# Gold decoration of silica by low-T decomposition of aqueous gold(III) hydroxide

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#### ESI-1. Equilibria of Au(III) species in alkaline solutions

To achieve the Au(OH)<sub>3</sub> precipitation, a strong alkali like NaOH is added into aqueous solutions of HAuCl<sub>4</sub> (gold precursor). When the pH of a solution HAuCl<sub>4</sub> is increased, the ligand exchange (Cl<sup>-</sup> by OH<sup>-</sup>) takes place gradually producing anionic species like [Au(OH)Cl<sub>3</sub>]<sup>-</sup>, [Au(OH)<sub>2</sub>Cl<sub>2</sub>]<sup>-</sup> or a red precipitate of gold hydroxide (Au(OH)<sub>3</sub>, Kps =  $3.16 \times 10^{-48}$ )<sup>1</sup> according to:

$$\left[\operatorname{AuCI}_{4}\right]_{(ac)}^{-} + \operatorname{3HO}_{(ac)}^{-} \longrightarrow \operatorname{Au}(\operatorname{HO})_{3(s)}^{-} + \operatorname{4CI}_{(ac)}^{-}$$
(1)

A further increase of hydroxyl concentration leads to the formation of soluble uncolored complex species like  $[Au(OH)_4]^-$  accordingly with the amphoteric behavior of  $Au(OH)_3$ ,<sup>2–4</sup> as follows:

$$Au(HO)_{3(s)} + HO_{(ac)} \longrightarrow \left[Au(HO)_{4}\right]_{(ac)}^{-}$$
(2)

#### ESI-2. Characterization of the SiO<sub>2</sub>MPs

**Figure S1a** shows the typical decreasing UV-Visible spectrum of SiO<sub>2</sub>MPs. Dynamic Light Scattering (DLS) measurements (**Figure S1a inset**) indicate that the obtained SiO<sub>2</sub>MPs are not agglomerated. Hydrodynamic diameter values are in the range from 140 to 300 nm. The raw estimation for diameter provided by DLS is consistent with the average diameter value obtained from TEM images: 227 nm (**Figure S1b**). We will call these particles as "microparticles" (SiO<sub>2</sub>MPs) to clearly differentiate them from the AuNPs.



**Figure S1. a.** UV-Visible spectrum of the aqueous SiO<sub>2</sub>MPs stock suspension synthesized; inset: distribution of the particles by DLS\*; **b.** TEM image of the SiO<sub>2</sub>MPs.

\*DLS measurements were performed using a Beckman Coulter-Delsa Nano C to perform measurements with a laser light source at 658 nm and a detection angle of 165°.

# ESI-3. Instability of alkaline Au(III) solutions in different acetone:water environments

In this section, the results of the experiment performed by fixing the concentration of Au(III) and NaOH, and the incubation time (15 minutes) but increasing acetone proportion between 10% and 90% are shown (**Figure S2**). For the acetone percent 10%, 25% and 50%, the spectra exhibit AuNPs SPR peaks with similar intensities at 503.0 nm, 504.5 nm and 505.0 nm, respectively. These spectral features show that AuNPs nucleation is very fast under these conditions. Otherwise, for higher acetone fraction (75%), broad AuNPs SPR maximum is observed at larger wavelength (639 nm) indicative of the presence of larger AuNPs. For 90% of acetone, a decreasing extinction profile between 400 and 1100 nm with small extinction values was observed, consistent with the dispersion of large particles. The presence of larger particles at higher rates of acetone is indicative that AuNPs nucleation is slowed down under these conditions since AuNPs growth takes place rather than continuous nucleation. Consequently, 90:10 acetone:water appears to be the optimal condition for the decoration of substrate

particles because it allows to speed up Au(OH)<sub>3</sub> precipitation/decomposition but delay homogeneous nucleation enough in order to favor heterogeneous nucleation.



**Figure S2.** UV-Visible spectra corresponding to solutions of HAuCl<sub>4</sub> 0.1 mM and NaOH 5 mM incubated for 15 minutes in different acetone:water environments.

#### ESI-4. Synthesis of SiO2MP|AuNPs in aqueous media

**Figure S3** shows the spectral evolution during the incubation at room temperature of aqueous alkaline Au(III) solution in the presence of SiO<sub>2</sub>MPs. The initial spectrum (blue line) includes the typical decreasing extinction contribution of suspended SiO<sub>2</sub>MPs (**Figure S1**) in addition to the extinction coming from Au(III) species (either soluble hydroxilated complexes of Au(III) or Au(OH)<sub>3</sub> precipitate). After 13 days of reaction (light blue line), a clear evidence of AuNPs formation is detected as a shoulder centered at 534 nm. As time elapses, such a feature evolves to define a maximum of increasing intensity that shifts to larger wavelength values: 550 nm (2 months), 554 nm (4 months) and 581 nm (7 months). These spectral changes confirm the formation of AuNPs.



Figure S3. Spectral evolution of an aqueous suspension of  $HAuCl_4 0.1 \text{ mM}$ , NaOH 1 mM and 4.43 x  $10^{12}$  SiO<sub>2</sub>MPs per L (pH=8.5) incubated at room temperature.

## ESI-5. Characterization of the SiO2MP|AuNPs

Figure S4 shows different bright field TEM images of the NSs obtained by low-T protocol.



Figure S4. Bright field TEM images of the NSs obtained by low-T protocol.

**Figure S5** shows the X ray spectrum of the sample in which it can be seen the presence of the desired elements: Si, O and Au.



Figure S5. X-ray spectrum of the sample.



Figure S6. STEM images of the NSs obtained by low-T protocol.

STEM images of bright and dark field obtained with the JEM-200ARMF JEOL operating at 200 kV (**Figure S6**) reveals the correspondence between both operation modes and the AuNPs location over the  $SiO_2MP$ .

## **References**

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