

Monomer Adsorption of Indocyanine Green to Gold Nanoparticles

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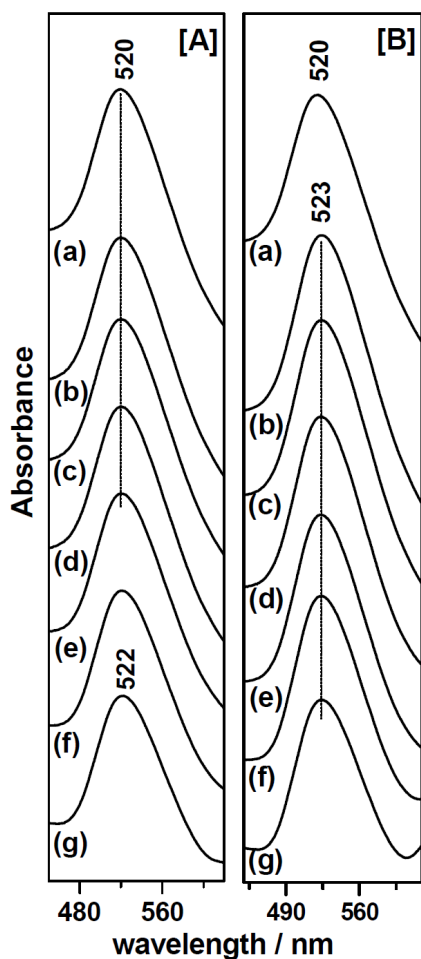


Figure S1. Detail of the low wavelength region of the ICG absorption spectra in [A] Br/GNP and [B] Br/Ag/GNP suspension at increasing dye concentration: (a) 0, (b) 7×10^{-6} M, (c) 1×10^{-5} M, (d) 1.5×10^{-5} M, (e) 2×10^{-5} M, (f) 3×10^{-5} M and (g) 5×10^{-5} M. The plasmon absorption band appearing at ~ 520 nm undergoes a slight red-shift only for very high ICG concentration ($> 5 \times 10^{-5}$ M). This shift is attributed to the change in refractive index resulting from the large dye adsorption on the gold surface and indicates the absence of GNP aggregation.

Figure S2. Absorption spectra of Citrate-capped gold NPs (AuCT) after the addition of different aliquots of KBr 0.5 M aqueous solution (the final bromide concentration in the colloidal suspension is reported in the figure). The extinction spectra of the gold NPs were monitored over 10 minutes after the bromide addition (experimental time scale). The results indicate that a final concentration of Br in the colloidal suspension of 10^{-3} M (2 μ L aliquot of the Br stock solution), corresponds to the highest halide concentration which does not produce significant NPs aggregation.

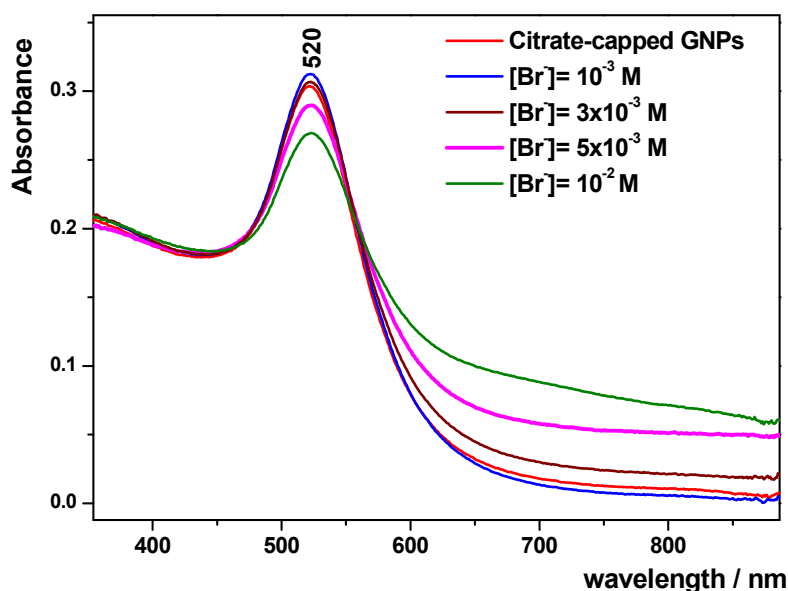


Figure S3. Extinction spectra of redispersed precipitate and supernatant of CTAB-capped Au NPs (CTA/Br/NPs) after 3 steps of centrifugation: (1) 12000 rpm for 30 minutes, (2) 12000 rpm for 30 minutes and (3) 12000 rpm for 20 minutes.

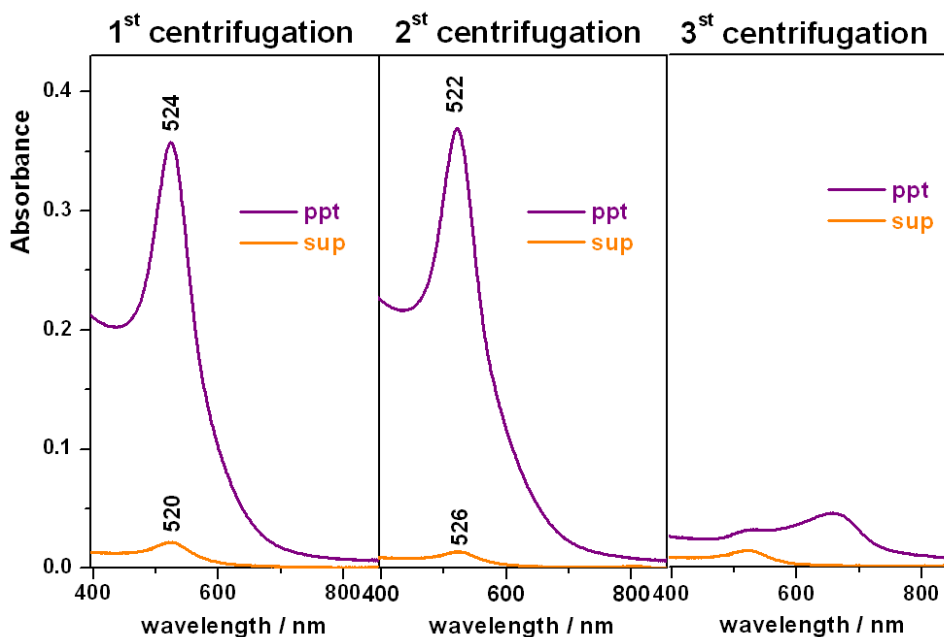
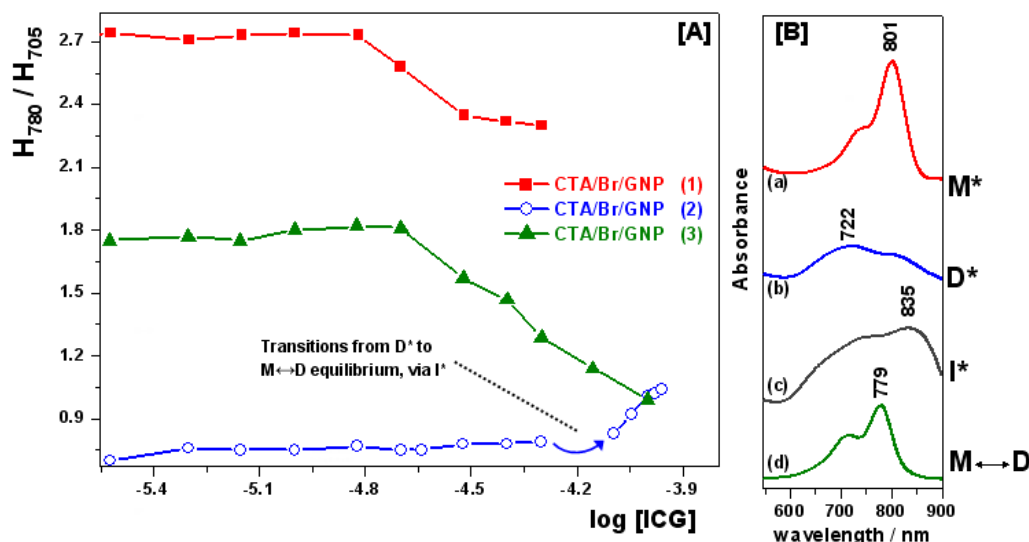


Figure S4. [A] Experimental values of the spectral parameter H_{780}/H_{705} for ICG in CTA/Br/NPs and CTA/Br/Ag/NPs colloids after (1), (2) and (3) centrifugation steps at different dye concentration (logarithmic scale). [B] Absorption spectra of ICG 3×10^{-5} M in (a) CTA/Br/GNPs (1), (b) CTA/Br/GNPs (2) and (d) CTA/Br/GNPs (3) colloids. (c) Absorption spectrum of ICG 7.8×10^{-5} M in CTA/Br/GNPs (2) colloid.



The results reported in Figure 4 suggest that the surfactant concentration in solution strongly affects the ICG state. Based on these findings, we capped citrate-gold NPs with a large excess of CTAB ($\gg \text{cmc}$) and performed several centrifugation steps in order to test the ICG adsorption at different surfactant concentrations, both in the bulk and at the metal-liquid interface (CTAB constantly exchanges from the bilayer at the metal-solvent interface to the solution). However, we cannot determine the exact surfactant concentration after each centrifugation.

Figure S3 shows that the first two centrifugation steps do not produce significant GNP aggregation, whereas the third one causes an irreversible assembly of metal nanoparticle into large cluster, also observed by the deposition of large amount of GNP at the bottom of the vial regardless of the time of centrifugation. This suggests a decrease of CTAB concentration at the metal-liquid interface induces the disruption of the surfactant double layer around the GNP leading to their irreversible aggregation. We labelled these CTAB-capped GNP suspensions as CTA/Br/GNP (1), CTA/Br/GNP (2) and CTA/Br/GNP (3), where the number into brackets refers to the centrifugation steps carried out on the colloidal system.

Absorption data (Figure S4) indicates that the dye exists as M^* in the CTA/Br/GNP (1), and as highly stabilized dimer D^* in CTA/Br/GNP (2). As previously observed for ICG in CTAB $50 \mu\text{M}$ salt solution (Figure 4), a transition from $D^* \rightarrow I^* \rightarrow M/D$ occurs when increasing the dye concentration. In the CTA/Br/GNP (3) system, ICG molecules exist in M and D forms at all dye concentrations but, again, the position of the $M \leftrightarrow D$ equilibrium is largely affected by the remaining surfactant molecules in the bulk solution. By comparison to the data illustrated in Figure 4, these results suggest that we progressively decrease the unbound CTAB amount in CTA/Br/GNP suspensions from surfactant concentration above cmc , to ~ 1 order of magnitude smaller and, finally, to ~ 2 order of magnitude smaller after each step of centrifugations, respectively. On the whole, the ICG behaviour in CTAB solution (Figure 4) and in CTA/Br/GNP suspensions (Figure S4) is very similar. This seems to indicate that the optical properties of ICG molecules are largely determined by the unbound surfactant molecules in the bulk solution rather than by the interaction with the metal surface, even though it is not possible to separate these two effects.