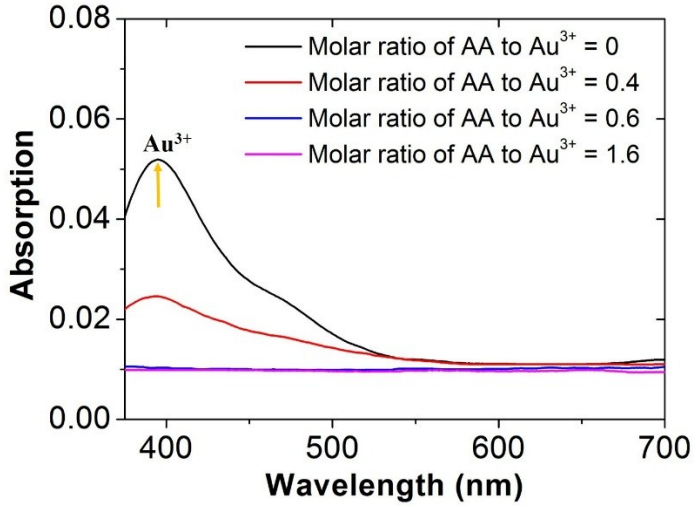

Figure. S16. Absorption spectra of growth solution (II) acquired corresponding to molar ratios of AA to Au^{3+} from 0 to 1.6. The absorption peak intensity of Au^{3+} decreased with the increasing molar ratio of AA to Au^{3+}.

References

(1) Attia Y A, Buceta D, Requejo F G, et al. Photostability of gold nanoparticles with different shapes: the role of Ag clusters. *Nanoscale.* **2015**, 7, 11273-11279.

(2) Link, S.; Mohamed, M.; El-Sayed, M. Simulation of the optical absorption spectra of gold nanorods as a function of their aspect ratio and the effect of the medium dielectric constant. *J. Phys. Chem. B* **1999**, 103, 3073-3077.