Electronic Supplementary Material (ESI) for Nanoscale.
This journal is © The Royal Society of Chemistry 2019

Supporting Information

Aromatic Thiols-modulated Ag Overgrowth on Gold Nanoparticles: Tracking Thiol's Position in the Core-shell Nanoparticle

*Jiaqi Chen, Dejing Meng, Hui Wang, Haiyun Li, Yinglu Ji, Xinghua Shi, and Xiaochun Wu**

Experimental Section

Materials: Chloroauric acid ($HAuCl_4 \cdot 3H_2O$), silver nitrate ($AgNO_3$) and hydrochloric acid (HCl) were purchased from Beijing Chemical Reagent Company. L-ascorbic acid (AA) and L-Ascorbic Acid Sodium Salt (NaA) was obtained from Alfa. $NaNO_2$ was from Aladdin Regent Co., Shanghai, China. Ethanol (≥99.7%) was purchased from Damao Chemistry Reagent Factory. Cetyltrimethylammonium bromide (CTAB) were purchased from Amresco. 4-aminothiophenol (4-ATP), 4-Mercaptophenylboronic acid (4-MPBA), 4-Mercaptobenzoic acid (4-MBA), 4-Mercaptophenol (4-MP), and Mercaptobenzene (MB) were purchased from Sigma-Aldrich. 3-Aminothiophenol (3-ATP) and 2-aminothiophenol (2-ATP) were supplied by Shanghai Macklin Biochemical. Milli-Q water (18MΩ·cm) was used for the preparation of all solution.

Synthesis of Au@Ag core-shell NPs assisted by 4-ATP and other ATs: The AuNSs with diameter of ca. 20 nm and Au NRs with the LSPR peak at ca. 710 nm were synthesized according to our previous works.[1,2] The suspensions of as-prepared AuNSs and AuNRs were centrifuged using a Sigma 3K15 centrifugal machine once (9500 rpm, 13 min) and twice (9200 rpm, 10 min), respectively. 1mL of AuNSs or AuNRs suspension was prepared with Au atomic concentration at 0.1 mM and [CTAB] at 10 mM. Stock solution of 4-ATP (10 mM) was prepared in ethanol and then diluted into water to 1 mM for further use. 5, 10, 20 and 40 μL of 4-ATP (1mM) were added to modify the surface of Au cores, respectively. After incubating in a 30℃ water bath for 1 h, $AgNO_3$ (20 μL, 10 mM) and AA (20 μL, 0.1 M) were added. The mixture was then put in a 70 ℃ water bath for 1 h to make Ag shell overgrow. The final core-shell NPs with AuNSs and AuNRs as cores were termed as AuNS@4-ATP@Ag and AuNR@4-ATP@Ag, respectively. 1 mM of 4-MBA, 4-MPBA, 4-MP, 2-ATP, 3-ATP and MB solution were prepared in the same procedure as 4-ATP. And these molecules were used to replace 4-ATP to synthesize Au@Ag NPs as stated.

Ag overgrowth process was monitored using the kinetic scan mode of spectrophotometer. 1 mL of AuNS@4-ATP@Ag and AuNR@4-ATP@Ag samples were centrifuged twice (9500 rpm, 5min) by centrifuge (TGL-16C, Anting Scientific Instrument Factory, Shanghai, China), and the concentrated NPs with [CTAB] lower than 50 μM were used for TEM imaging.

Methods: A 1 cm path-length cell was used to record ultraviolet-visible (UV-vis) extinction spectra on a Varian Cary 60. The kinetic scanning mode was chosen from the menu by setting 2 min scan interval. The extinction data were collected at a wavelength range from 1100 to 200 nm with a scan speed of 1000 nm/min. The Ag growth temperature was set at 70°C by the temperature-control accessory. TEM images

were captured with a Tecnai G2 20 S-TWIN, HRTEM and energy dispersive X-ray (EDX elemental mapping images were obtained by Tecnai G2 F20 U-TWIN operating at an acceleration voltage of 200 kV. Raman spectra were acquired from aqueous dispersions of the samples excited by 514 (20 mW), 633 (10 mW) and 785nm (30 mW) lasers using a Renishaw InVia Raman microscope. 200 μL sample was extracted from original aqueous suspension and added in a cell. Upon illuminating with the laser, Raman spectra were measured. SEM images were captured with Zeiss JC-Merlin SEM at a voltage of 5 kV.

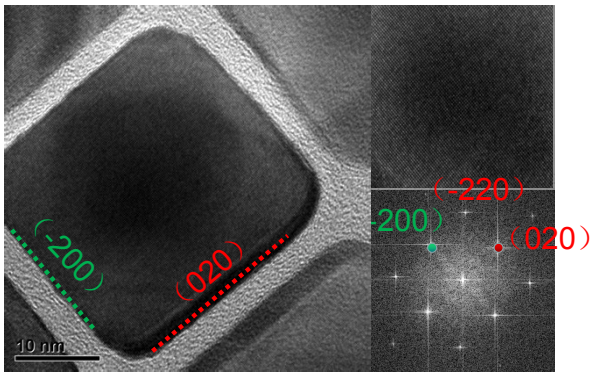
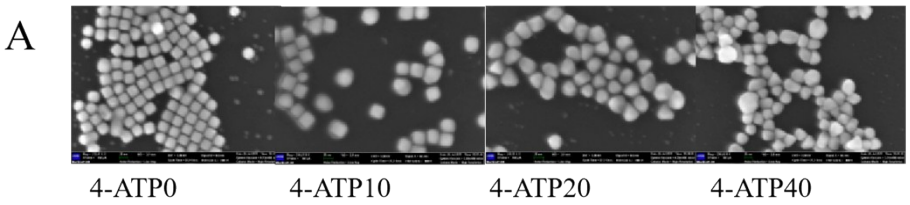


Figure S1. Typical HR-TEM images and the corresponding FFT pattern of one Au20@4-ATP0@Ag2 NP.



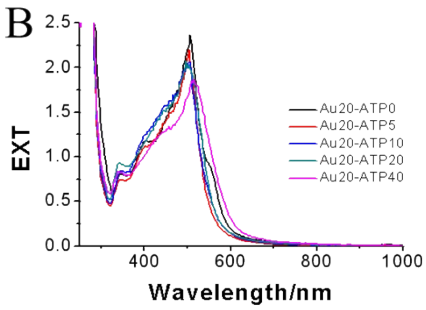


Figure S2. SEM images (A) and extinction spectra (B) of Au20@Ag NPs with different [4-ATP].

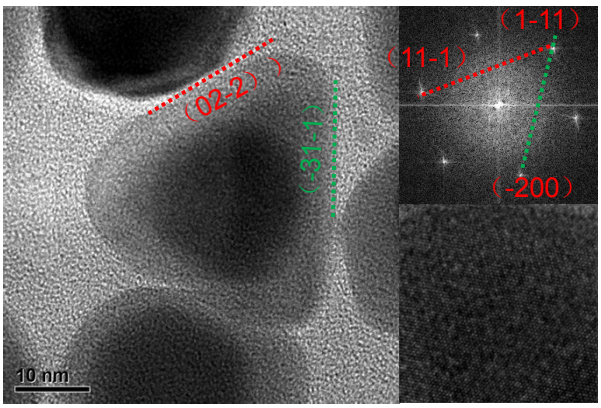


Figure S3. HR-TEM images and FFT pattern of Au20@4-ATP40@Ag2 NP.

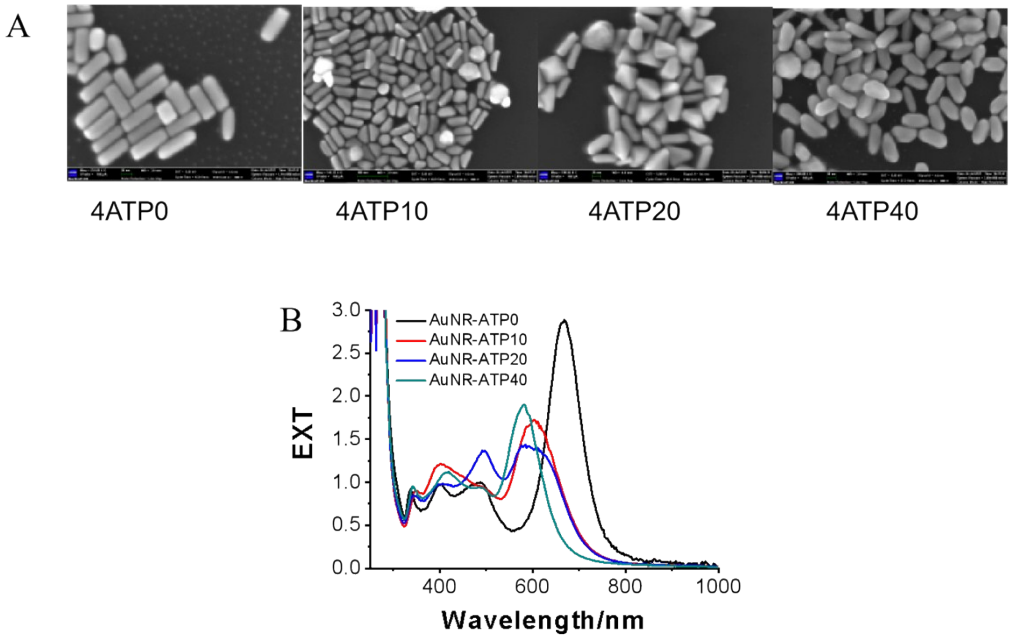


Figure S4. SEM images (A) and extinction spectra (B) of AuNR@Ag NPs with different [4-ATP].

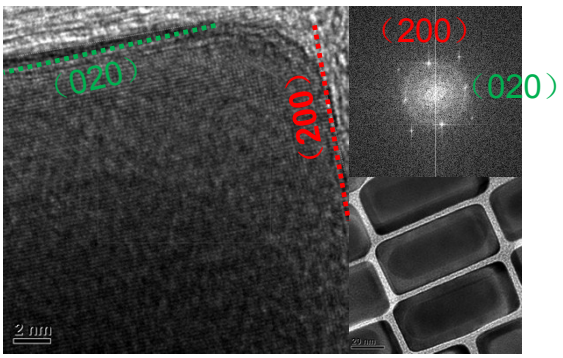


Figure S5. HR-TEM images and FFT pattern of AuNR@4-ATP0@Ag2 NPs.

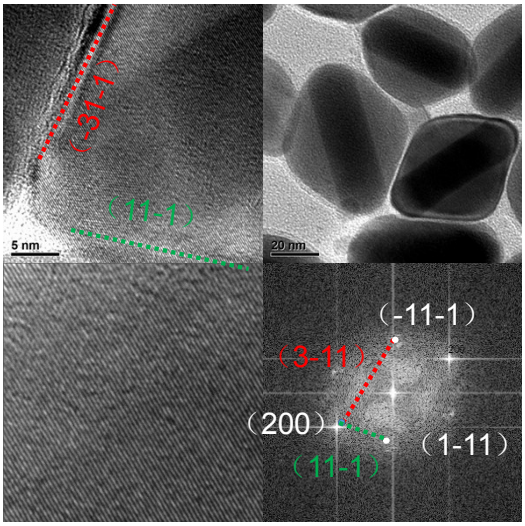


Figure S6. HR-TEM images and FFT pattern of AuNR@4-ATP40@Ag2 NPs.

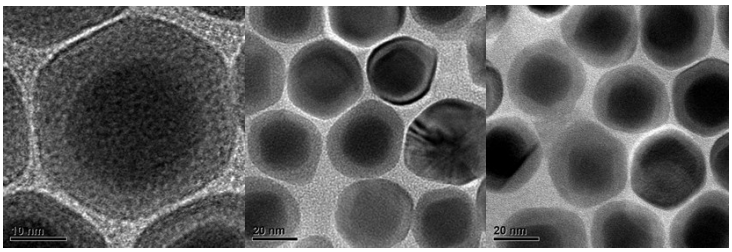


Figure S7. TEM images of Au20@Cys10@Ag2 NPs.

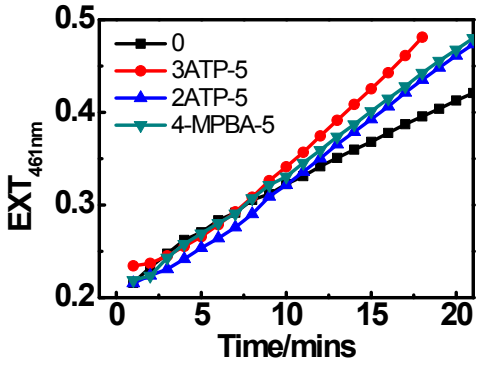


Figure S8. The acceleration effect of 3-ATP, 2-ATP and 4-MPBA on Ag overgrowth.

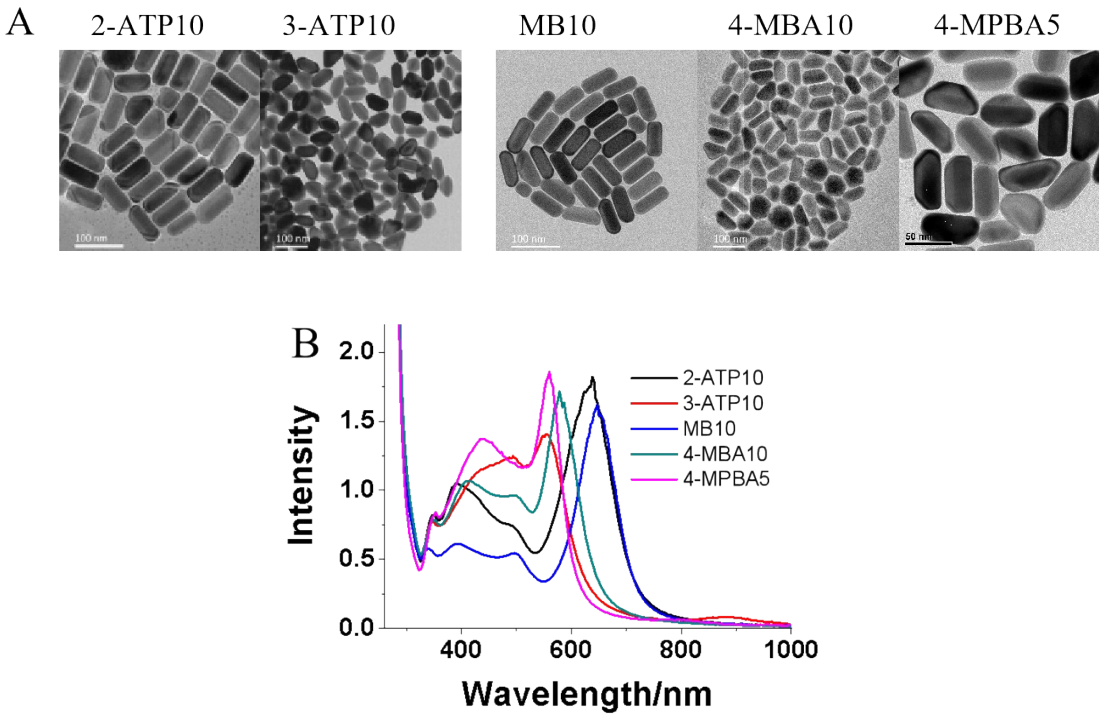


Figure S9. The morphology (A) and the extinction spectra (B) of AuNR@Ag assisted with 10 μM 2-ATP, 3-ATP, MB, 4-MBA and 5 μM 4-MPBA.

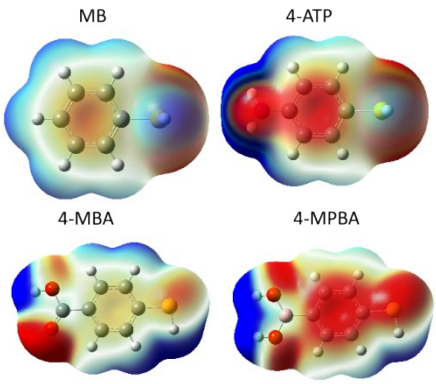


Figure S10. The Mulliken charge distributions of atoms in MB, 4-ATP, 4-MBA, and 4-MPBA molecules, respectively.

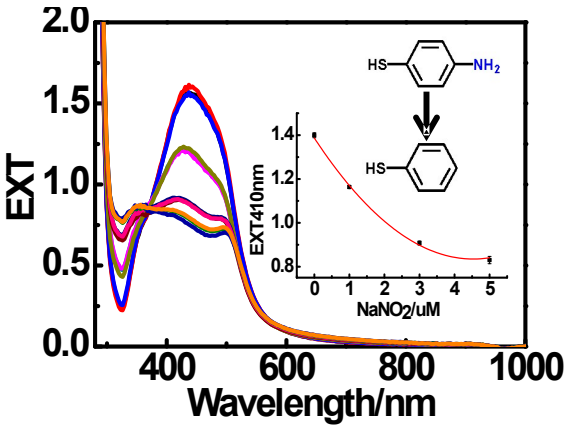


Figure S11. The extinction spectra of AuNS@ATP5@Ag after deamination reaction of 4-ATP with 0 ~ 5 μM nitrite, inset is the EXT_{410nm} vs. [$NaNO_2$].

The deamination reaction experiment followed these three steps：(1) **4-ATP incubation:** The AuNSs suspension containing 5 mM CTAB, 5 μM 4-ATP, 1mM HCl and 10% ethanol was firstly incubated at 60℃ for 3 h. (2) **Deamination reaction of 4-ATP:** Subsequently, $NaNO_2$ (0.1mM) was freshly prepared before using. A series of volume of nitrite (0.1 mM) was added to 1 mL of the incubated Au core suspension. Then, the mixture was heated at 95℃ for 45 minutes. (3) **Ag overgrowth:** After deamination process, $AgNO_3$ (20 μL,10 mM) and NaA (20 μL,0.1 M) were

added to coating Ag shell at 70℃ for 20 minutes. The control NPs were grown with no deamination reaction step of 4-ATP.

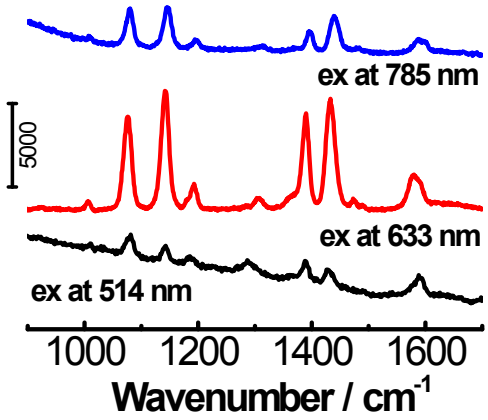


Figure S12. Raman spectra of AuNS@4-ATP10@Ag NPs excited by 514, 633 and 785 nm lasers, respectively.

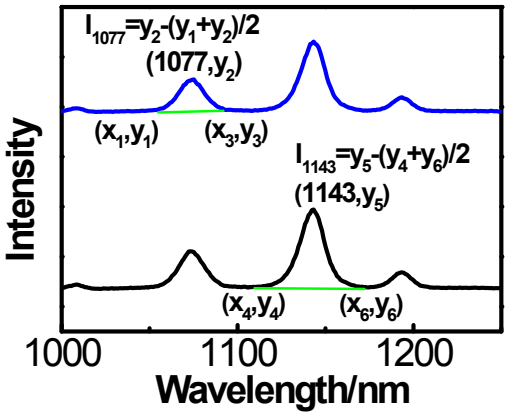


Figure S13. The schematic demonstration of calculating Raman peak intensity at 1077 and 1143 cm^{-1}.

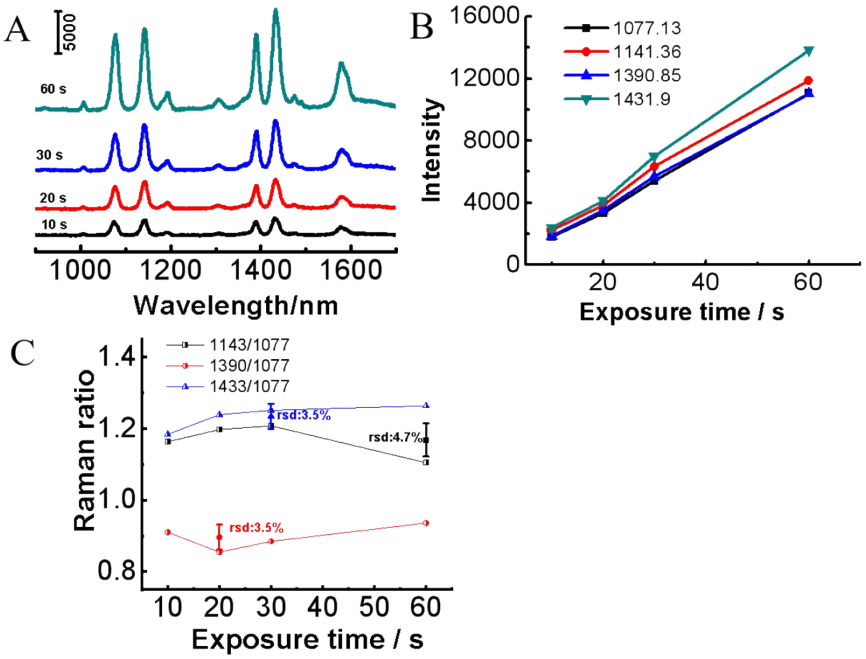


Figure S14. The Raman spectra (A), the intensities of Raman bands(B) and the DMAB ratios (C) of AuNS@4-ATP10@Ag NPs excited with 633 nm laser by changing exposure time to 10，20，30 and 60 s, respectively.

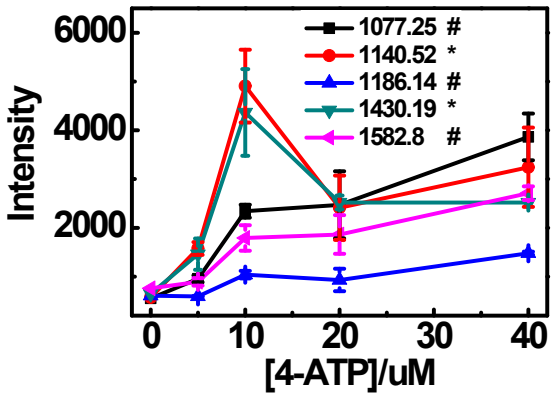


Figure S15. The intensities of Raman bands of Au20@4-ATP@Ag NPs assisted with different [4-ATP].

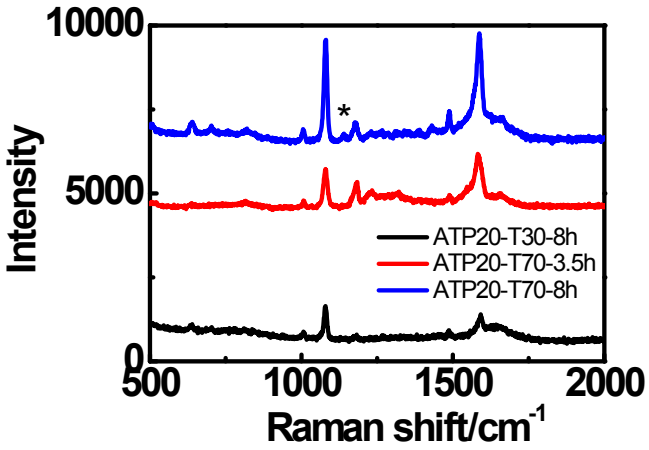


Figure S16. Raman spectra of Au20@4-ATP10 at higher incubation temperature and with prolonged incubation time.

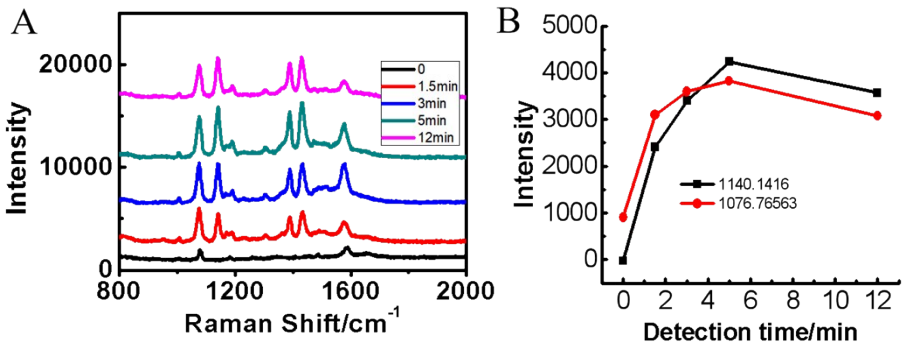


Figure S17. Raman spectra (A) and intensities of Raman bands (B) vs. detection time of Au20@4-ATP10 NPs after adding 0.2 mM Ag^{+}.

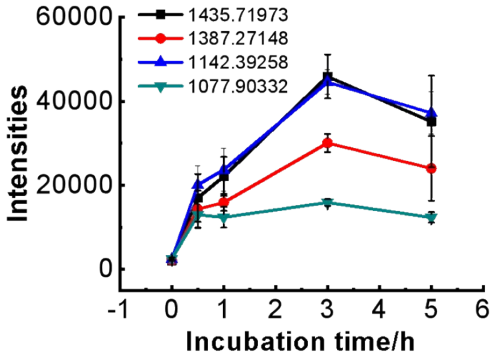


Figure S18. The intensities of Raman bands of Au20@4-ATP10@Ag with prolonged incubation time.

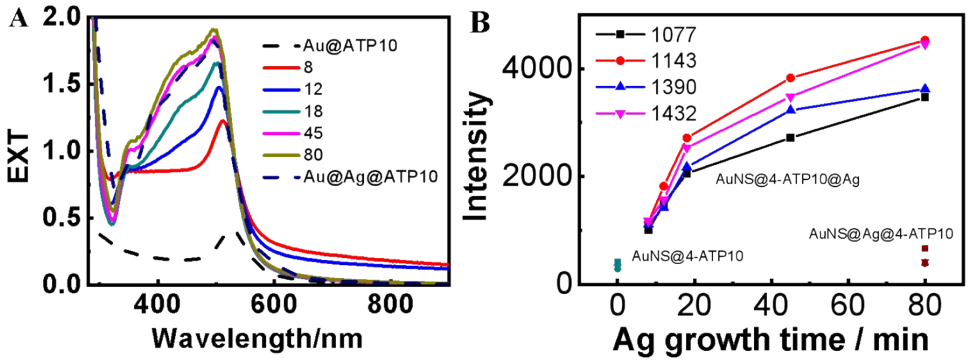


Figure S19. The extinction spectra (A) and intensities of Raman bands (B) of AuNS@ATP10@Ag NPs at different growth time.

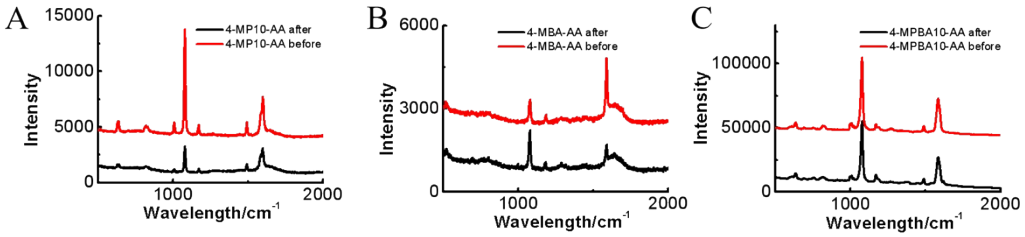


Figure S20. The GERS signal of NPs embedded with 10 μM 4-MP (A), 4-MBA (B) and 4-MBA (C) with AA added after or before Ag^{+}.

1. J. Chen, J. Yan, Y. Chen, S. Hou, Y. Ji and X. Wu, Nano Research, 2018, 11, 614-624.

2. S. Hou, T. Wen, H. Zhang, W. Q. Liu, X. N. Hu, R. Y. Wang, Z. J. Hu and X. C. Wu, Nano Research, 2014, 7, 1699-1705.