Supporting Information

Simultaneous and Sequential Protein and Organothiol Interactions with Gold Nanoparticles

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Table S1. Catalog number and purities of the chemical used in the experiments. All the chemicals were obtained from Sigma-Aldrich unless specified otherwise.

Chemical	Product No	Lot No	CAS	Purity
Gold(iii) Chloride trihydrate	520918-5 G	MKBH8873V	16961-25-4	≥99.9%
BSA	A-4503	75H0110	9048-46-8	≥96%
Mercaptobenzimidazole	M3205	09218JJ	583-39-1	98%
Cysteine	C 8755	14H3462	56-89-3	
Homocysteine	H4628	098K3793	454-29-5	≥95%
Glutathione	(Acros organics)	A0279520	70-18-8	98%
Thioguanine	A4882	110M1274V	154-42-7	≥98%
6-Mercaptopurine	852678	MKBJ8785V	6112-76-1	98%
2-Mercaptopurine	M6875		28128-19-0	≥95%
Sodium citrate dihydrate	W302600	19797DJ	6132-04-3	≥99%
KCl	(Fisher Scientific)	964665	7447-40-7	99.9%

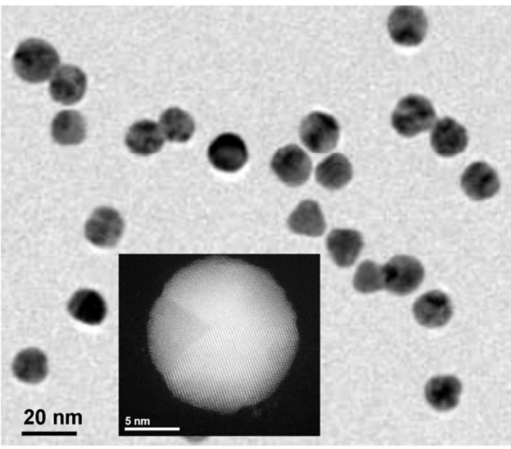

Figure S1. TEM images of the as-synthesized AuNPs. The average particle size was estimated as 12.8±1.3 using image J software. Inset, the high resolution TEM image of a single AuNP.

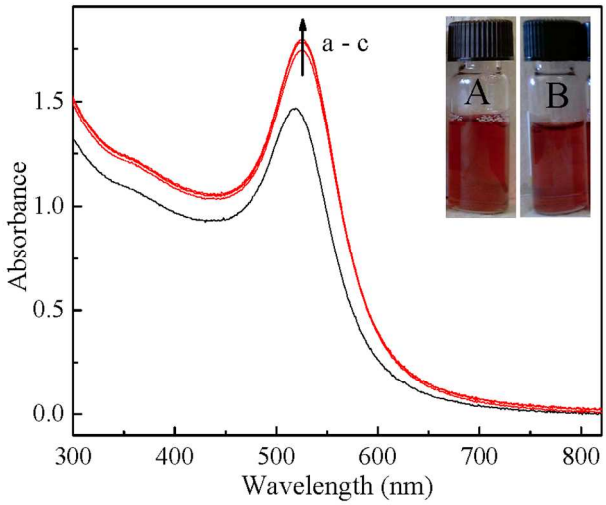

Fig. S2: UV-vis spectrum of (black) the AuNP control, and (red) a AuNP/BSA mixture that is aged (a-c) for 5 mins, overnight, and 3 days. The concentrations of the AuNP and BSA were 5.6 nM and 3 μM respectively. Inset: Photograph of (A) freshly prepared, and (B) three-day aged AuNP/BSA mixture. The absence of an AuNP LSPR peak around ~700 nm indicates the AuNP stability.

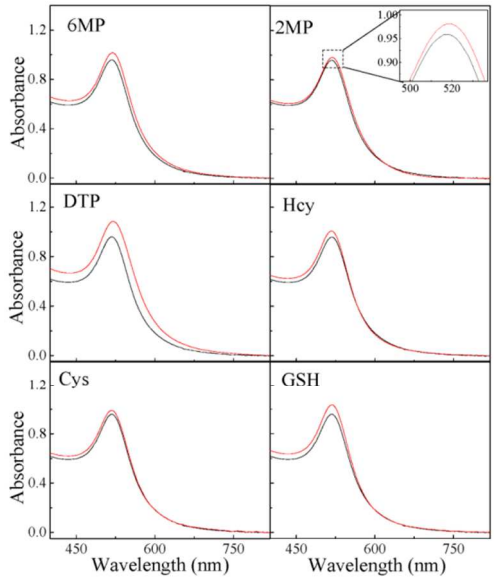

Figure S3. UV-vis spectra of AuNPs (red) with, and(black) without OTs. The inset in the 2MP plot shows a zoom-in of the AuNP LSPR region centered around 520 nm. The concentrations of AuNPs and OTs used were 3.7nM, and 3.3μM, respectively. All AuNP/OT spectra were acquired 5mins after organothiol addition to the AuNPs. The UV-LSPR spectra of AuNP/TG and AuNP/MBI samples are not shown in figure S3 because the AuNP interaction with MBI and TG can be directly inferred from the AuNP aggregation induced by MBI and TG addition (see Figure 2 in main text).

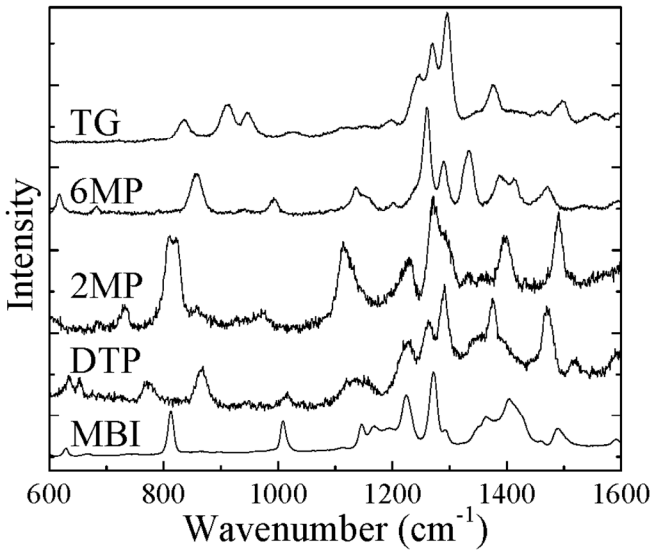

Figure S4. SERS spectra of AuNP/TG, AuNP/6MP, AuNP/2MP, AuNP/DTP, and AuNP/MBI samples. The AuNP and OT concentrations used were 3.7nM, and 3.3μM, respectively. The spectra were scaled and offset for clarity.

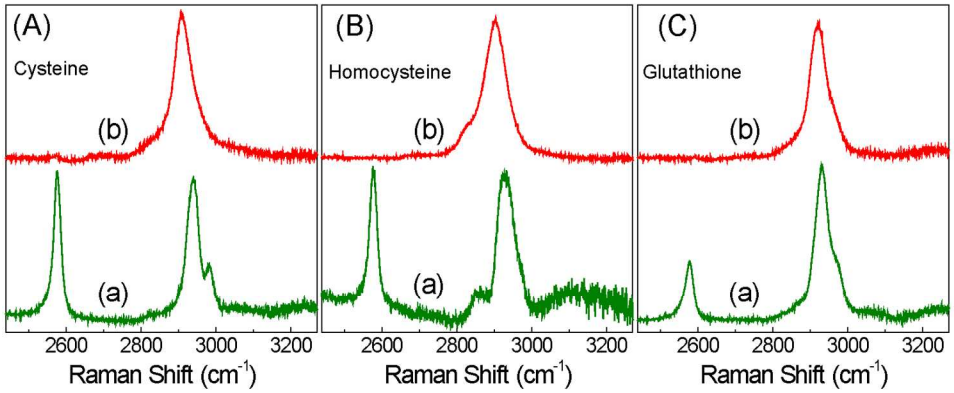

Fig. S5: Comparison of the (a) normal Raman and (b) SERS spectra of (A) Cysteine, (B) Homocysteine, and (C) glutathione. The disappearance of the S-H stretch feature (~2500 cm^{-1}) in the SERS spectra obtained with the amino acid thiols indicates the cleavage of the S-H peak upon the organothiol adsorption onto the AuNP surfaces.

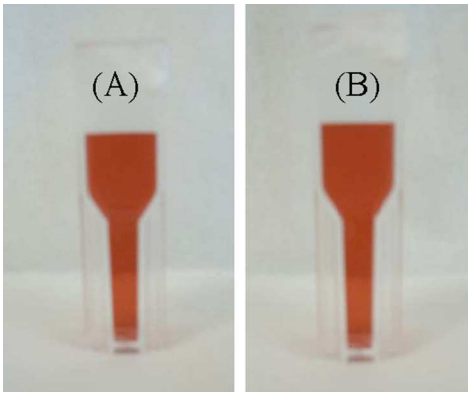

Fig. S6: Photograph of (A) a freshly prepared AuNP/Cys and (B) a three-day aged AuNP/Cys solution. There is no color difference between these two samples even though the time-resolved UV-vis measurements in the main text showed that there is a small degree of AuNP aggregation in the aged AuNP/Cys mixture.

Table S2. Comparison of the MBI adsorption onto the BSA stabilized AuNP with and without mixing with other organothiols.

Sample	Γ_{MBI} (μM)
(((AuNP/BSA)/H_2O)/MBI)	4.8 ± 0.5
(((AuNP/BSA)/GSH)/MBI)	3.5 ± 0.5
(((AuNP/BSA)/DTP)/MBI)	2.6 ± 0.6

The as-synthesized AuNP was mixed with BSA for 5 mins before the addition of third component (H_2O, GSH, or DTP). MBI was added 5 mins after addition of the third component. Quantification of the MBI adsorbed was carried out using the ratiometric SERS method we recently described.[1] The nominal concentrations of AuNP, BSA, GSH, DTP, MBI were 2.5 nM, 3.0 μM, 8 μM, 8 μM, and 8 μM, respectively.

(1) Vangala, K.; Ameer, F.; Salomon, G.; Le, V.; Lewis, E. A.; Liu, D.; Yu, L.; Zhang, D. *The Journal of Physical Chemistry C* 2012.