One-step green synthesis of gold and silver nanoparticles with ascorbic acid and their versatile surface post-functionalization

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SI-1- Au NP and Ag NP Synthesis

SI-1-1 $HAuCl_4$ pH effect: relation between R_1 and V_{NaOH}

The solutions of 50mL fresh gold salt ($HAuCl_4$) solution at 0.5 mM was tuned by adding different amounts of a 0.10 M sodium hydroxide (NaOH) solution in order to reach different ratios R_1=[NaOH]/[$HAuCl_4$] from 0 to 6.4.

R_1	0	0.3	0.6	0.9	1.3	1.6	1.9	2.3	2.6	2.9	3.3	3.6	3.8
V_{NaOH} mL	0	0.075	0.150	0.225	0.325	0.400	0.475	0.575	0.650	0.725	0.825	0.900	0.950

R_1	4	4.2	4.4	4.6	4.8	5	5.2	5.4	5.6	5.8	6	6.2	6.4
V_{NaOH} mL	1	1.05	1.1	1.15	1.2	1.25	1.3	1.35	1.4	1.45	1.5	1.55	1.6

SI-1-1 AA pH effect: relation between R_2 or R_3 and V_{NaOH}

The pH of 50mL Ascorbic acid solutions at 0.1 mM was tuned by adding different amounts of a 10 M NaOH solution in order to reach different ratios R_2=[NaOH]/[AA] from 0 to 2 (for gold NP synthesis) or R_3=[NaOH]/[AA] from 0 to 4 (for silver Np synthesis)

Relation between R_2 and V_{NaOH}

R_2	0	0.2	0.4	0.6	0.8	1	1.2	1.4	1.6	2
V_{NaOH} mL	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	1

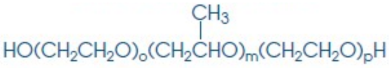
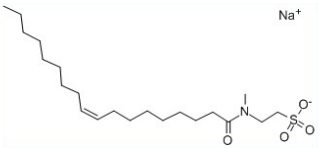
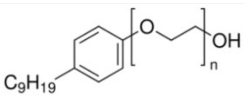
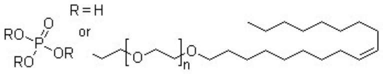
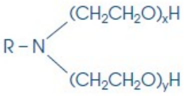
Relation between R_3 and V_{NaOH}

R_3	0.4	1	1.2	1.45	1.55	1.65	1.7	1.8
V_{NaOH} mL	0.2	0.5	0.6	0.725	0.775	0.825	0.85	0.9

R_3	1.9	2	2.2	2.45	2.7	2.9	3.5	4.4
V_{NaOH} mL	0.95	1	1.1	1.225	1.35	1.45	1.75	2.2

SI-2- Description of commercial surfactants

Short description of the Solvay surfactants used for the surface modification of the nanoparticles stabilized with ascorbic acid.

Antarox L64	 $HO(CH_2CH_2O)_o(CH_2\overset{CH_3}{C}HO)_m(CH_2CH_2O)_pH$
Geropon T77	
Igepal CO-630	
Lubrhophos LB-400	
Rhodameen PN-430	 $R-N\genfrac{}{}{0pt}{}{(CH_2CH_2O)_xH}{(CH_2CH_2O)_yH}$ R = hydrocarbonated chain

SI-3- Comparison of Au@AA with more monodisperses particles

SI-2-1 Synthesis of Au@CTAB NPs

CTAB-coated Au NPs were prepared using water-based method reported by Liz-Marzan.[1] Briefly, a solution of ascorbic acid is injected into a solution of gold salt $HAuCl_4$ and CTAB under a vigorous stirring. This injection is quickly followed by the addition of gold seeds previously prepared using the Turkevich method. The size of the particles is tuned by the amount of seeds injected in the solution. Therefore five batches of nanoparticles with different sizes have been synthesized: A: 12 ± 8% _ B: 30 ± 7% _ C: 39 ± 5% _ D: 54 ± 4% _ E: 63 ± 5% (Fig SI-1).

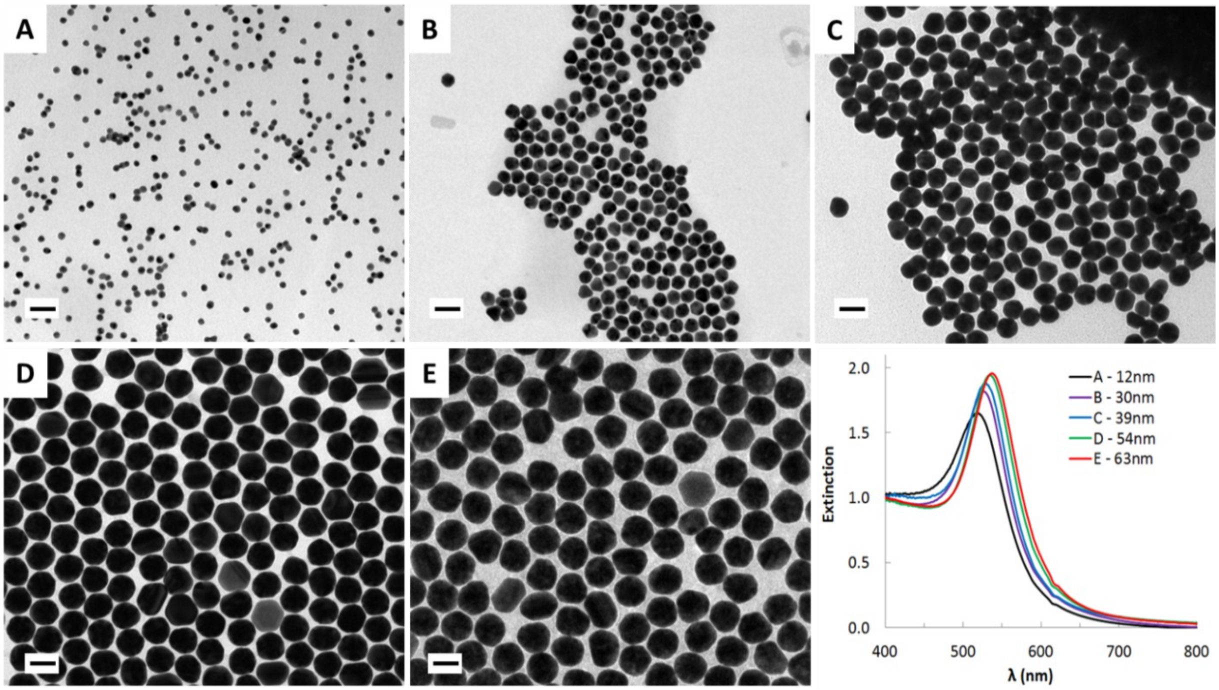


Fig. SI-1 : TEM images of Au@CTAB NPs (scale bars = 50nm) and their exctinction spectrum normalized at 400nm
A: 12 ± 1 nm _ B: 30 ± 2 nm _ C: 39 ± 2 nm _ D: 54 ± 2nm _ E: 63 ± 3nm

[1] J. Rodríguez-Fernández, J. Pérez-Juste, F. J. García de Abajo and L. M. Liz-Marzán, *Langmuir*, 2006, **22**, 7007–7010

SI-2-2 Extinction spectrum: Au@AA versus Au@CTAB

These calibrated particles are compared to the corresponding Au@AA particles. As it can be seen in the Fig. SI-2, there are only on small variations in the optical properties. The graphic D2 Fig SI-2 shows that an important polydispersity of Au@AA particles is needed to notably deviate from the monodisperse particles.

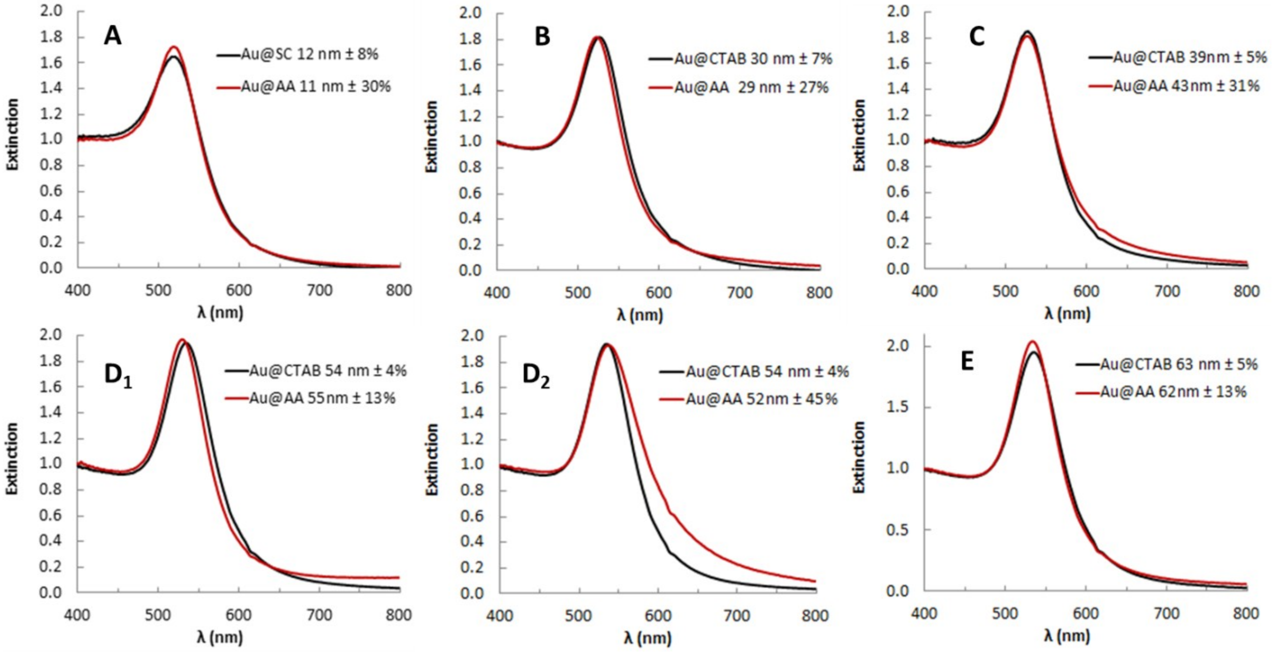


Fig SI-2: Comparison of Au@CTAB and Au@AA extinction spectrum (normalized at 400nm)

- A- Turkevich NP VS Au@AA R_2=1.2
- B- Au@CTAB 30nm VS Au@AA R_1=0
- C- Au@CTAB 39nm VS Au@AA R_1=2.6
- D_1- Au@CTAB 54nm VS Au@AA R_1=5
- D_1- Au@CTAB 54nm VS Au@AA R_1=3.8
- E- Au@CTAB 63nm VS Au@AA R_1=5.2