Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information

Stable ligand-free stellated polyhedral gold nanoparticles for sensitive plasmonic detection

Rachel Keunen, Danielle Macoretta, Nicole Cathcart and Vladimir Kitaev

Experimental

Reagents

Tetrachloroauric acid (99%), hydrogen peroxide (30-32 wt.% in water, 99.999% trace metal basis, with potassium stannate inhibitor), sodium hydroxide (99.99%), potassium iodide (99%), arginine (98-101% TLC), potassium bromide (99%), hydrochloric acid (37%, semiconductor grade), L-cysteine, 97%, ampicillin sodium salt (95%) and ascorbic acid (99.9%) were supplied by Aldrich and used as received. High-purity deionized water (>18.3 MΩ·cm) was produced using Millipore A10 Milli-Q.

Synthesis of AuStNPs

In a typical preparation of stellated gold NPs, 4.33 mL of deionized water, 0.500 mL of 0.005 M $HAuCl_4$, and 0.067 mL of 10.4 M hydrogen peroxide are combined in a 20 mL vial. The reaction vial was stirred at ca. 700 rpm using a 12.7 mm by 3.2 mm magnetic stir bar. Immediately after mixing first reagents, 0.350 mL of 0.1 M NaOH was added to this mixture to increase the pH of the system. The addition of NaOH triggers the reduction of the gold precursor by the hydrogen peroxide leading to the immediate formation of blue dispersion of AuStNPs (Fig. S1); the

reaction development is visualized in Fig. S2. To complete AuStNP formation the reaction was continued stirring for 40-60 min. More details on specific sample preparation conditions are summarized in Table S1.

Seeded synthesis of AuStNPs

First, 1.31 mL (1.875 µmol of gold) of previously synthesized AuStNPs were centrifuged for 15 min at 3000 rpm followed by decanting the supernatant and redispersing the pellet in 0.10 mL of H_2O. The total amount of gold used was kept the same as for the non-seeded AuStNP synthesis (2.50 µmol of gold). The reaction vial was continuously stirred at ca. 700 rpm using a 12.7 mm by 3.2 mm magnetic stir bar. Reagents were combined in the following order: 4.4 mL of deionized water, 0.375 mL of 0.005 M $HAuCl_4$, 0.40 mL of concentrated seed particles (ca. 1.875 µmol of gold), 0.040 mL of 10.4 M H_2O_2, and finally 0.350 mL of 0.1 M NaOH. After the addition of NaOH, the solution turned blue almost immediately (Fig. S1) and the stirring was continued for 40-60 min to complete the synthesis.

Synthesis of AuStNPs with nucleation by ascorbic acid

To prepare AuStNPs nucleated with ascorbic acid, first 0.350 mL of 0.1 M NaOH and 0.050 mL of 0.01 M ascorbic acid were combined in a 20 mL vial. In another 20 mL vial, 4.31 mL of deionized water, 0.500 mL of 0.005 M $HAuCl_4$, and 0.040 mL of 10.4 M hydrogen peroxide were mixed together at ca. 700 rpm. Adding at once 0.400 mL of the NaOH and ascorbic/ascorbate mixture to the gold precursor with hydrogen peroxide triggers the reduction of gold and formation of AuStNPs. The solution turned blue immediately and was allowed to stir for 40-60 min to complete the synthesis. Note that it is crucial to use freshly prepared NaOH solution (not older than 48 h), otherwise smaller AuStNPs with the less defined stellation are more likely to form.

Synthesis of AuStNPs with iodide

The preparation of AuStNPs in the presence of iodide followed the same procedure as with the typical synthesis with one exception; different amounts of potassium iodide (varied from 0 to 0.007 mM total iodide concentration) were added directly following the addition of $HAuCl_4$ and prior to the addition of H_2O_2 and NaOH.

Synthesis of AuStNPs with arginine

Arginine was tested in the AuStNP synthesis in three different manners. Firstly, it was added similarly to KI after the addition of the $HAuCl_4$ and prior to the addition of the H_2O_2 reducing agent. Secondly, it was added following the addition of the NaOH and triggering the reduction by H_2O_2. Finally, it was combined with ascorbic acid and NaOH prior to addition to the reaction vial similarly to the conditions described above for AuStNP synthesis with ascorbic acid. The total concentration of arginine varied from 0.0025 to 0.49 mM (see Table S1).

Characterization

Electron microscopy (EM), both transmission (TEM) and scanning (SEM), was performed using a Hitachi S-5200. Nanoparticle dispersions were deposited and dried on a carbon-coated Formvar grid (EMS Corp.). The operating voltage was 30.0 kV. UV-vis spectra were recorded with either an Ocean Optics QE65000 fiber-optic spectrophotometer or a Cary 50Bio UV-vis spectrophotometer. Malvern Nano ZS Zetasizer was used for zeta potential measurements.

SPR measurements were performed with OpenSPR instrument by Nicoya Lifesciences. Optical cells with the path lengths of 1 and 0.5 cm were used to hold 1-2 ml of AuStNP solutions. AuStNP concentration range varied from as prepared (0.23 to 0.85 mM gold) to diluted 2-4 times with the absorbance values at LSPR maxima ranging from 0.3 to 1.1.

Table S1. Summary of representative synthetic conditions for AuStNP samples shown in electron microscopy images including information on particle size and surface plasmon resonance maxima, λ_{LSPR}.

$HAuCl_4$ (mM) (1)	H_2O_2 (mM) (2)	NaOH (mM) (3)	Arginine (μM) (4)	Ascorbic Acid (mM) (5)	Addition Order	Stir Rate (rpm)	λ_{LSPR} (nm)	Avera gesize (nm)	Corre-sponding Figure Image
0.51	84	4.0	---	---	1-2-3	200	748	150	Fig. 2A,D
0.85	13.6	11.9	---	---	1-2-3	swirlin	667	127	Fig. 2B
0.26	28.7	6.3	---	---	1-2-3	700	750	201	Fig. 2C, S5A
0.45	66	6.3	---	---	1-2-3	700	773	149	Fig. 2E
0.46	86	6.5	---	---	1-2-3	700	753	125	Fig. 2F
0.43	79	6.7	---	0.07	1-2-3,5[B]	500	548	40	Fig. 3A1
0.48	79	6.7	---	0.17	1-2-3,5[B]	700	585	65	Fig. 3A2
0.48	79	6.7	---	0.10	1-2-3,5[B]	700	622	100	Fig. 3A3
0.48	79	6.7	---	0.10	1-2-3,5[B]	700	643	115	Fig. 3A4
0.48	133	6.7	---	---	2-3-1	700	698	150	Fig. 3A5
0.48	133	6.7	---	---	2-3-1	700	753	155	Fig. 3A6
0.48	79	6.7	---	---	1-2-3	300	780	137	Fig. 3A7, S6A
0.48	79	3.8	---	---	1-2-3	700	876	212	Fig. 3A8
0.48	79	4.8	---	---	1-2-3	400	750	132	Fig. S3A
0.48	79	6.7	2.9	0.095	1-2-	700	596	89	Fig. S3B
0.48	133	2.9	9.5	---	1-2-3-4	700	687	63	Fig. S3C
0.82	19.7	11.5	---	---	1-2-3	~700	621	102	Fig. S3D
0.48	133	6.7	9.5	---	1-2-3-4	700	643	86	Fig. S3E
0.45	66	6.3	---	---	1-2-3	700	685	109	Fig. S3F
0.48	133	6.7	480	---	1-4-2-3	700	554	27	Fig. S3G
0.23	130	8.4	---	---	1-2-3	700	664	118	Fig. S3H
0.48	133	6.7	9.5	---	1-4-2-3	700	620	30	Fig S5B
0.48 [C]	79	6.7	---	---	1-2-3-1[C]	700	649	134	Fig. S5C
0.48 [D]	79	6.7	---	---	1-3-2	700	840	164	Fig. S5D
0.48	79	4.8	---	---	1-2-3	700	562	49	Fig. S6B
0.48	79	6.7	---	0.095	1-2-3,5[B]	700	634	88	Fig. S6C,D

*Concentrations are total concentration in the reaction.

[A] NaOH, arginine, and ascorbic acid combined prior to addition to sample vial. Added simultaneously to gold precursor and hydrogen peroxide combined.

[B] NaOH and ascorbic acid combined prior to addition to sample vial.

[C] Centrifuged previously formed AuStNPs for 15 min at 3000 rpm and redispersed the pellet in 400 µL of H_2O. Used 100 µL of redispersed AuStNP sample and 375 µL $HAuCl_4$ 0.005 M solution. Redispersed stars were the first component added following by $HAuCl_4$ that was added dropwise over a one minute interval.

[D] Centrifuged previously formed AuStNPs for 15 min at 3000 rpm and redispersed the pellet in 400 µL of H_2O. Used 100 µL of redispersed AuStNP sample and 375 µL $HAuCl_4$ 0.005 M solution. $HAuCl_4$ was added first followed immediately by the redispersed AuStNP solution.

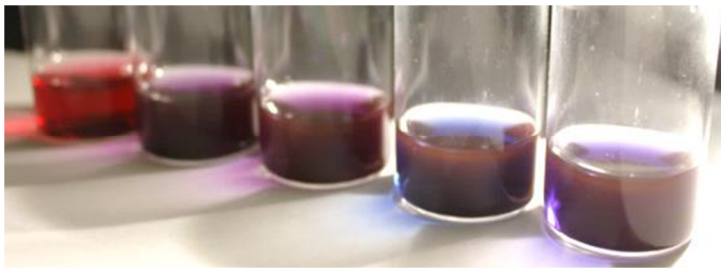

Figure S1. Photographs of a series of AuStNPs representative of the diversity of sizes and LSPR; the samples are shown as prepared in original reaction vials.

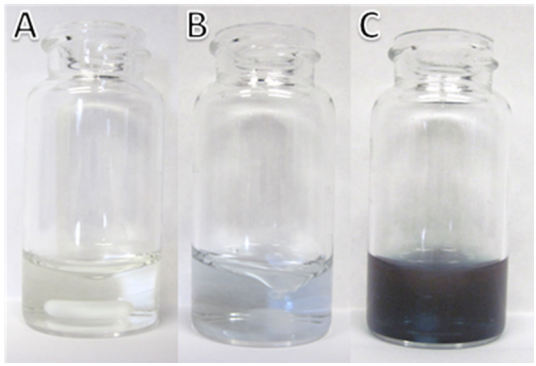

Figure S2. Photographs of the development stages of AuStNPs after the addition of both NaOH and H_2O_2. **A)** After H_2O_2 addition; **B)** ca. 1 s after NaOH addition; **C)** Within 30 s after NaOH addition.

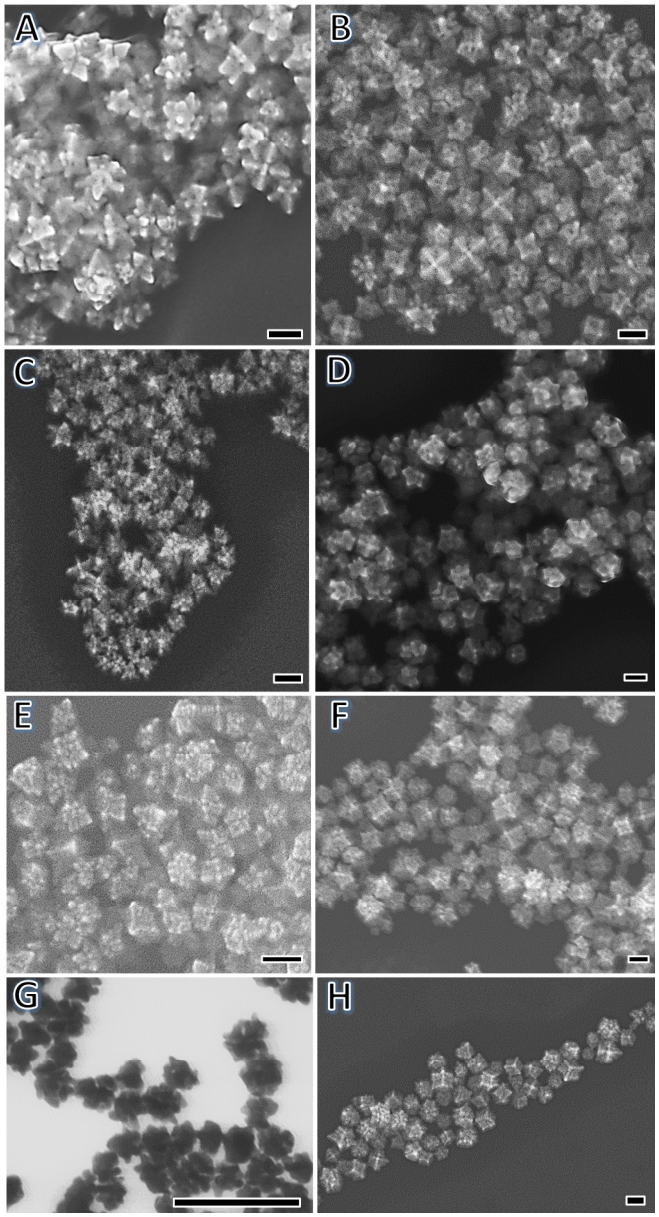

Figure S3. EM images of representative AuStNPs corresponding to reaction conditions itemized in **Table S1.** All scale bars are 100 nm.

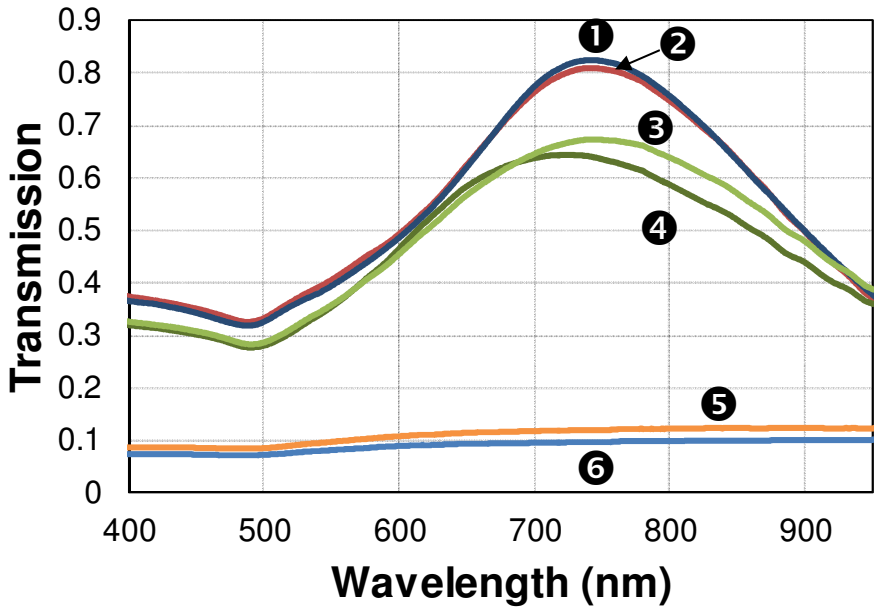

Figure S4. UV-vis spectra illustrating the effect of the order of reagent addition on AuStNP development. The order or reagents is as the following: ❶ H_2O_2, NaOH, $HAuCl_4$; ❷ NaOH, H_2O_2, $HAuCl_4$; ❸ $HAuCl_4$, H_2O_2, NaOH; ❹ H_2O_2, $HAuCl_4$, NaOH; ❺ NaOH, $HAuCl_4$, H_2O_2; ❻ $HAuCl_4$, NaOH, H_2O_2. The final concentrations of the 3 reagents were 6.7 mM for NaOH, 133 mM for H_2O_2, and 0.28 mM for Au.

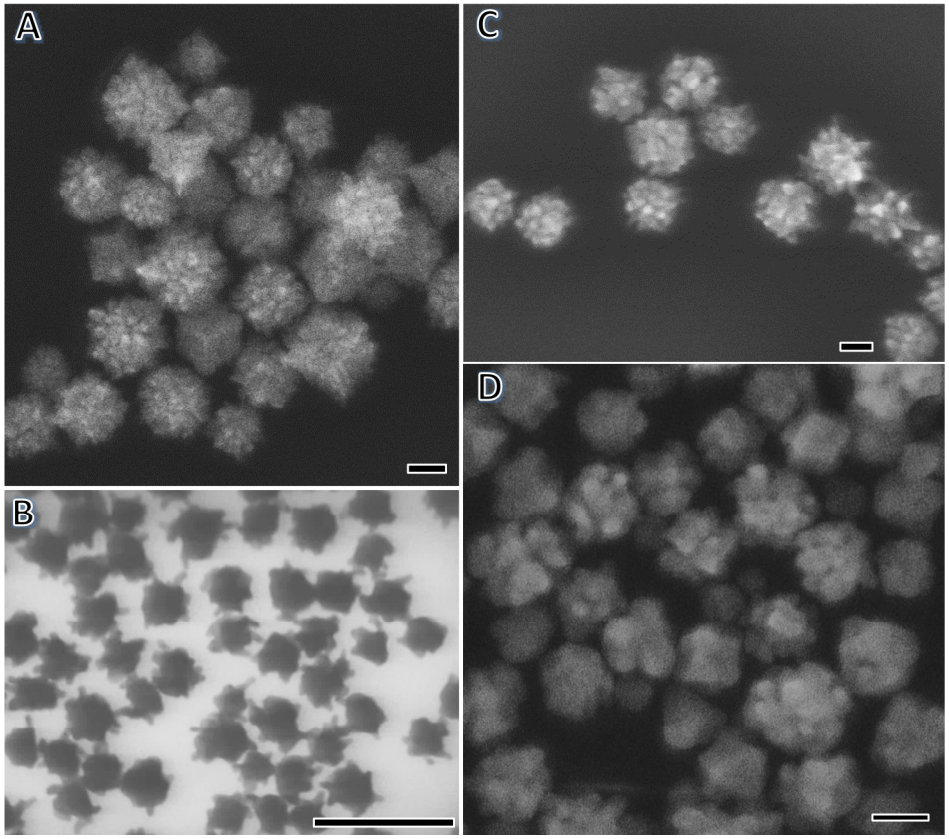

Figure S5. Electron microscopy (EM) images of **A)** AuStNPs prepared with lower gold precursor concentration (0.26 mM); **B)** Au stars synthesized using arginine (9.5 µM total concentration); **C)** and **D)** AuStNPs synthesized using concentrated previously synthesized AuStNP seeds (see Experimental). All scale bars are 100 nm.

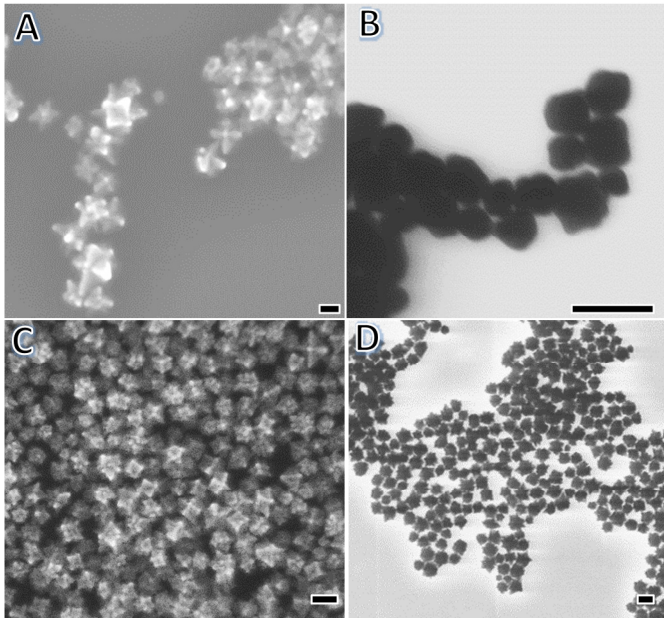

Figure S6. EM images illustrating the effects of nucleation by ascorbic acid on AuStNP size dispersity: **A)** no ascorbic acid, **B)** 0.15 μM, **C)** and **D)** 95 nM. All scale bars are 100 nm.

Sample Name:	nt422-goldstars 20x dil 1		
SOP Name:	mansettings.nano		
File Name:	Install Tests.dts	**Dispersant Name:**	Water
Record Number:	1732	**Dispersant RI:**	1.330
Date and Time:	September-28-15 3:14:15 PM	**Viscosity (cP):**	0.8872
		Dispersant Dielectric Constant:	78.5

Temperature (°C):	25.0	**Zeta Runs:**	12
Count Rate (kcps):	330.3	**Measurement Position (mm):**	2.00
Cell Description:	Clear disposable zeta cell	**Attenuator:**	9

			Mean (mV)	**Area (%)**	**St Dev (mV)**
Zeta Potential (mV):	-61.1	**Peak 1:**	-65.7	88.9	11.6
Zeta Deviation (mV):	26.0	**Peak 2:**	-35.2	9.6	6.56
Conductivity (mS/cm):	0.0869	**Peak 3:**	-15.4	1.2	4.00

Result quality : See result quality report

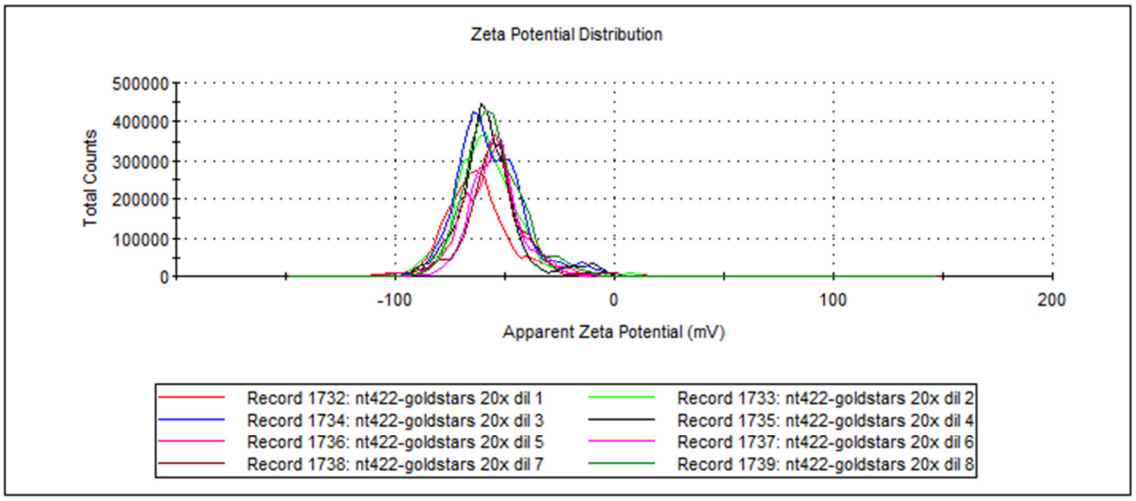

Figure S7. Zeta potential measurements (8 independent runs) for AuStNP sample diluted 20 times.

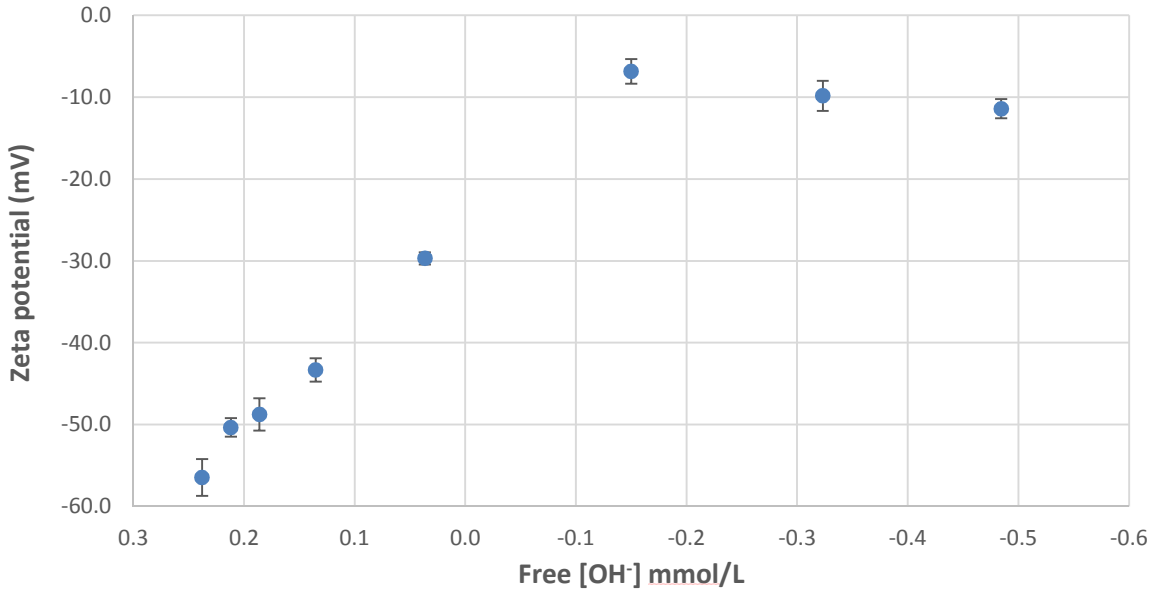

Figure S8. Zeta potential titration measurements for AuStNP sample diluted 20 times from original 0.43 mM Au concentration of as prepared sample. HCl is added to neutralize NaOH. Zeta potential is shown as a function of calculated concentration of free OH^- ions. Negative values represent HCl excess. For further details see **Table S2**.

Table S2. Zetasizer data for AuStNP titration with HCl.

Sample	Free [OH-] (mmol/L)	ζ average (mV)	σ_ζ (mV)	# Runs
NT422- 20 x diluted	0.238	-56.5	2.3	8
+5 µL 0.005 M HCl	0.212	-50.4	1.1	8
+10 µL 0.005 M HCl	0.186	-48.8	2.0	8
+20 µL 0.005 M HCl	0.135	-43.3	1.4	8
+40 µL 0.005 M HCl	0.037	-29.7	0.7	8
+80 µL 0.005 M HCl	-0.150	-6.8	1.5	8
+120 µL 0.005 M HCl	-0.323	-9.8	1.8	80
+160 µL 0.005 M HCl	-0.484	-11.4	1.2	40

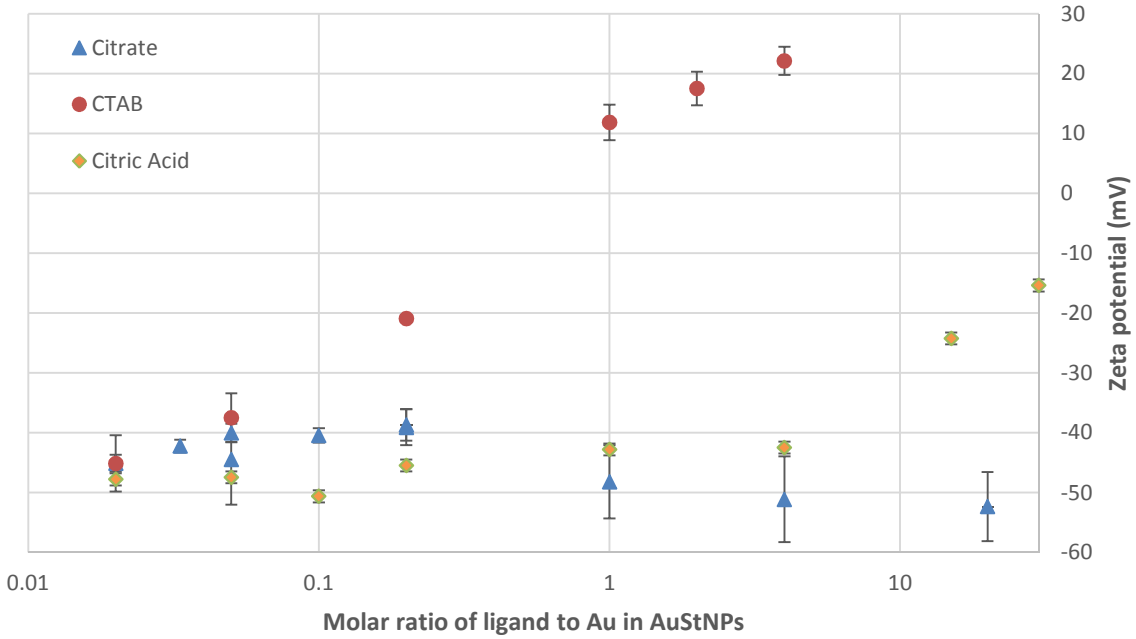

Figure S9. Zeta potential measurements for AuStNP (diluted 20 times from original Au concentration of 0.43 mM) upon addition of CTAB (red circles), citrate (blue triangles) and citric acid (orange diamonds).

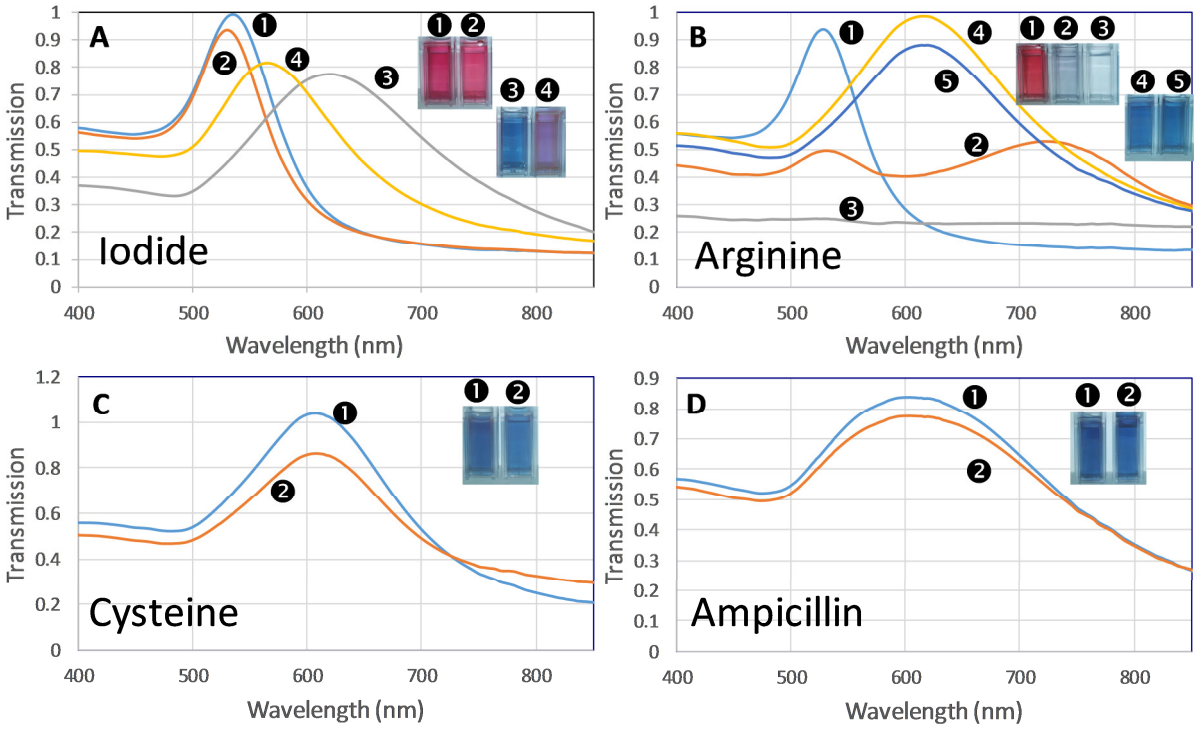

Figure S10. UV-vis spectra with photograph insets of control AuStNP samples and AuStNP samples exposed to different reagents. **A**) KI – 1) smaller AuStNP control sample, 2) 10^{-3} M KI, 3) larger AuStNP control sample, and 4) 10^{-5} M KI. **B**) Arginine -1) smaller AuStNP control sample, 2) 10^{-2} M, 3) 10^{-1} M, 4) larger AuStNP control sample, and 5) 10^{-1} M. **C**) Cysteine – 1) larger AuStNP control sample, 2) 10^{-1} M cysteine. **D**) Ampicillin – 1) larger AuStNP control sample, and 2) 10^{-2} M ampicillin.