ELECTRONIC SUPPLEMENTARY INFORMATION

New insights on the Au$_{core}$/Pt$_{shell}$ nanoparticle structure in the sub-monolayer range: SERS as surface analyzing tool.

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Experimentals

Materials

Lucigenin dinitrate (LG) was purchased from Sigma-Aldrich with a purity of >97% w/w. Thiophenol (TP) was purchased from Fluka with a purity of >98% w/w. LG aqueous stock solution and TP ethanol stock solution were prepared to a final concentration of 10^{-3} M. Gold(III) chloride hydrate and Chloroplatinic acid hexahydrate (H_2PtCl_6) were purchased from Sigma-Aldrich. An aqueous H_2PtCl_6 stock solution of 10^{-3} M was prepared in Milli-Q water.

Synthesis of colloids and SERS measurements

Gold citrate colloid (AuCT) was prepared by reduction of chloroauric acid with sodium citrate according to the method reported by Sutherland and Winefordner [1].

Both $Au@PtCl_6^{2-}$ and $Au@Pt^0$ samples were classified according to the value R, which denotes the ratio between total number of Pt atoms added as $PtCl_6^{2-}$ anions to the Au NPs seeds versus the estimated total numbers of Au atoms on the NP surfaces. The estimated total numbers of Au atoms on the NP surfaces were calculated for gold NPs prepared of 15 nm diameter and assuming that these NPs are perfect spheres constituted of Au atoms in a close-packed *fcc* structure with an atomic radius of 0.144 nm [2].

The $PtCl_6^{2-}$ covered gold NPs ($Au@PtCl_6^{2-}$) were prepared by adding aliquots of hexachloroplatinate stock solution to 0.5 ml of AuCT colloid. Each sample was then diluted to 1 ml volume with Milli-Q water. According to Waibel et al. [3], $PtCl_4^{2-}$ and $PtCl_6^{2-}$ adsorb on Au(111) and Au(100) surfaces forming similar ordered adlayers.

Core-shell Au-Pt nanoparticles ($Au@Pt^0$) were prepared according to the method reported by Lu et al. [4] with slight modifications. 5 ml of AuCT colloid were mixed with different aliquots of an appropriate H_2PtCl_6 aqueous solution (from 10^{-4}M to 10^{-2}M) and diluted with Milli-Q water to a final volume of 7 ml, then cooled at 4°C. 3 ml of freshly prepared Ascorbic Acid (AA) solution at different concentrations were first cooled at 4°C and then added under stirring to the gold NPs/platinum mixture. The molar ratio Ascorbic Acid/$PtCl_6^{2-}$ in the final mixture was always kept constant at 1.5. The final mixture was left to react at room temperature. Within ca. 30 min, the red color of the gold colloid changes to the dark brown color of a platinum colloid. The use of the weak reducing agent AA results in a slower reduction rate, leading to the fabrication of $Au@Pt^0$ core-shell structures with high monodispersity and uniform morphology [4].

In the case of TP SERS measurements, the activation of the colloidal suspension was performed by adding 30 µL of 0,5 M potassium nitrate solution before the addition of TP stock solution (final concentration in the colloid 10^{-5} M). In the case of LG SERS measurements, the activation of the colloidal suspension was performed by adding 30 µL of 0,5 M sodium chloride solution before the addition of LG stock solution (final concentration in the colloid 10^{-5} M). The activation process consists of the aggregation of the colloidal NPs by addition of electrolytes, which promote the formation of colloidal clusters showing much larger SERS enhancement than that of individual particles [5]. We optimized the salt addition to induce a mild aggregation of the nanoparticles providing a stable suspension on the timescale of the experiment. In the case of TP, a molecule capable to directly interact with the metal surface through the formation of the sulphur bond, we used a KNO_3 salt, which merely acts by increasing the ionic strength of the colloid and, in turn, decreasing the screened Coulomb interaction and favouring the aggregation process [5]. Whereas, for LG we employed a halide salt (NaCl), which in addition to the modification of the colloidal ionic strength, allows the adsorption of halide anions on the metal surface. These

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superficial chloride anions promote the extensive adsorption of LG on the NPs (LG requires a "bridging" anion to bind the metal surface) [6]. As a control experiment, the SERS study for TP was also performed by substituting KNO_3 with NaCl as the aggregating agent and no significant changes were observed.

Instrumentations

The SERS spectra were measured with a Renishaw Raman Microscope System RM2000 equipped with a diode laser at 785 nm, a Leica microscope, and an electrically refrigerated CCD camera. The laser power in the sample was 2.0 mW. The spectral resolution was set at 4 cm^{-1}. Samples for UV-visible absorption spectroscopy were prepared in the same way as those for the corresponding SERS spectra and were recorded in a Shimadzu UV-3600 UV-VIS-NIR Spectrophotometer. The colloidal suspensions were diluted to 20% in water and placed in 1-cm optical path quartz cuvettes.

X-ray Diffraction (XRD) data were collected on a Bruker D8 Advance diffractometer using Cu KR radiation (λ= 1,5406 Å) equipped with LyxnEye detector. The measurements were done in reflection geometry and the diffraction (Bragg) angles 2θ were scanned at a step of 0.05°. Each data point was measured for 4 s and several scans were taken of each sample. The XRD data was collected from 35 to 55 degree 2θ at a rate of 0.58 degrees/min at room temperature.

SERS Spectra of the Probe Molecules

The platinum coating of the Au NPs affects the SERS response of the nanostructures in two main ways:

1. Modification of the NP chemical properties of the NPs, as revealed by the changes in the SERS spectra profiles of the probe molecules LG and TP. In particular, as can be seen in Figure S1A, LG exhibits drastic changes for the bands at ca. 1581 and 1427 cm^{-1}, assigned to $\nu(C=N)$ modes [7]; ca. 1394 cm^{-1}, attributed to $\nu(N^+-CH_3)$ modes [7]; and ca. 463, 444 and 418 cm^{-1}, associated with the $\delta(C-C)$ vibrations [7]. The same bands proved to be very sensitive to the presence of different anions on the silver surface [6]. Because of the direct interaction of the N^+ in the acridine moiety with the chloride anion adsorbed onto the metal surface, these bands are strongly affected by the nature of the substrate. By contrast, the SERS spectra of TP (Fig. S1B) display slight modifications of the spectral profile. The most pronounced changes are observed in the 1100-950 cm^{-1} range, where bands at 1073 cm^{-1}, assigned to C-C asymmetric stretching [8], and 997 cm^{-1}, associated to ring out-of plane deformation and C-H out-of-plane bending modes [8], significantly vary their relative intensities. TP chemisorbs as benzenthiolate, forming -S-metal covalent bonds but possibly adopting different orientation and interaction strength depending on the surface composition [9].

2. Quenching of the EM enhancement felt by the probe molecules, as revealed by the decreasing of the overall intensity of their SERS spectra. The platinum coating of the gold nanostructures works as spacer between the SERS active substrate and the adsorbate (for both $Au@PtCl_6^{2-}$ and $Au@Pt^0$) and progressively damps the plasmon absorption of Au core (only for $Au@Pt^0$).

Therefore, the modification of the surface chemical properties of the NPs by progressive coating of Pt was monitored by using the peak height ratios H_{1395}/H_{1580} for LG and H_{997}/H_{1073} for TP as spectral parameters displaying a large sensitivity to the surface coverage. On the other hand, the quenching of the Au NP SERS enhancement during the deposition process was followed by measuring the sums of the band height of the features at 1395 and 1580 cm^{-1} for LG ($H_{1395}+H_{1580}$) and at 997 and 1073 cm^{-1} for TP ($H_{997}+H_{1073}$).
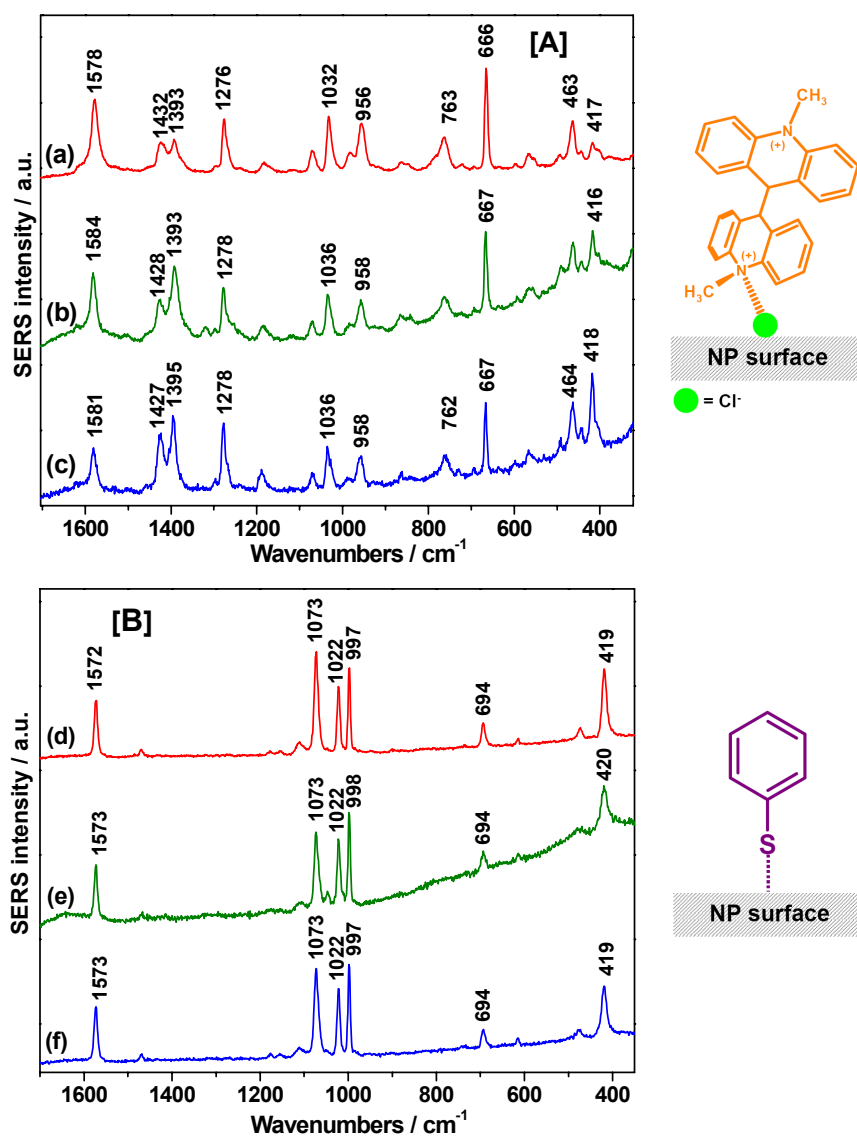
Figure S1. [A] SERS spectra of LG 10^{-5} M on (a) pure AuCT, (c) Au@Pt^0 (R= 0.27) and (o) Au@PtCl$_6$$^{2-}$ (R= 0.27). [B] SERS spectra of TP 10^{-5} M on (d) pure AuCT, (e) Au@Pt^0 (R= 0.27) and (f) Au@PtCl$_6$$^{2-}$ (R= 0.27).

Competitive adsorption of LG, TP and $PtCl_6^{2-}$ on Au NPs

The affinity of $PtCl_6^{2-}$ toward the gold surface was also investigated in competition with LG or TP molecule. Gold NPs pre-functionalized with TP and LG were added with an aliquot of $PtCl_6^{2-}$ solution (R=0.21) and the SERS spectral parameters H_{998}/H_{1073} for TP and H_{1395}/H_{1580} for LG were monitored over time, from t=0 to t=30 minutes (Fig. S2A). The results suggest that $PtCl_6^{2-}$ anions fully displaced the LG molecule from the gold surface in ca. 10-15 minutes after the platinum addition (the H_{1395}/H_{1580} ratio converges to the same value observed for LG added to preformed $Au@PtCl_6^{2-}$ substrate, R=0.21), whereas the initial TP spectral ratio maintained roughly the same value, indicating that the strong covalent –S-Au bond is not affected by $PtCl_6^{2-}$ addition (the scheme in Figure S2B outlines these two different processes). This interesting results highlight the extreme affinity of $PtCl_6^{2-}$ molecules for gold surfaces, which are not only capable of forming well-organized adlayer to the detriment of weakly adsorbed compounds as citrate anions, but also displace strong interacting LG probes.
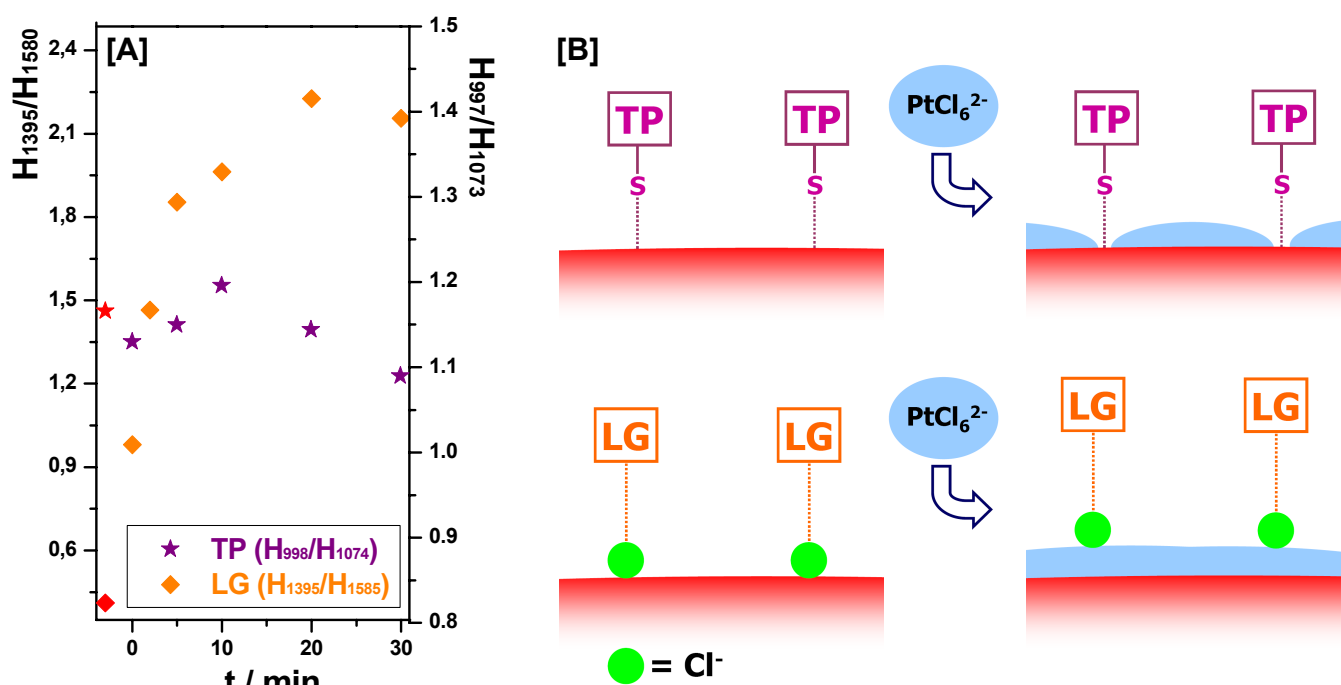
Figure S2. [A] Effect of $PtCl_6^{2-}$ addition to TP- and LG- functionalized Au NPs on the SERS spectral parameters H_{997}/H_{1073} (TP) and H_{1395}/H_{1580} (LG) over different time after the initial addition of the chloroplatinic solution (t=0, 2, 5, 10, 20 and 30 min). [C] Scheme of the suggested $PtCl_6^{2-}$ deposition mechanism on TP- and LG-functionalized Au NPs.

## Plasmon resonance spectra of Au@Pt bimetallic systems

The exact position of the plasmon band is extremely sensitive both to the particle geometry (size and shape) and to the optical and electronic properties of the medium surrounding the particles [5, 10]. Figure S3A and B show the Absorption spectra of Au@Pt^0 and Au@$PtCl_6^{2-}$ NPs, respectively, at different R. In the first case, the plasmon absorption of Au core is progressively damped (Fig. S3C) and slightly blue-shifted (Fig. S3D) as the Pt^0 shell becomes first complete and then thicker to such an extent that the plasmon absorption of the gold core becomes almost invisible and the total optical properties of the core-shell structure are now inferred solely by the Pt external shell [11-13]. By contrast, when aliquots of $PtCl_6^{2-}$ solution are added to the AuCT suspension without performing the reduction reaction, we observe a slight red-shift of the plasmon resonance as the platinum concentration is increased (Fig. S3D), whereas the absorption intensity looks poorly affected (Fig. S3C). Therefore, on the basis of the results shown in Figure S3, we suggest that when Pt is adsorbed as $PtCl_6^{2-}$ adlayer is electronically inert (i.e. it does not exchange charge with the gold particles) but still its refractive index differs from that of both water and gold. Thus, the $PtCl_6^{2-}$ deposition is not significantly reducing the intensity of the plasmon absorption but does induce a red-shift of the absorption maximum as a result of the increase of the refractive index around the particles [10].
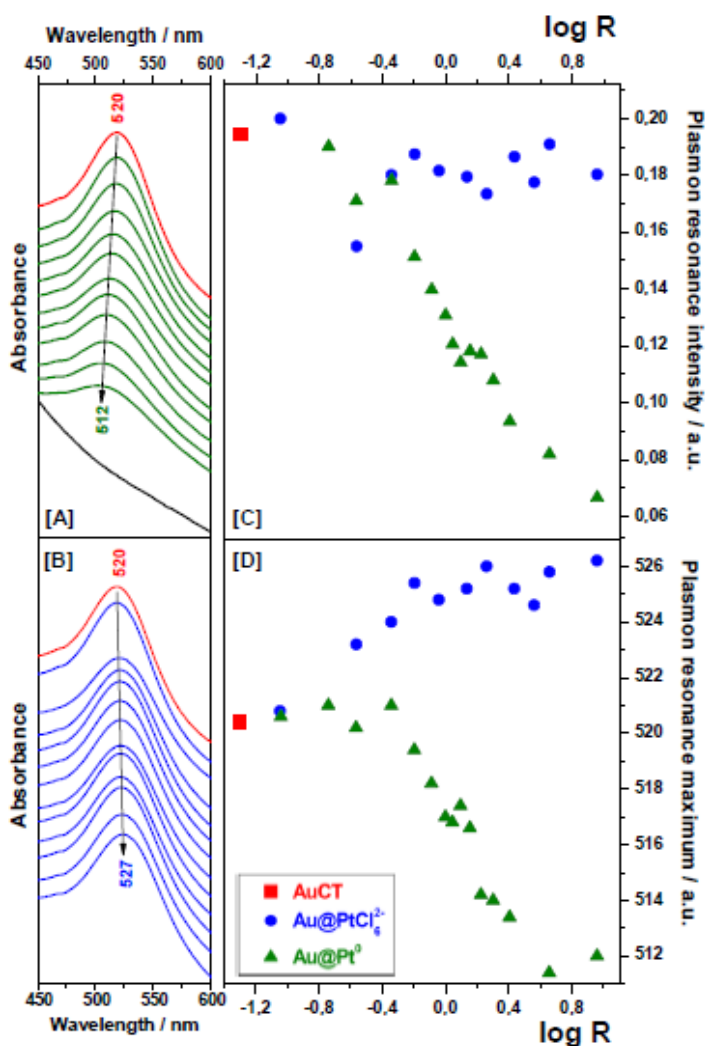
Figure S3. Absorption spectra of pure AuCT and mixed colloids ([A] Au@Pt^0 and [B] Au@$PtCl_6^{2-}$ colloids) at different ratios, R. The R value decreases from the top spectrum to the bottom spectrum. [C] Plasmon resonance intensity and [D] Plasmon resonance maximum (nm) at different ratios, R (logarithmic scale) for Au@Pt^0 and Au@$PtCl_6^{2-}$. The red dots correspond to the absorption values for pure AuCT colloid and are arbitrary placed in the graph at log R=-1.3.

Effect of time in the $PtCl_6^{2-}$ deposition on Au NPs

The formation of the $PtCl_6^{2-}$ adlayer is a competitive process which implies the adsorption of $PtCl_6^{2-}$ complexes on the gold surface to the detriment of previously adsorbed residual ions and molecular species resulting from the colloidal synthesis, as NO_3^-, Cl^- and citrate anions with its oxidation products [14]. Therefore, the deposition time is a critical experimental parameter to control which may affect the extension of $PtCl_6^{2-}$ self-assembled adlayer. The SERS spectra of LG and TP were acquired at different times after the $PtCl_6^{2-}$ addition to the gold colloid and the corresponding spectral parameters (Fig. S4, for R=0.21) show that LG spectrum requires ca. 5 minutes to reach a constant signal, whereas TP probe interaction is poorly affected by the time variable. As a result, all the $PtCl_6^{2-}$ deposition data presented in this article have been obtained by using 10 minutes aged $Au@PtCl_6^{2-}$ colloids.
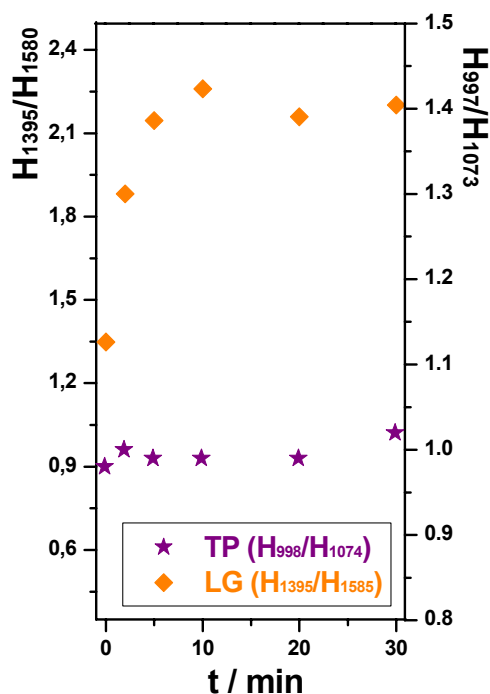
Figure S4. Values of spectral parameters H_{998}/H_{1073} (TP) and H_{1395}/H_{1580} (LG) acquired on $Au@PtCl_6^{2-}$ colloid (R=0.21) at different time after the initial addition of the $PtCl_6^{2-}$ solution to the bare Au NPs (t=0, 2, 5, 10, 20 and 30 min).

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