# Supporting Information for

## Gold Nanorods Synthesis with Small Thiolated Molecules

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## EXPERIMENTAL SECTION

### Materials

Cetyltrimethylammonium bromide (CTAB, ≥99%), hydrogen tetrachloroaurate trihydrate ($HAuCl_4 \cdot 3H_2O$, ≥49% gold basis), silver nitrate ($AgNO_3$, ≥99%), hydroquinone ($C_6H_6O_2$, ≥99.5%), sodium borohydride ($NaBH_4$, 99%), L-Glutathione reduced (GSH, ≥98%), L-Glutathione oxidized (GSSG, ≥98%), L-cysteine (L-cys, ≥98%) and L-methionine (L-met, ≥98%) and potassium carbonate ($K_2CO_3$, 99.99%) were purchased from Sigma-Aldrich. Thiol-terminated methoxypoly(ethylene glycol) (2 kDa, 2K PEG-SH) was purchased from Laysan Bio. All solutions were freshly prepared before use except for $HAuCl_4$ (stored at 4 °C) and CTAB solutions (stored at 28 °C).

### Functionalization of AuNRs with PEG-SH and MUTAB

AuNRs synthesized by the seedless method with and without distinct bioadditives were used for the ligand exchange reactions with 2 kDa thiol-terminated poly(ethylene glycol) (2K PEG-SH) and 11-mercaptoundecyltrimethylammonium bromide (MUTAB). The nanorods obtained in the presence of GSH, GSSG and L-cys had the same final molar concentration of bioadditive (165 nM) which was added at 30 min after the start of the reaction. AuNRs solution (1.5 mL) was centrifuged once at 14 500 rpm for 30 min and the pellet was redispersed in 1.5 mL of Milli-Q water in a 2 mL centrifuge tube. Before PEGylation, 15 μL of 20 mM $K_2CO_3$ was added to the nanorods solution. Next, 30 μL of 10 mM PEG-SH or MUTAB was added to the solution and the tube was placed in the rocking platform for 1 day. PEG-SH and MUTAB coated AuNRs were purified twice by centrifugation at 14 000 rpm for 30 min and redispersed in 1.5 mL of Milli-Q water

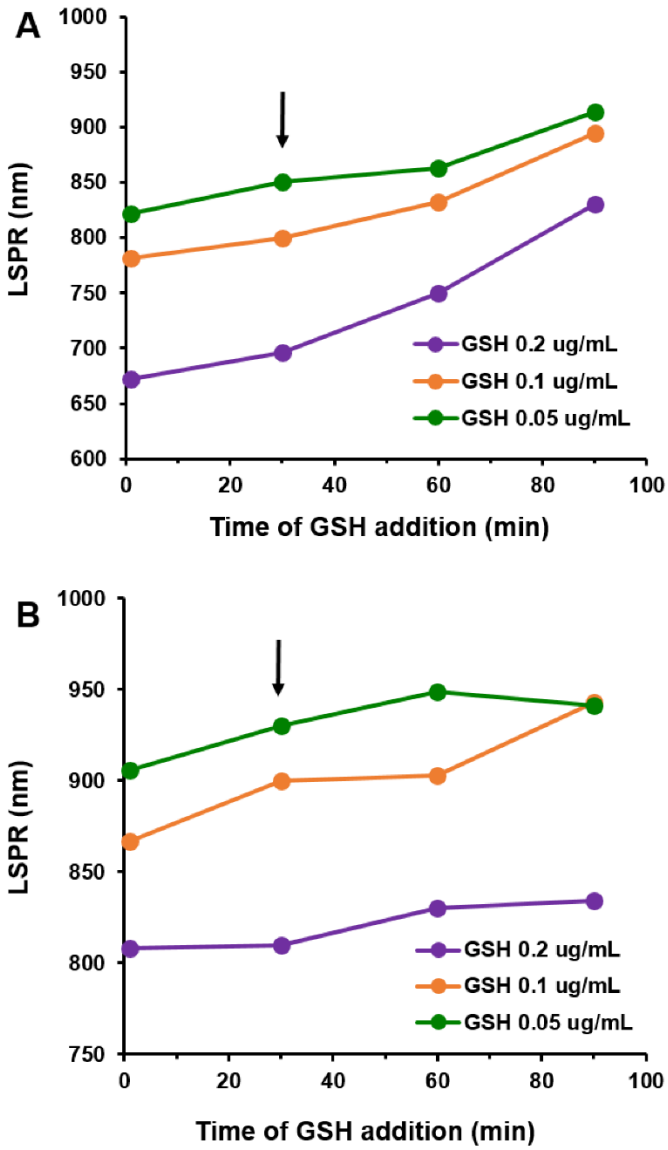


**Figure S1.** Variation of the LSPR band as a function of glutathione (GSH) addition time for AuNRs by the (A) seeded and (B) seedless methods. Distinct concentrations of GSH from 0.05 to 0.2 μg/mL are added during growth (1-90 min). Vertical arrow indicates GSH addition at 30 min of reaction.

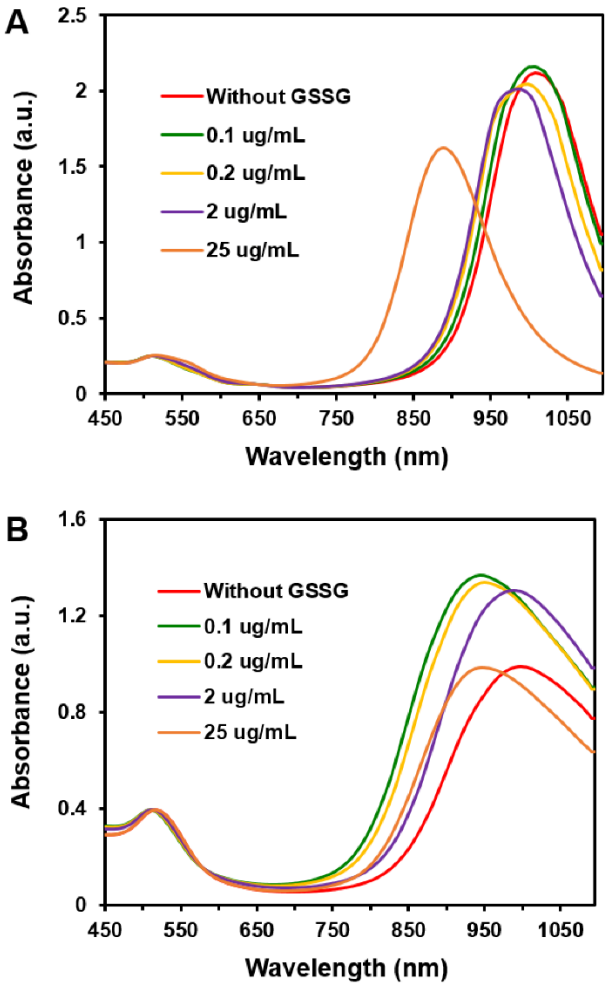


**Figure S2.** Concentration dependent normalized UV-Vis spectra of AuNRs obtained with oxidized glutathione (GSSG) by the (A) seeded and (B) seedless syntheses in 100 mM CTAB. Distinct weight concentrations of GSSG from 0.1 to 25 μg/mL added at 30 min after initiation of growth. A control sample prepared without bioadditive is shown in red.

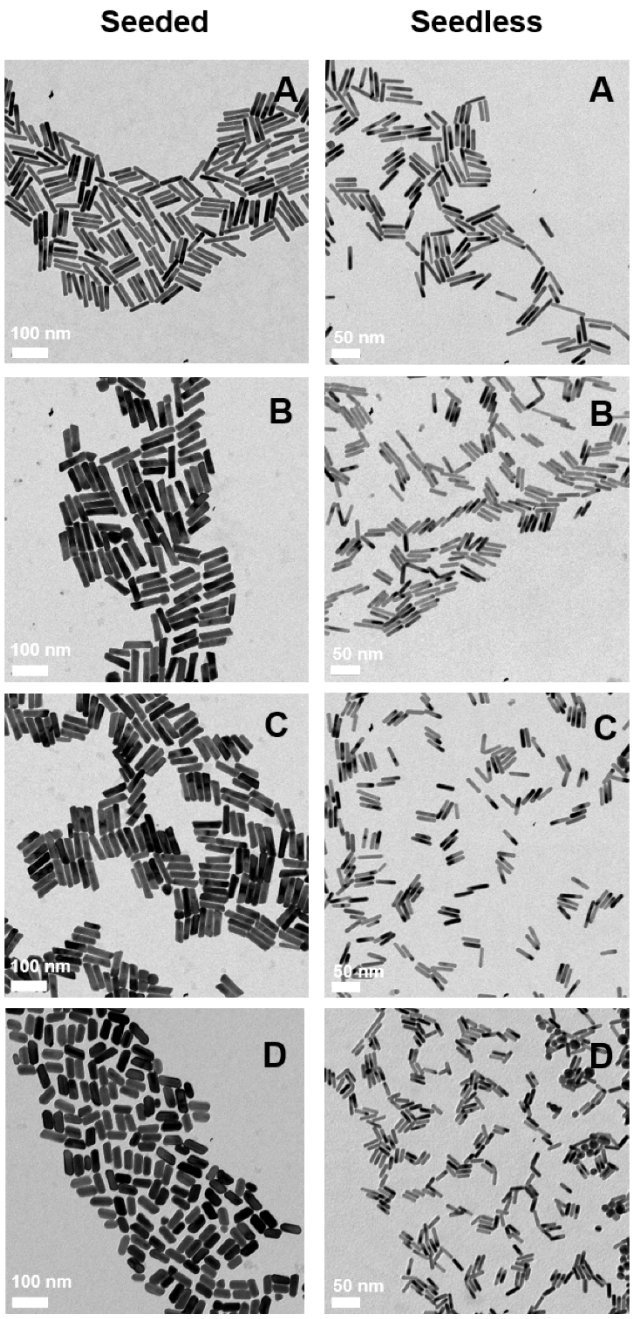


**Figure S3.** TEM images of AuNRs for the seeded (left column) and seedless (right column) syntheses after overnight growth in 100 mM CTAB. AuNRs (A) without GSH, with GSH for (B) 0.05 μg/mL, (C) 0.1 μg/mL and (D) 0.2 μg/mL added at 30 min after initiation of growth. Scale bars indicate 100 and 50 nm.

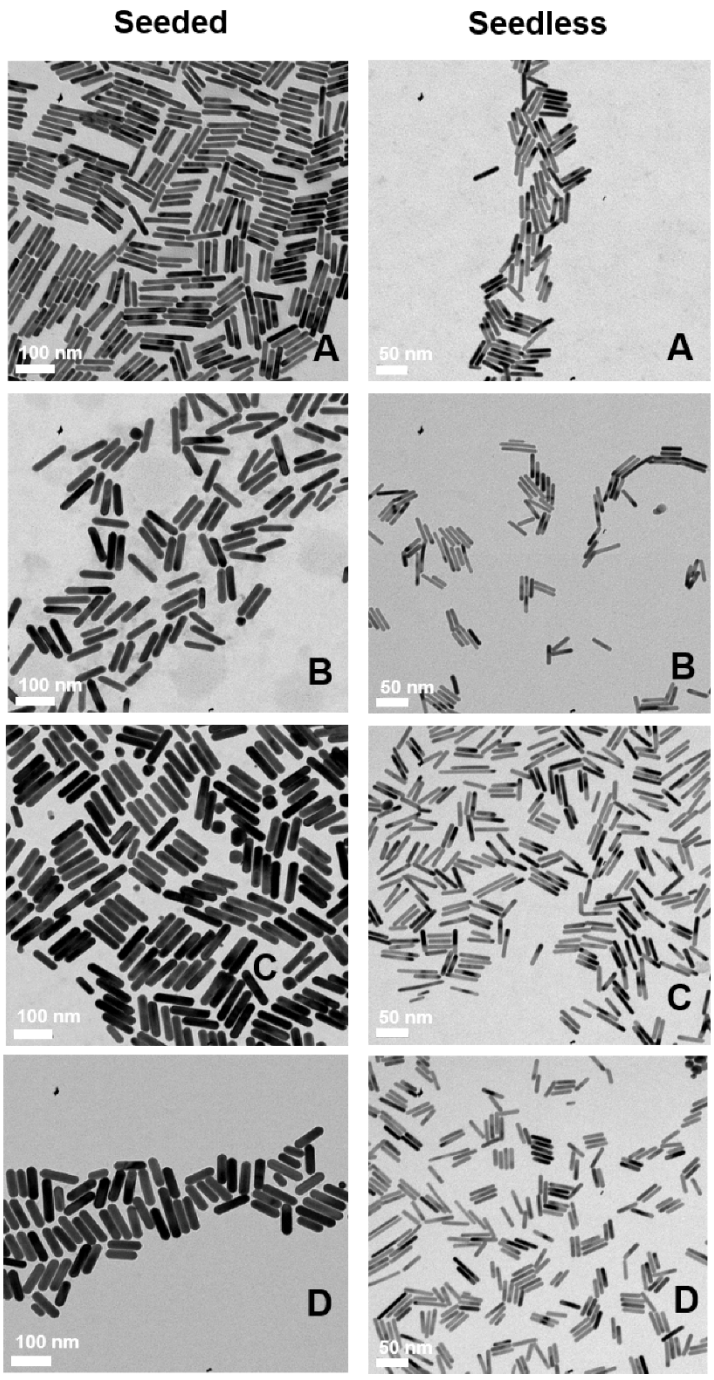


**Figure S4.** TEM images of AuNRs for the seeded (left column) and seedless (right column) syntheses after overnight growth in 100 mM CTAB. AuNRs (A) without GSSG, with GSSG for (B) 0.1 μg/mL, (C) 2 μg/mL and (D) 25 μg/mL added at 30 min after initiation of growth. Scale bars indicate 100 and 50 nm.

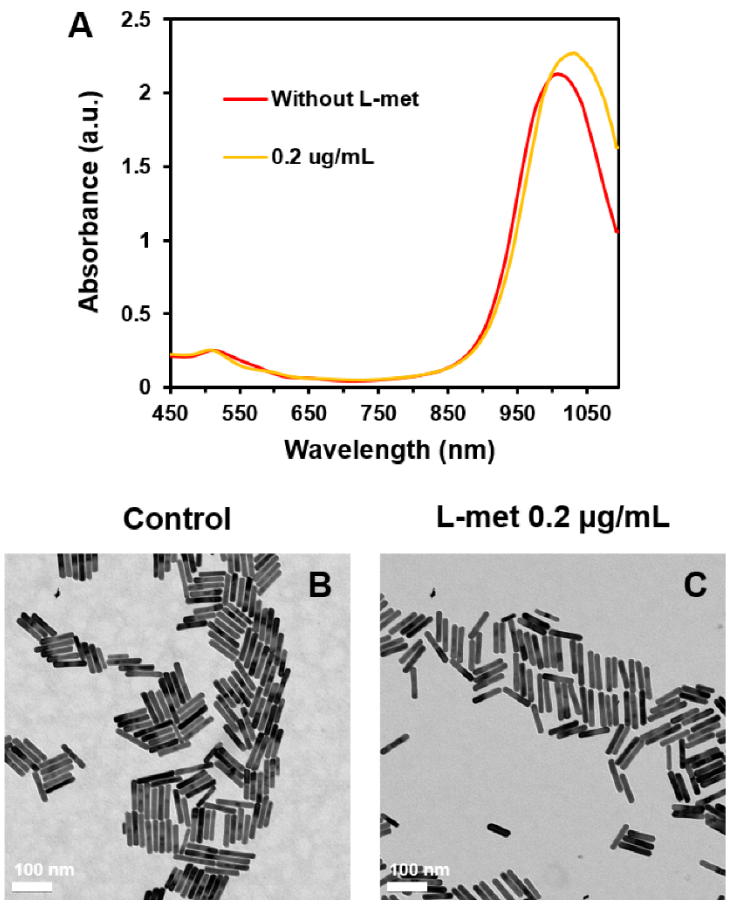


**Figure S5.** (A) Normalized UV-Vis spectra of AuNRs synthesized by the seeded method without and with L-methionine (L-met) at 0.2 µg/mL added at 30 min after seeds. TEM images of AuNRs (B) without L-met and with (C) 0.2 µg/mL L-met. Scale bars indicate 100 nm.

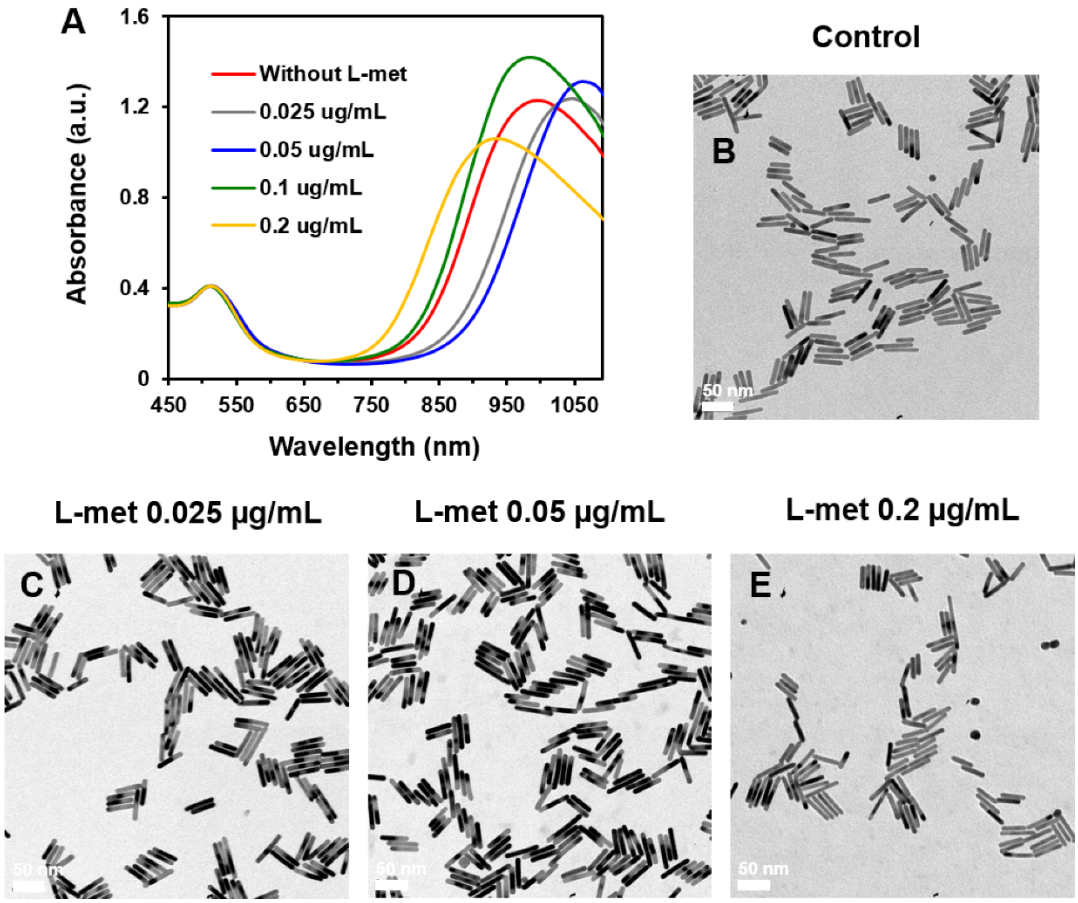


**Figure S6.** (A) Normalized UV-Vis spectra of AuNRs synthesized by the seedless approach with different concentrations of L-methionine (L-met) from 0.025 to 0.2 µg/mL added at 30 min after $NaBH_4$. A control sample prepared without bioadditive is shown in red. TEM images of AuNRs (B) without L-met, with L-met for (C) 0.025 µg/mL, (D) 0.05 µg/mL and (E) 0.2 µg/mL. Scale bars indicate 50 nm.

**Table S1.** LSPR band position, shape yield and dimensions for AuNRs synthesized by the seeded approach without bioadditive and with different amounts of small molecules.

| Sample | [Bioadditive] μg/mL | LSPR or λmax* (nm) | % Shape yield | Length/Width (nm) | AR |
|---|---|---|---|---|---|
| Control | - | 1015 | 96 | L: 84.7 ± 5.27<br>W: 12.8 ± 0.42 | 6.62 ± 0.43 |
| GSSG | 0.2 | 998 | 95 | L: 100.6 ± 4.42<br>W: 18.2 ± 0.54 | 5.52 ± 0.28 |
| GSSG | 2 | 985 | 93 | L: 100.9 ± 4.04<br>W: 20.3 ± 0.68 | 4.97 ± 0.20 |
| L-cys | 0.2 | 574* | <30 | L: 37.3 ± 4.08<br>W: 18.2 ± 1.98 | 2.06 ± 0.27 |
| L-met | 0.2 | 1032 | 98 | L: 89.2 ± 4.05<br>W: 13.4 ± 0.36 | 6.66 ± 0.33 |

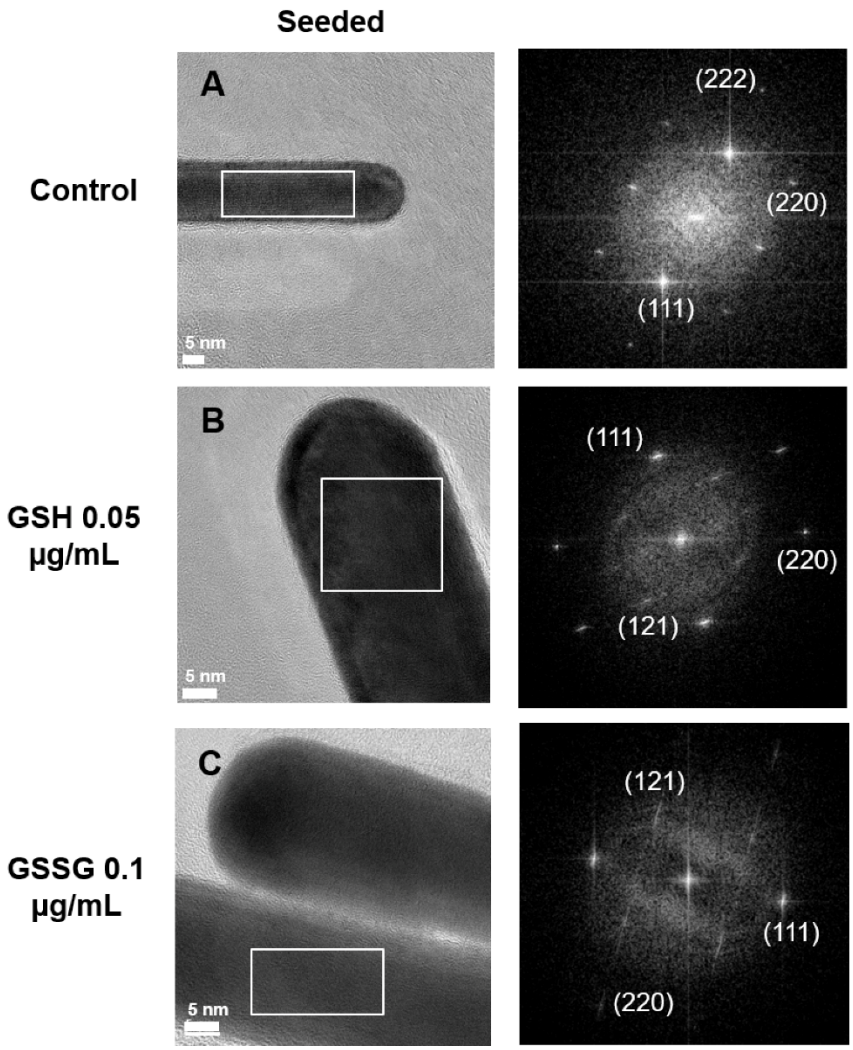


**Figure S7.** HR-TEM images of AuNRs for the seeded method after overnight growth. AuNRs (A) without bioadditive, with (B) 0.05 µg/mL GSH and (C) 0.1 µg/mL GSSG added at 30 min after seeds. Scale bars indicate 5 nm. Right column shows the Fast Fourier Transform (FFT) pattern of AuNRs for the white rectangle area.

**Table S2.** LSPR band position, shape yield and dimensions for AuNRs synthesized by the seedless method without bioadditive and with distinct amounts of small molecules.

| Sample | [Bioadditive] µg/mL | LSPR (nm) | % Shape yield | Length/Width (nm) | AR |
|---|---|---|---|---|---|
| Control | - | 1000 | 86 | L: 44.9 ± 4.12<br>W: 6.59 ± 0.31 | 6.82 ± 0.67 |
| GSSG | 0.1 | 946 | 92 | L: 36.8 ± 3.88<br>W: 6.12 ± 0.23 | 6.00 ± 0.71 |
| GSSG | 2 | 989 | 90 | L: 40.9 ± 2.56<br>W: 6.45 ± 0.25 | 6.34 ± 0.34 |
| L-cys | 0.02 | 947 | 78 | L: 38.8 ± 2.53<br>W: 6.48 ± 0.20 | 5.99 ± 0.40 |
| L-cys | 0.2 | 710 | 40 | L: 14.7 ± 1.60<br>W: 6.41 ± 0.30 | 2.30 ± 0.28 |
| L-met | 0.025 | 1047 | 87 | L: 49.7 ± 4.35<br>W: 6.69 ± 0.22 | 7.42 ± 0.73 |
| L-met | 0.2 | 934 | 80 | L: 34.6 ± 2.37<br>W: 6.01 ± 0.25 | 5.76 ± 0.43 |

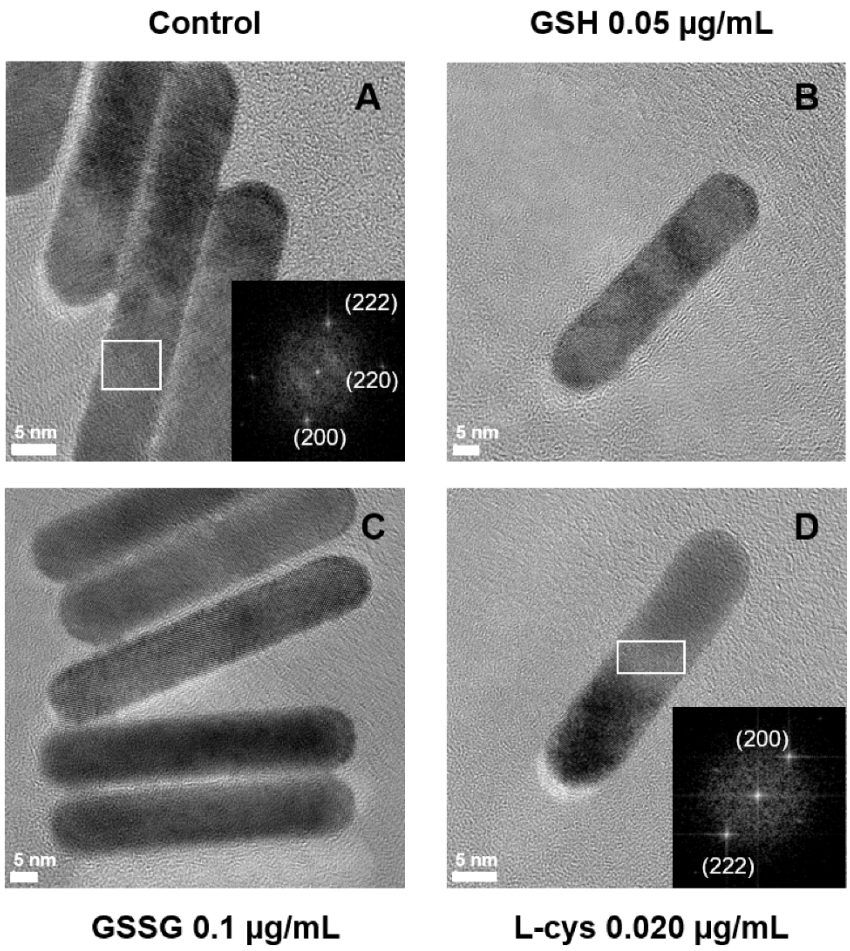


**Figure S8.** HR-TEM images of AuNRs for the seedless approach after overnight growth. AuNRs (A) without bioadditive, with (B) 0.05 µg/mL GSH, (C) 0.1 µg/mL GSSG and (D) 0.02 µg/mL L-cys added at 30 min after $NaBH_4$. Scale bars indicate 5 nm. Insets in (A) and (D) show the Fast Fourier Transform (FFT) pattern of AuNRs for the white rectangle area.

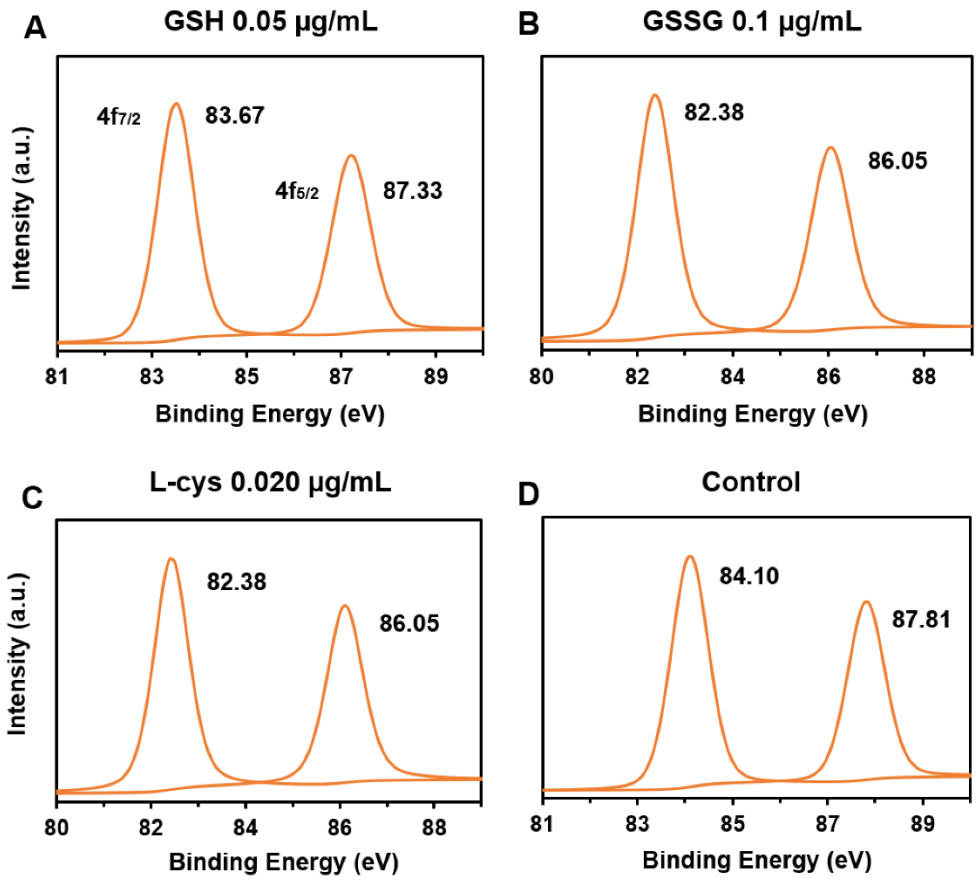


**Figure S9.** High resolution XPS spectra of Au 4f for AuNRs with (A) 0.05 µg/mL GSH, (B) 0.1 µg/mL GSSG, (C) 0.02 µg/mL L-cys added at 30 min after $NaBH_4$ and (D) without bioadditive for the seedless approach.

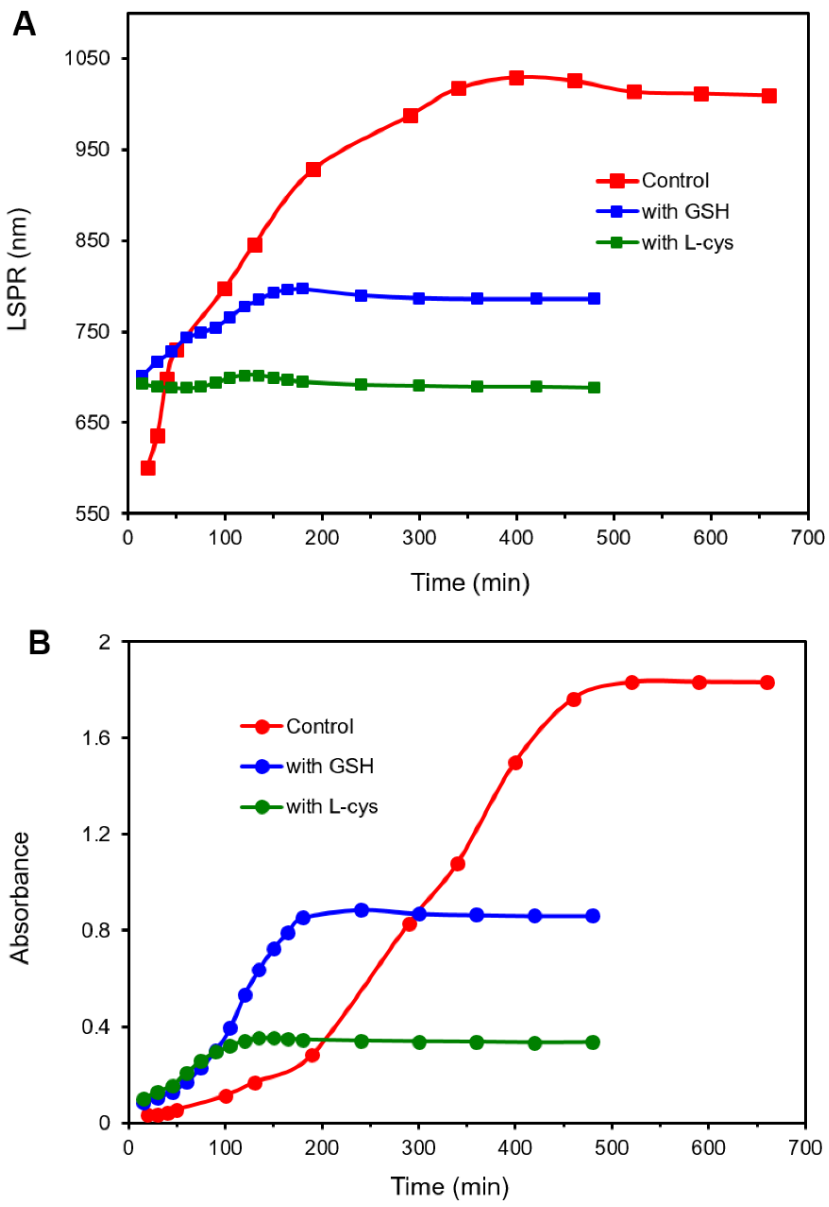


**Figure S10.** Variation of AuNRs LSPR band position (A) and its absorbance (B) as a function of time for the seedless method in 100 mM CTAB. AuNRs without bioadditive (control, red), with 0.2 μg/mL glutathione (GSH, blue) and L-cysteine (L-cys, green) added at 30 min after $NaBH_4$.

**Table S3.** Zeta potential (mV) of AuNRs before (CTAB) and after surface modification with 2K PEG-SH and MUTAB. AuNRs synthesized by the seedless method without and with different bioadditives at the same molar concentration (165 nM).

| Sample | Control | GSH | GSSG | L-cys |
|---|---|---|---|---|
| CTAB | 44.5 ± 3.00 | 49.9 ± 1.17 | 41.1 ± 1.17 | 40.4 ± 2.53 |
| PEG-SH | -27.1 ± 1.30 | -37.8 ± 0.52 | -31.7 ± 1.07 | -31.4 ± 0.42 |
| MUTAB | 44.4 ± 6.00 | 61.7 ± 2.19 | 42.6 ± 0.91 | 55.8 ± 3.00 |