Electronic Supplementary Material (ESI) for Nanoscale Advances.
This journal is © The Royal Society of Chemistry 2023

Electronic Supplementary Information

for

Magnetoplasmonic gold nanorods for the sensitive and label-free detection of glutathione

Zexiang Han[a,#], Wajid Ali[a,b,c,#], Ting Mao[d], Fei Wang[a,b], Xiaoli Wang[a,b]*

[a.] *CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, National Center for Nanoscience and Technology, Beijing, 100190, P. R. China*

[b.] *Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, P. R. China*

[c.] *Key Laboratory for Micro-Nano Physics and Technology of Hunan Province, Hunan Institute of Optoelectronic Integration, College of Materials Science and Engineering, Hunan University, Changsha, Hunan 410082, P. R. China*

[d.] *Institute of Materials, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland*

# These two authors contributed equally.

Synthesis of gold nanorods.

Briefly, for seed solution, 0.25 mL of 10 mM of gold salt $HAuCl_4$ was mixed with 1.6 mL of Milli-Q water and 7.5 mL of 100 mM hexadecyltrimethylammonium bromide (CTAB). The mixture was gently stirred for two minutes at 30˚C, following which 0.6 mL of fresh, ice-cold sodium borohydride ($NaBH_4$) was added as a reducing agent. The solution was left undisturbed for two hours in a temperature-controlled bath. For the growth solution, 0.5 mL of 10 mM $HAuCl_4$ solution was added to 10 mL of 100 mM CTAB, which was stirred for one minute at the same temperature as before. Upon adding 0.6 mL of 10 mM of silver nitride and the same amount of 100 mM of ascorbic acid under rapid stirring, the solution became colorless. At this instant, quickly add 12 mL of the prepared seed solution. The entire mixture was aged for 12 hours at 30 ˚C in a heated bath. The obtained colloid was washed three times using Milli-Q water by performing ultracentrifugation at 10,000 rpm for a few minutes each time in order to remove the excess CTAB. Colloids were briefly sonicated before use.

Additional data.

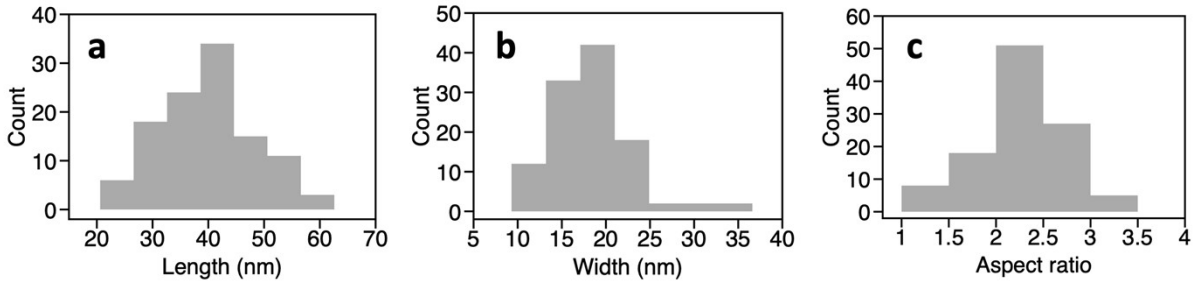

Figure S1. Distribution histograms for the (a) length, (b) width and (c) aspect ratio of the as-synthesized GNRs.

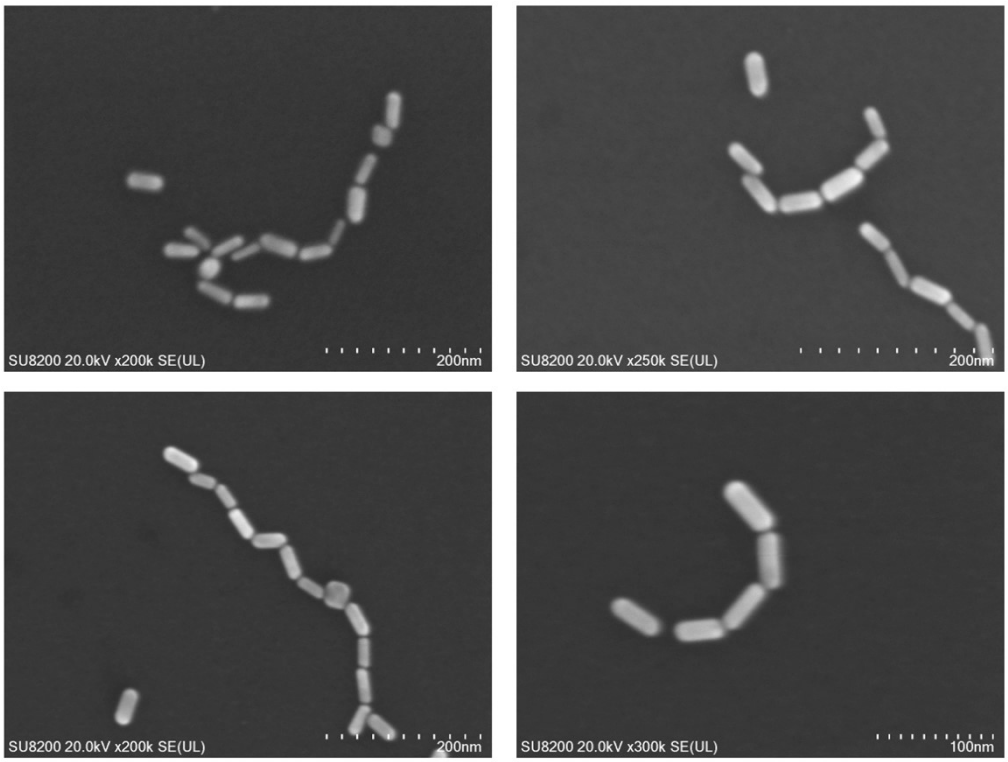

Figure S2. Representative SEM images showing the preferential end-to-end assembly of GNRs induced by glutathione.

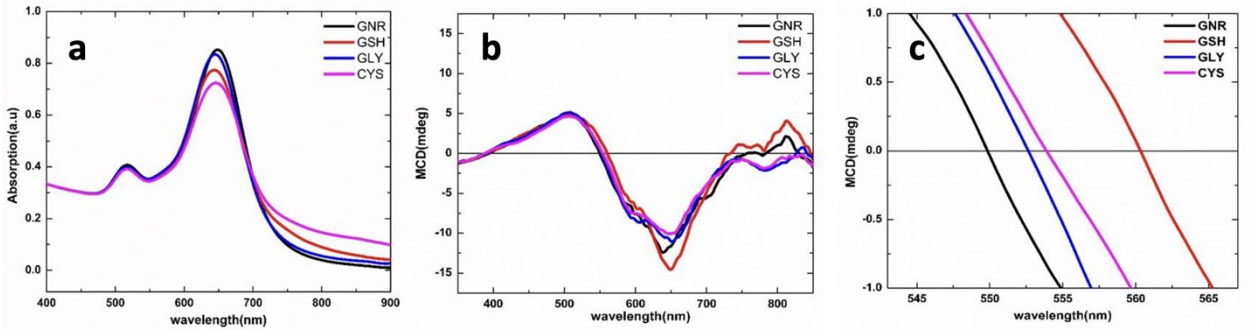

Figure S3. (a) Absorption spectra of GNRs in the presence of different analytes at a concentration of 0.5 µM. (b) The corresponding MCD spectra. (c) A magnetified view of the zero-line crossing point around 555 nm for each spectrum in (b). The corresponding normalized $|MCD|^{-1}$ plot is shown in Figure 3d.

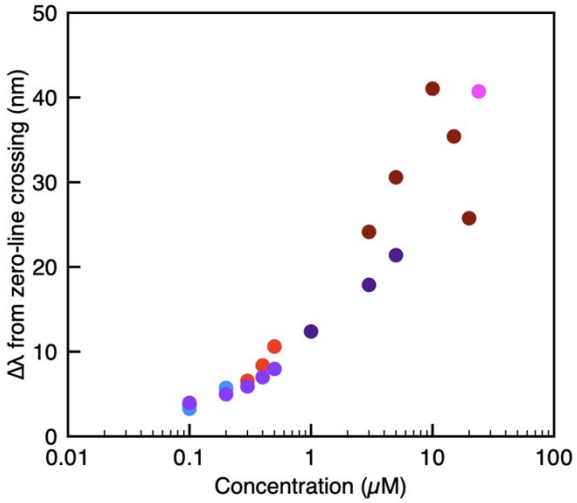

Figure S4. Same data as per Figure 4. Calibration curve showing the spectral shift versus GSH concentration. Each color indicates one batch of GNRs used for GSH sensing.

Table S1. Summary of linear regression fitting parameters for Figure 4a.

Best-fit values (mean ± standard deviation)	
Slope	15.4 ± 1.7
y-intercept	1.7 ± 0.5
Goodness of fit	
R^2	0.967
Standard deviation of the residuals, Sy.x	0.755
Significance test	
p-value	0.0004
Deviation from horizontal?	Significant

Numerical Simulations.

Numerical simulations were performed using the commercial COMSOL Multiphysics software based on the finite element method (FEM). We used the Wave optics module with scattering boundary condition and perfect matching layer in the spherical layered geometrical model's outer domain. In order to avoid any back reflection from the domain walls, the domain was configured in 3D and truncated with perfectly matched layers. The system setup is shown in Figure S3. For our GNRs, the dielectric function of gold is adopted from Jonson and Christy.[1] A relative permittivity tensor is added to the electric displacement field to include the effect of an external magnetic field with a strength of 1.6 T in the simulation.[2] A user-defined free tetrahedral mesh of maximum element size $\lambda/5$ was applied to the physical domain and finally swept for perfectly matched layer.

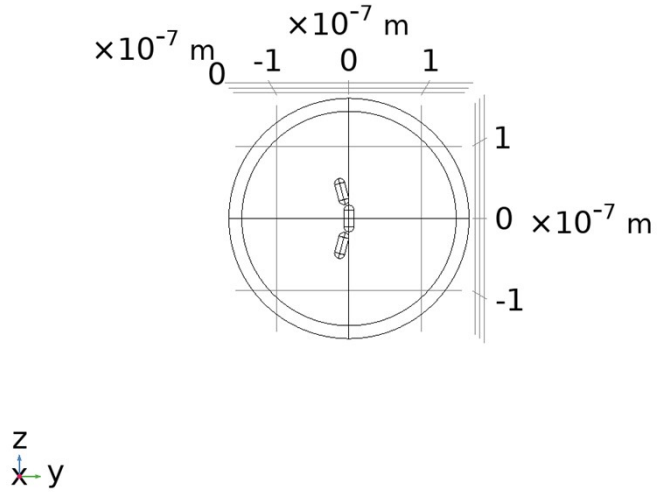

Figure S4. COMSOL system setup of the GNR trimer assembly in an end-to-end configuration.

Table S2. Two sets of measurements for the refractive indices of water and GSH solutions at 20˚C.

Concentration	Measured RI #1	Measured RI #2
0 (water)	1.3331	1.3330
100 nM	1.3327	1.3328
200 nM	1.3330	1.3329
300 nM	1.3332	1.3240
400 nM	1.3331	1.3328
500 nM	1.3332	1.3330
1 µM	1.3332	1.3330

Table S3. Comparison of the performance of some colloidal GSH sensors.

System (Reference)	Signal monitored	Linear range	LoD
Fe_3O_4 magnetic nanoparticles (*Analyst* **2012**, *137*, 485-489)	Changes in absorbance at a given wavelength ΔA_i	3–30 µM	3 µM
Carbon quantum dots (*New J. Chem.*, **2018**, *42*, 5814–5821)	Changes in fluorescence at a given wavelength ΔPL_i	5–20 µM	1.7 µM
Cu nanoclusters (*Appl. Mater. Interfaces*, **2020**, *12*, 42521–42530)	Changes in absorbance at a given wavelength ΔA_i	1–150 µM	890 nM
5,5'-Dithio-bis(2-nitrobenzoic acid)-modified Au nanoparticles (*Anal. Chim. Acta*, **2013**, *794*, 90–98)	Changes in absorbance at a given wavelength ΔA_i	0.55–29.4 µM	680 nM
Mixture of Au nanoparticles and carbon quantum dots (*Biosens. Bioelectron*. **2014**, *56*, 39–45)	Changes in fluorescence at a given wavelength ΔPL_i	100–600 nM	50 nM
Fe-doped MoS_2 nanoflowers (*Mater. Chem. Phys.*, **2021**, *267*, 124684)	Changes in absorbance at a given wavelength ΔA_i	1–30 µM	577 nM
Carbon nanoparticles (*RSC Adv.*, **2022**, *12*, 595–601)	Changes in absorbance at a given wavelength ΔA_i	2.5–50	260 nM
Arg-conjugated Au nanoparticles (*Small* **2015**, *11* (41), 5510)	Changes in absorbance ratio at difference wavelengths $\Delta(A_i/A_j)$	25–375 nM	10.9 nM
CTAB-conjugated Au nanorods (**This work**)	Magnetic circular dichroism spectral shift Δλ_MCD	100–500 nM	97 nM

Supplementary References

1. P. B. Johnson and R. W. Christy, *Phys. Rev. B*, 1972, **6**, 4370–4379.

2. J. Q. Liu, S. Wu, P. Wang, Q. K. Wang, Y. B. Xie, G. H. Sun and Y. X. Zhou, *Opt. Express*, 2019, **27**, 567.