Electronic Supplementary Information (ESI)

Gold-plated silver nanoparticles engineered for sensitive plasmonic detection amplified by morphological changes

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Experimental section

Reagents

Silver nitrate (99.9%), tetrachloroauric acid (99.5%), hydrogen peroxide (30-32 wt.%, (ca. 10.4 M) solution in water, semiconductor grade, 99.99%), L-arginine (TLC, 98%), sodium citrate tribasic dihydrate (99+%), sodium borohydride (99%), poly(sodium 4-styrene sulfonate) (PSS, M_w = 70K), L-cysteine (97%), reduced glutathione (98%), L-histidine (TLC, >99%), potassium bromide (99%), potassium iodide (99%) and ampicillin sodium salt were supplied by Sigma Aldrich and used as received. High-purity deionized water (> 18.3 MΩcm) was produced using Millipore A10 Milli-Q.

Synthesis of silver decahedral nanoparticles (AgDeNPs)

AgDeNPs were synthesized using a new-generation photochemical synthetic protocol[1,2] adapted to use of PSS as a steric stabilizer[3] instead of PVP. To a 20-mL vial containing 14.00 mL of high-purity deionized water, the following solutions were added in the listed order: 0.520 mL of 0.050 M sodium citrate, 0.0225 mL of 0.050 M PSS (total concentration of monomer units), 0.050 mL of 0.005 M L-arginine, 0.400 mL of 0.050 M silver nitrate, and freshly prepared 0.200 mL of 0.100 M sodium borohydride. A pale yellow solution is first formed which subsequently turns bright yellow upon continuous

stirring (600 rpm, using a 3 mm by 12.7 mm magnetic stir bar) for ca. 45 min. Subsequently, 0.300 mL of ca. 10.4 M hydrogen peroxide was added. The solution was left stirring until the bubble evolution vanishes. The resulting solution was exposed to royal blue LED (λ= 449 ± 2 nm) for 14 hrs.

Synthesis of uniformly gold plated decahedral nanoparticles (u-Au@AgDeNPs)

In a typical synthetic procedure to prepare uniformly gold-plated silver decahedral nanoparticles (**u-**Au@AgDeNPs, shell@core), 3.00 mL of freshly prepared aqueous solution (in a 5.0 ml plastic syringe) containing 0.0077 to 0.154 mL of 0.0005 M tetrachloroauric acid (for 1 to 20% molar ratios of gold relative to silver present in plated AgDeNPs, respectively) and 2.99-2.84 ml of high-purity deionized water was dispensed at a constant rate during 12 hours (3.21 nmol/hr) into a 20-mL vial containing 3.00 mL of as prepared AgDeNPs upon uniform stirring at 350 rpm.

Synthesis of thin-frame gold coated decahedral nanoparticles (tf-Au@AgDeNPs)

Optimal procedure to prepare thick-frame (or thin fragile) gold plated silver decahedral nanoparticles (**tf**-Au@AgDeNPs, shell@core) was a one stage addition of 1.00 mL freshly prepared aqueous solution containing 0.038 mL to 0.77 mL of 0.00005 M tetrachloroauric acid (for 0.5 to 10% molar ratios of gold to silver ions present in plated AgDeNPs) was dispensed at once via pipette into a 20-mL vial containing 3.00 mL of as prepared AgDeNPs upon uniform stirring at 350 rpm.

Instrumentation

AgNPs and Au@AgNPs were cleaned and concentrated, as needed, using a Clinical 100 Centrifuge (VWR). For slow controlled addition, a KDS100 syringe pump (KDS Scientific) was used. Light exposure was performed using 1-watt 350 mA LEDs powered by a TDC LED driver operating at 350 mA constant current. UV-vis spectra were obtained and recorded using Ocean Optics QE65000 fiber-optic UV-vis

spectrophotometer. EM imaging (TEM and SEM) was performed with a Hitachi S-5200 using a copper grid with a formvar/carbon film (FCF-200, Electron Microscopy Science). SPR signal were monitored using OpenSPR instrument (Nicoya Lifescience Inc., Waterloo, ON, Canada).

Real Time Plasmonic Response Measurements with OpenSPR

In a capped half-cell cuvette, 0.500 mL of as prepared AgDeNPs or Au@AgDeNPs was first equilibrated for 3 hours in the OpenSPR to achieve a stable signal background. Injection of 0.025 mL freshly prepared analyte to the cuvette was performed manually by removing the cuvette cap and immersing the pipette tip into solution for injection. After analyte injection, the recapped cuvette was removed from the holding cell, shaken, and then returned to the cell for the remainder of the test.

Figures

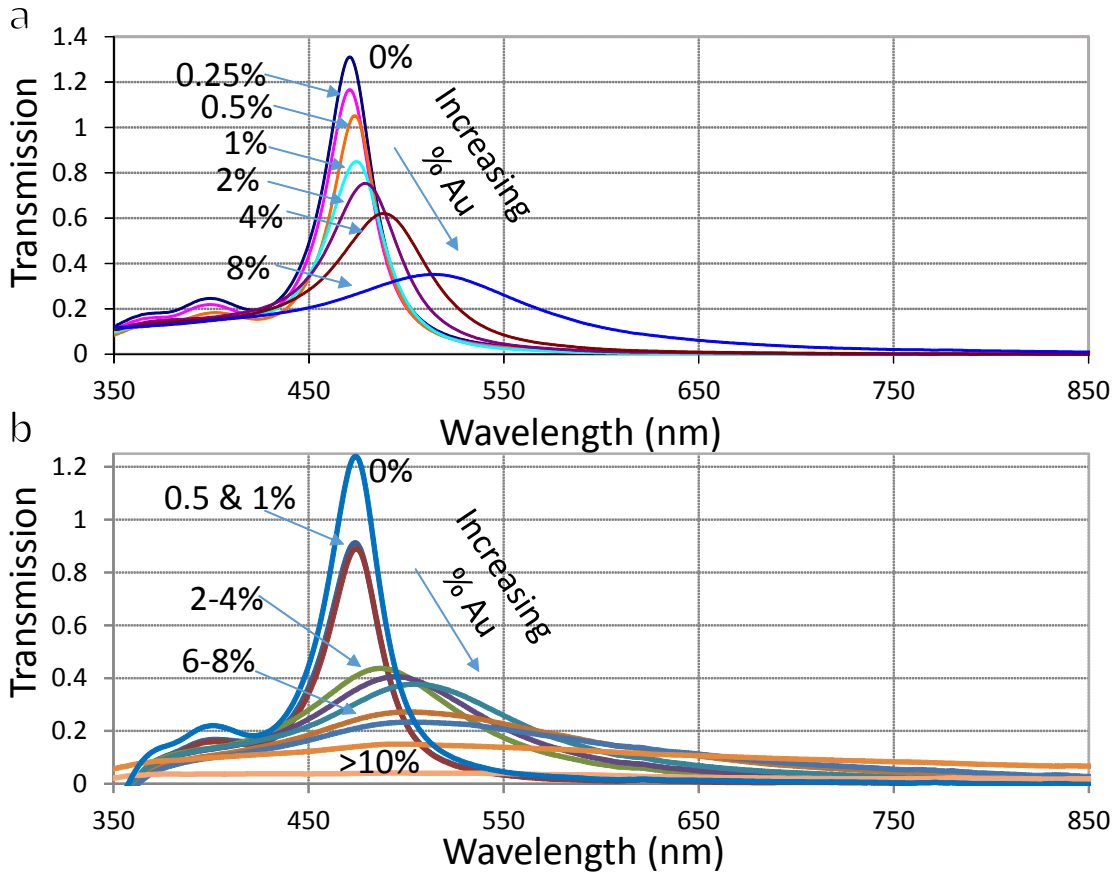


Figure S1. UV-vis spectra of two independent series of formation of tf-Au@AgNPs with varying mol. % Au relative to Ag in decahedra with the precursor AgDeNPs denoted as 0%. Spectra shown in **a)** correspond to TEM images of Figure 1 in the main text.

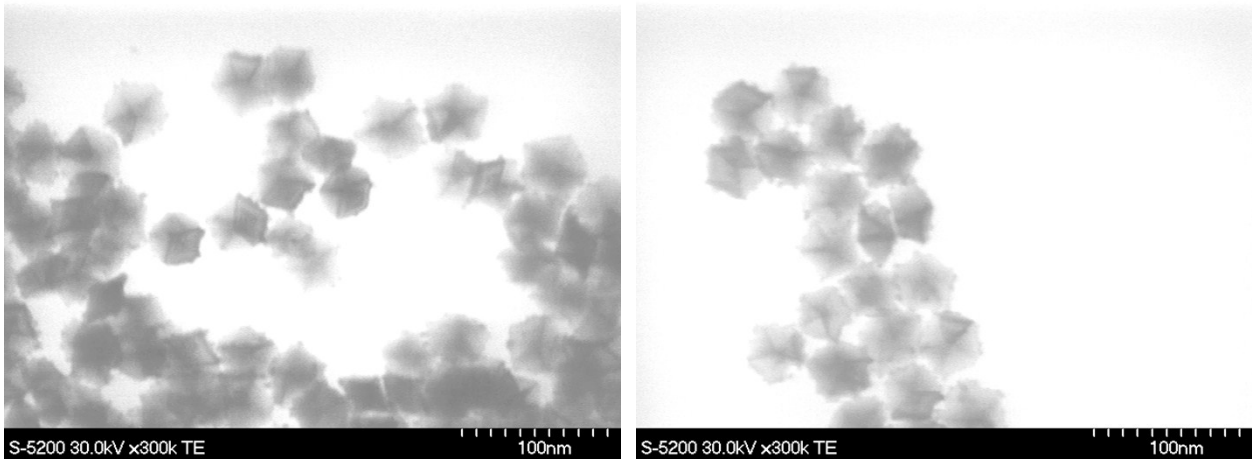


Figure S2. Transmission electron microscopy (TEM) images of tf-Au@AgNPs with 5 mol. % gold showing preferential gold deposition around the edges of decahedra.

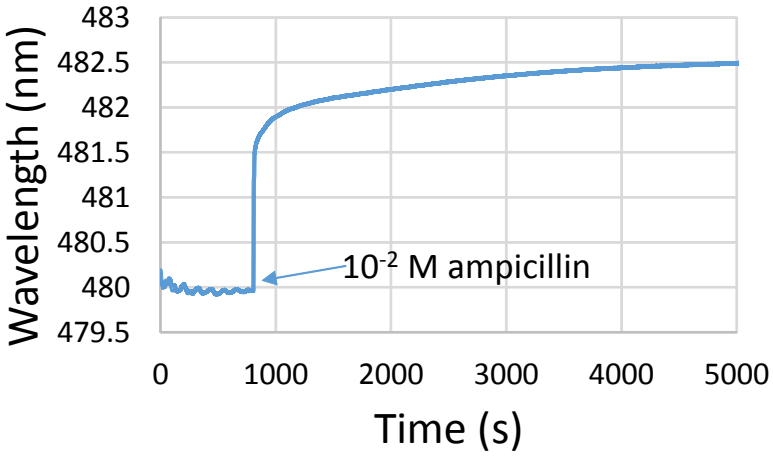


Figure S3. SPR response curve of u-Au@AgNPs with 10 mol. % Au upon exposure to 10^{-2} M ampicillin.

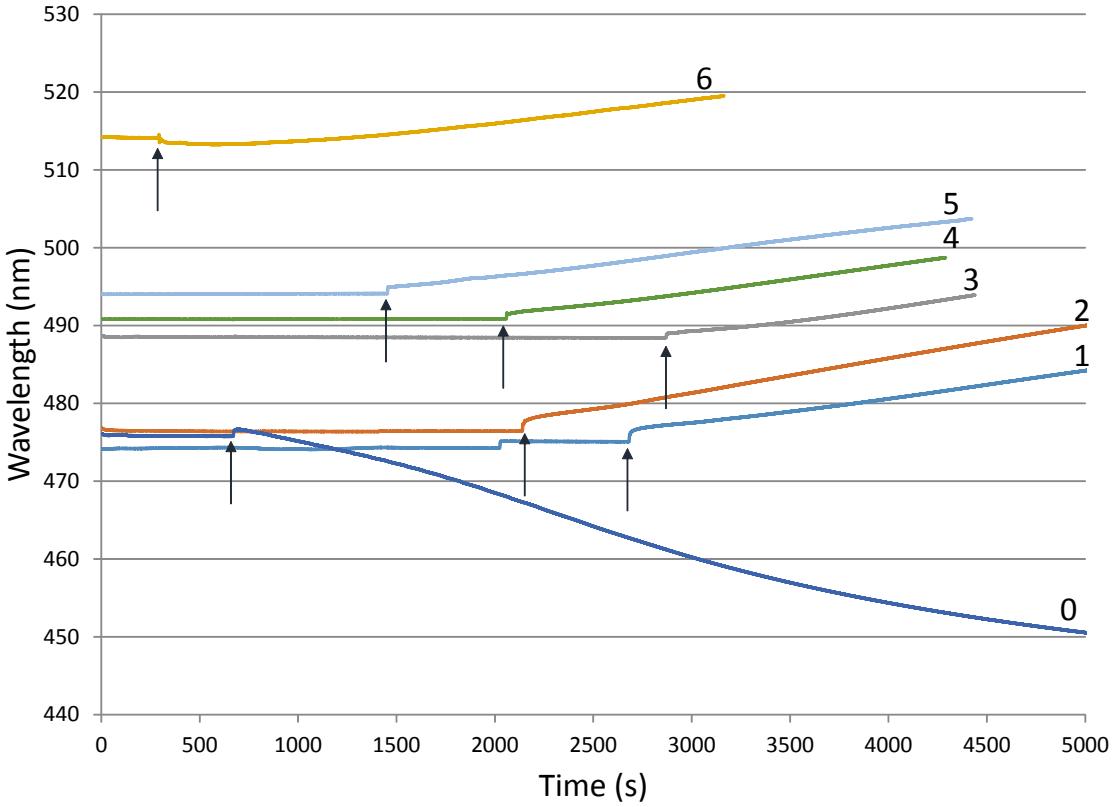
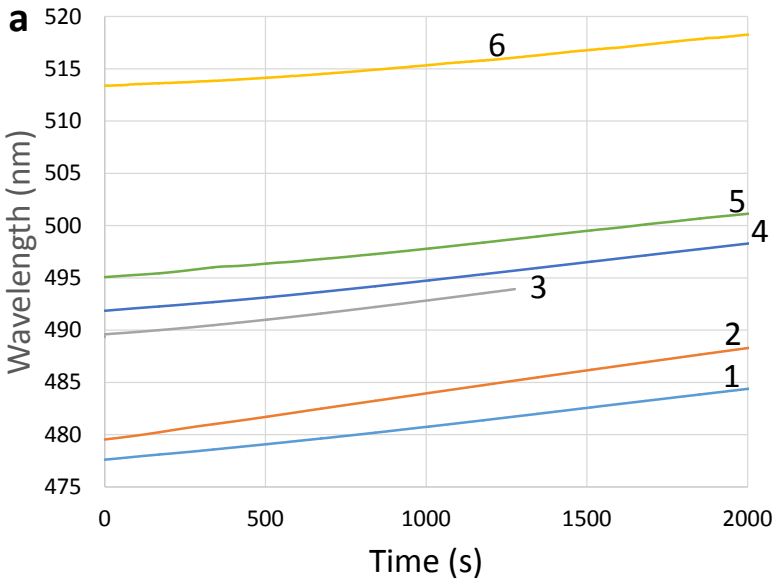


Figure S4. SPR response curve of tf-Au@AgNPs with different mol. % of gold upon exposure to 10^{-2} M ampicillin. Molar % of Au relative to Ag in precursor decahedra are the following: (**0**) - 0%, (**1**) - 0.5%, (**2**)- 1%, (**3**) - 2%, (**4**) - 3%, (**5**) - 4%, (**6**) - 5%. Ampicillin injection times are denoted by the arrows.



b

Curve	mol % Au	Slope ($\Delta\lambda_{max}$/s)
1	0.5	0.0035
2	1	0.0043
3	2	0.0035
4	3	0.0033
5	4	0.0031
6	5	0.0027

Figure S5. **a)** SPR curves showing morphological changes of tf-Au@AgNPs with varying gold coating exposed to 10^{-2} M ampicillin (from Figure S4). Mol. % of Au in tf-Au@AgNPs are: (**1**) - 0.5%, (**2**) - 1%, (**3**) - 2%, (**4**) - 3%, (**5**) - 4%, (**6**) -5%. Curves are set to 0 s for the ease of comparison. **b)** Tabular representation of the dependence of the rate of morphological change (slope of the SPR curves) as a function of mol. % of Au in tf-Au@AgNPs.

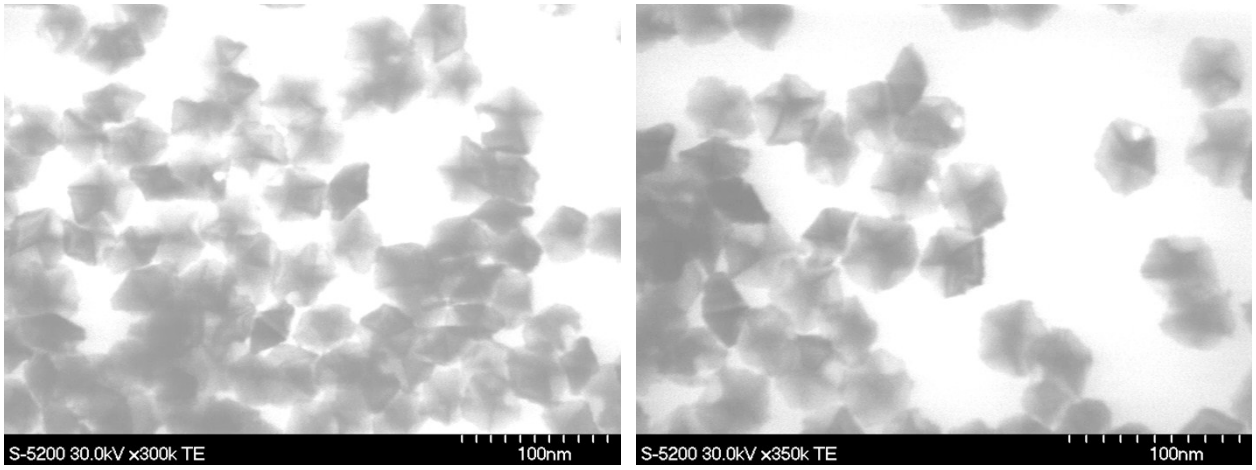


Figure S6. TEM images of tf-Au@AgNPs with 4 mol. % Au after exposure to 10^{-2} M ampicillin showing cavitation.

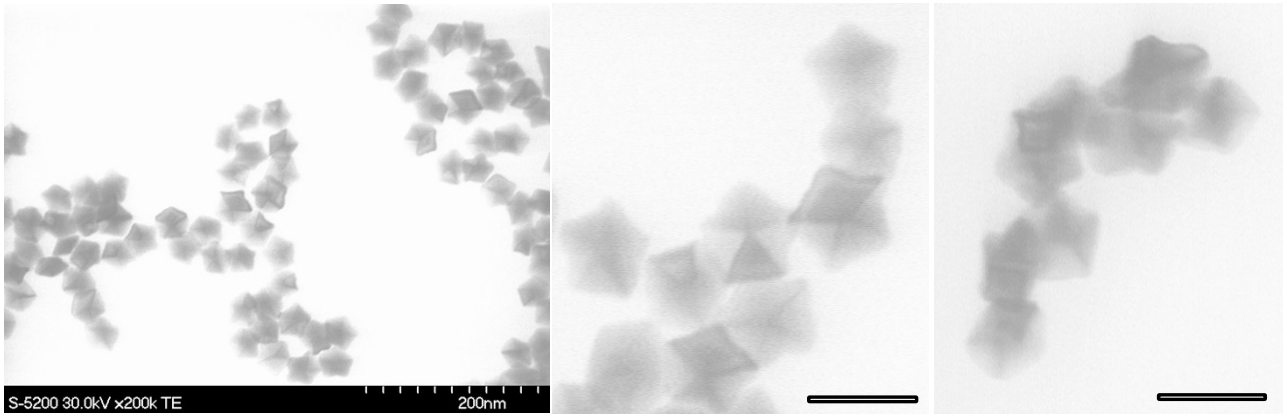


Figure S7. TEM images of tf-Au@AgNPs with 1 mol. % after exposure to 10^{-2} M ampicillin showing partial stellation. The scale bars are 50 nm.

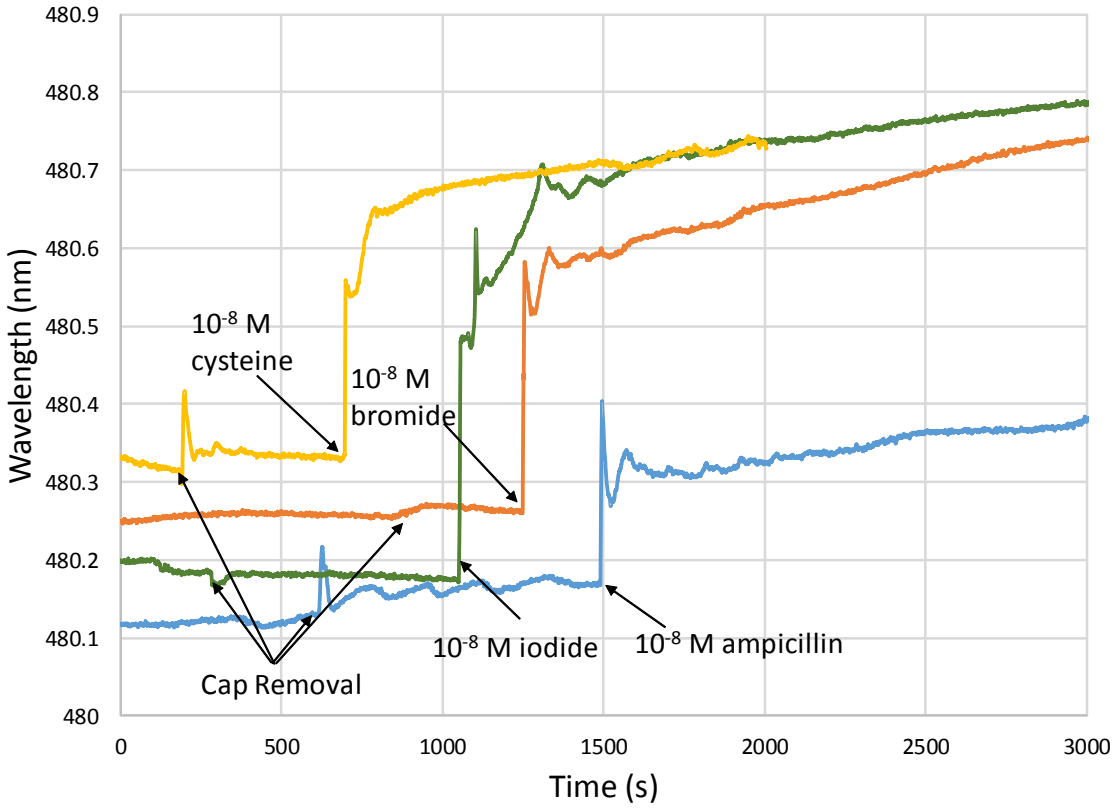


Figure S8. SPR response curve of tf-Au@AgNPs with 1 mol. % of gold upon exposure to 10^{-8} M cysteine, potassium bromide, potassium iodide and ampicillin. Time when injections took place and the cap of the cell was removed are denoted on the graph.

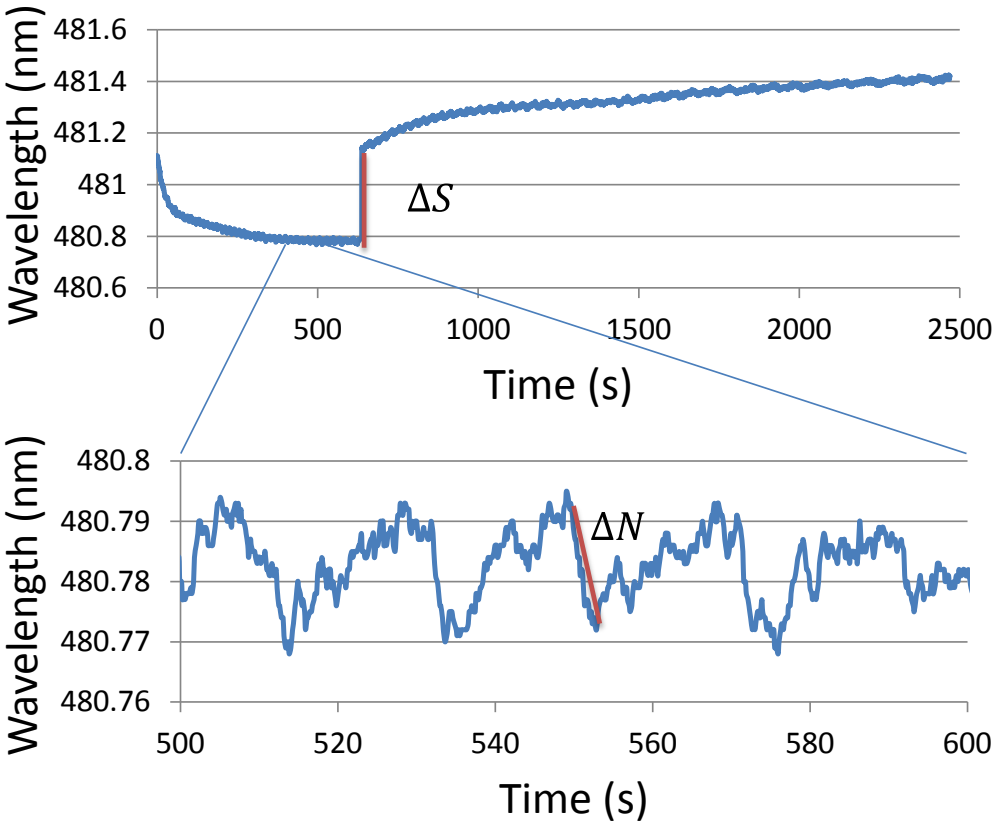


Figure S9. SPR response demonstrating typical signal noise in the system (tf-Au@AgNPs with 1 mol. % of gold upon exposure to 10^{-6} M cysteine).

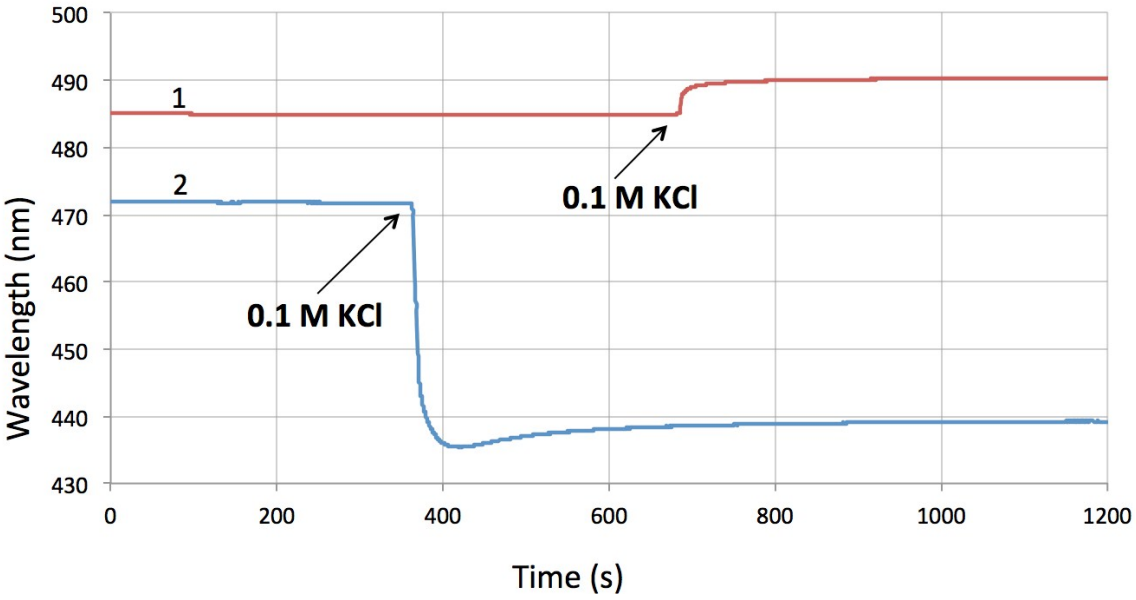


Figure S10. SPR response curves comparing **(1)** tf-Au@AgNPs with 1 mol. % of gold and **(2)** unmodified AgDeNPs upon exposure to 0.100 M potassium chloride. Time when injections took place is denoted on the graph by arrows.

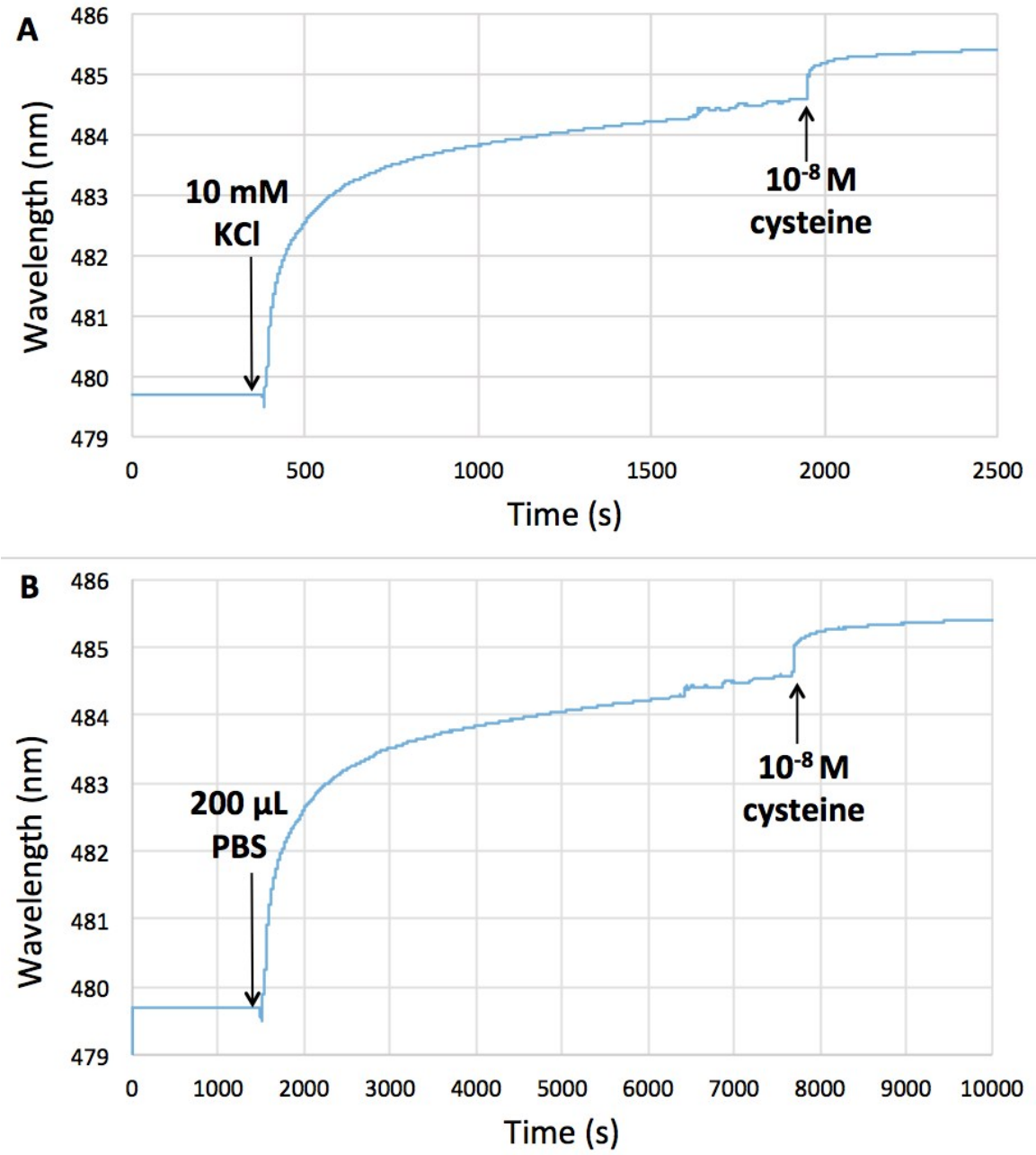


Figure S11. SPR response curves of tf-Au@AgNPs with 1 mol. % of gold upon sequential exposure to **(A)** 10 mM potassium chloride and then 10^{-8} M cysteine; and **(B)** to phosphate-buffered saline (PBS: 22 mM NaCl, 0.45 mM KCl, 1.6 mM Na_2HPO_4, 0.3 mM KH_2PO_4) and then 10^{-8} M cysteine. Time when injections took place is denoted on the graph by arrows.

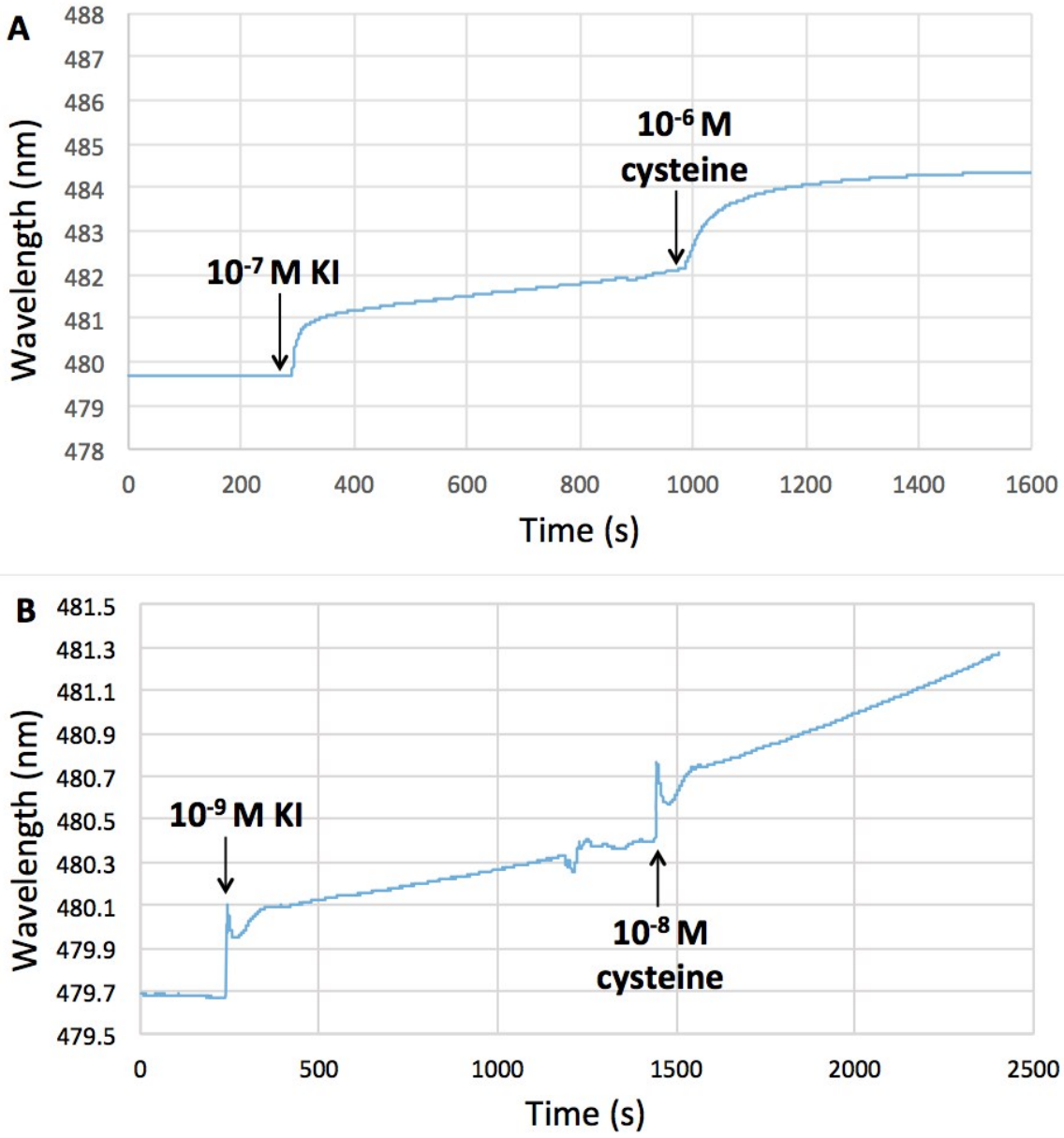


Figure S12. SPR response curves of tf-Au@AgNPs with 1 mol. % of gold upon sequential exposure to **(A)** first 10^{-7} M potassium iodide and then 10^{-6} M cysteine; and **(B)** first 10^{-9} M potassium iodide and then 10^{-8} M cysteine. Time when injections took place is denoted on the graph by arrows.

References

1. B. Pietrobon and V. Kitaev, *Chem. Mater.,* 2008, **20**, 5186–5190.

2. N. Murshid, D. Keogh, V. Kitaev, *Part. Part. Syst. Charact.* 2013*,* **31**, 178–189.

3. N. Murshid, I. Gourevich, N. Coombs and V. Kitaev, *Chem. Commun*., 2013, **49**, 11355–11357.