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SUPPORTING INFORMATION

Reactive solutions with chloride ions

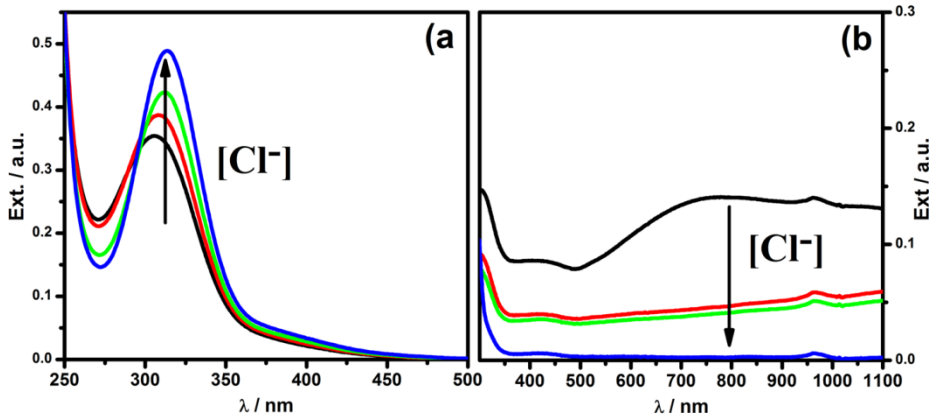

Figure S1. Extinction spectra of 0.1 mM Au(III) reactive solutions with increasing chloride ion concentration: (black) 7.5 mM, (red) 10 mM (green) 25 mM, (blue) 50 mM, (a) before and (b) after H_2Q addition ($[H2Q]_{final}$=0.15 mM).

In Figure S1-a are displayed the spectra obtained after chloride ions addition to solutions of $HAuCl_4$ 0.1 mM. The extinction maxima located between 300 and 325 nm correspond to the absorption of aqueous Au(III) complexes. When the chloride ion concentration rises, the peak is red-shifted and increase in intensity; this is due to the change in the Au(III) speciation caused by the replacement of hydroxyl ions by chloride ions in the coordination sphere of gold. When hydroquinone is added to these solutions, changes in the spectroscopic behaviour are detected (Figure S1-b). Similar to the observed for reactive solutions with bromide ions, at low chloride ions concentrations the extinction observed in the visible region indicates Au(0) formation (black, red and green lines). When the chloride ions concentration is high enough (50 mM, blue line), no spectral evidence of the presence of Au(III) and Au(0) is observed whatsoever indicating the presence of Au(I) metastable species and nucleation inhibition.

Reactive solutions with iodide ions

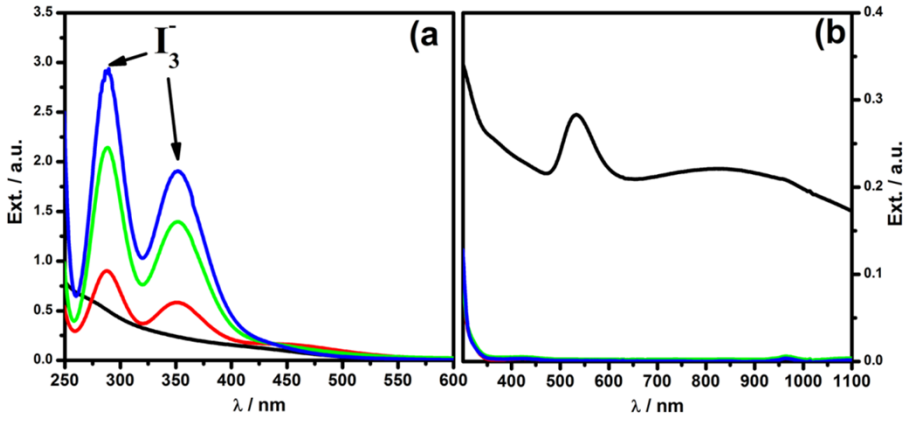

Figure S2. Extinction spectra of 0.1 mM Au(III) reactive solutions with increasing iodide ion concentration: (black) 0.1 mM, (red) 0.5 mM (green) 1 mM, (blue) 2.5 mM, (a) before and (b) after H_2Q addition ($[H2Q]_{final}$=0.15 mM).

In Figure S2-a are displayed the spectra obtained after iodide ions addition to solutions of $HAuCl_4$ 0.1 mM. At low iodide ions concentration (black line), the solution exhibits turbidity which is indicative of the presence of iodine. At higher iodide ion concentrations (red, green and blue lines) the characteristic peaks of triiodide ions, located at 288 and 352 nm,[1] are detected. The presence of iodine and triiodide ions can be explained by the iodide ions oxidation by Au(III). When H_2Q is added into these solutions (Figure S2-b) the spectroscopic characteristics of iodine and triiodide ions vanish, indicating their reduction by H_2Q back to the iodide ion form. At low iodide ions concentrations the characteristic extinction of large AuNPs (black line) indicates Au(0) formation. At iodide ions concentrations equal or higher than 0.5 mM (red, green and blue lines) no spectroscopic evidence of the presence of Au(III) or Au(0) is observed, indicating the formation of Au(I) metastable species and nucleation inhibition.

[1] Awtrey, A. D.; Connik, R. E. *J. Am. Chem. Soc.* **1951**, 73, 1842.

Temperature effect

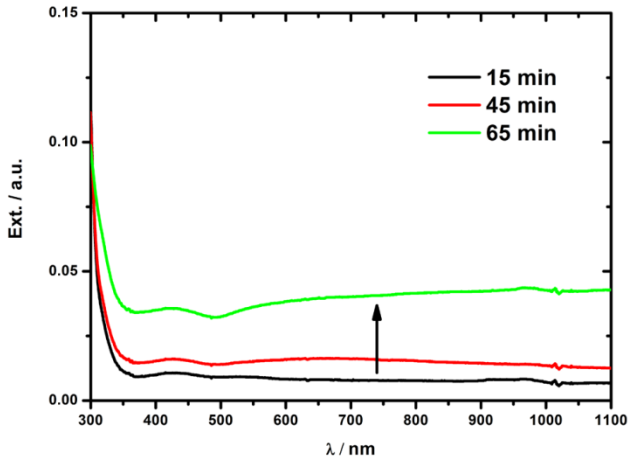

Figure S3. Extinction spectra evolution of a reactive solution containing 0.1 mM $HAuCl_4$, 50 mM KBr and 0.15 mM of H_2Q prepared at 98 °C.

15 minutes after the addition of H_2Q (black line) the solution exhibits a low but appreciable extinction in the visible range which is indicative of the formation of gold microparticles. This is further confirmed by the spectra evolution which shows that the extinction increases in time for all wavelengths. This result indicates that nucleation of gold is not inhibited under this conditions.

Reactive solution with Hexadecyltrimethylammonium Nitrate (CTAN)

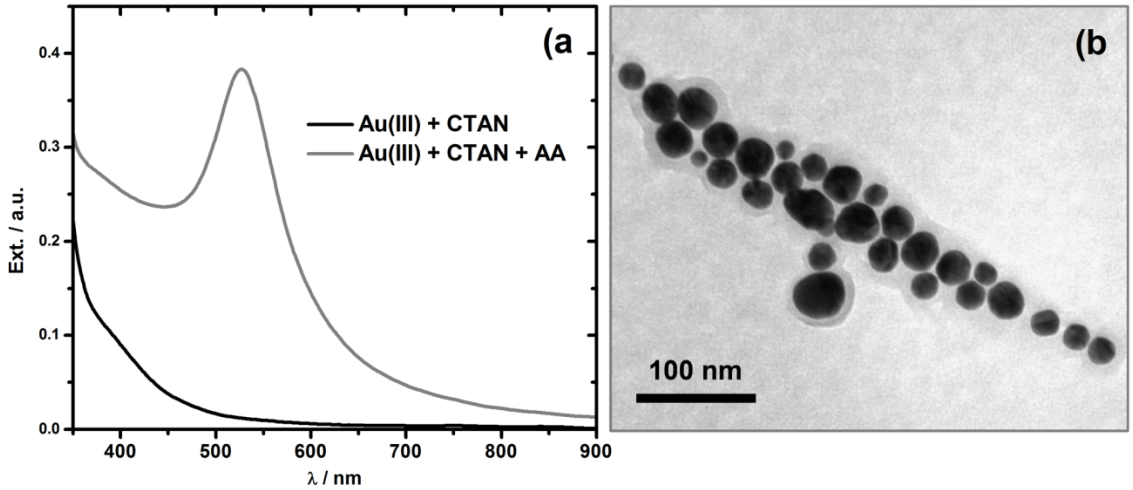

Figure S4. a) Extinction spectra of 0.1 mM $HAuCl_4$ reactive solution with 10 mM CTAN before (black line) and after ascorbic acid (AA) addition (gray line; $[AA]_{final}$=0.15 mM, pH=6.5). b) TEM image of the AuNPs formed.

The aqueous solutions formed by $HAuCl_4$ and CTAN have a pale yellow colour as consequence by its light absorption above the 400 nm associated with the Au(III)-chloride complexes (Figure S3, black line). When AA is added into this solutions the characteristic SPR peak at c.a. 520 nm of AuNPs is observed (grey line). This indicates that the Hexadecyltrimethylammonium cation (CTA^+) itself does not prevent AuNPs nucleation in absence of halide ions. The TEM image shows that the NPs produced are polydisperse in size and have spherical shapes.

Derivation of the equation to predict the AuNPs size after seeding

The following approximations are taken in to account: (i) Samples are monodisperse in size, (ii) the AuNPs are perfect spheres, (iii) all gold species are completely reduced to Au(0) in all the synthetic stages and (iv) the AuNPs have the same molar volume as the bulk gold.

The total mole of Au(0) after seeding can be calculated as the sum between the mole of Au(I) coming from the bath plus the mole of Au coming from the seeds:

$$n_{total}^{Au} = n_{bath}^{Au(I)} + n_{seeds}^{Au}$$

The mole of Au(I) can be calculated from the final concentration (M) and the final volume (L) after seeding:

$$n_{final}^{Au} = V_{final}[Au(I)] + n_{seeds}^{Au}$$

If the mole of Au are equally distributed among the AuNPs, dividing by the number of seeds AuNPs we can obtain the final mole of Au per NP:

$$\bar{n}_{final}^{Au} = \frac{V_{final}[Au(I)]}{N_{seeds}} + \bar{n}_{seed}^{Au}$$

N_{seeds}/V_{final} is the final concentration of AuNPs in number of NPs per litre; if it is divided by the Avogadro Number it gives the concentration in mol/L, so the above equation can be rewritten as:

$$\bar{n}_{final}^{Au} = \frac{N_A[Au(I)]}{[seeds]} + \bar{n}_{seed}^{Au}$$

where $[seeds]$ is the molar concentration of AuNPs. Multiplying by the molar volume, it is obtained the volume per NP:

$$\bar{V}_{final}^{NP} = \frac{V_m N_A[Au(I)]}{[seeds]} + \bar{V}_{seed}$$

Finally, using the relationship between the volume and the diameter of a sphere and solving for the diameter:

$$d_{final} = \sqrt[3]{\frac{6V_m N_A[Au(I)]}{\pi[seeds]} + d_{seed}^{3}}$$