SUPPLEMENTARY INFORMATION

Silver Colloids as Plasmonic Substrates for Direct Labelfree Surface-enhanced Raman Scattering Analysis of DNA

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Figure S1. (A) Normalized extinction spectra of AgCit, AgHX and AgSp colloids. The pH of the colloids is 6.5, 7.3, and 6.1, respectively. The ζ potential values are -40.7 ± 1.1 mV; -38.5 ± 0.9 mV; and +43 ± 1.1 mV. (B-D) Histograms of nanoparticle size distribution and representative TEM images of the dried (B) AgSp (30 ± 6 nm), (C) AgCit (75 ± 10 nm) and (D) AgHX (29 ± 5 nm) colloids.



Figure S2. SERS spectra obtained by aggregating each of the colloids with addition of (A) MgSO₄ solution (0.1 M) or (B) SpCl₄ solution (0.1 M). Upon addition of SpCl₄, citrate molecules are displaced from the surface of AgCit nanoparticles by the chloride anions as revealed by the SERS (the citrate features in **Fig. S2A** disappear while the new intense v(AgCl) band arises at low wavenumbers in **Fig. S2B**). On the other hand, chloride anions are not capable of removing bromide and iodide anions from the metal surface. Only a week shoulder at ca. 240 cm⁻¹ is visible in the SERS spectra of AgCit@Br upon aggregation with SpCl₄ solution, while the SERS background of AgCit@I remains completely unvaried.



Figure S3. Normalized extinction spectra of AgCit before and after the functionalization with halide anions: (A) AgCit@CI, (B) AgCit@Br and (C) AgCit@I. The spectra of the halide-modified colloids were acquired after (i) 30 minutes and (ii) overnight aging, from the incubation with KCI, KBr and KI solutions.



Figure S4. SERS spectra of pC on AgSp, AgHX (pH 7.3) either aggregated with MgSO₄ or SpCl₄, and AgHX (pH 3.5) aggregated with MgSO₄. Final pC concentration in the samples 1 μ M. Inset: molecular structure of the Cytosine base (R= H) and its corresponding pKa. ^{1, 2}.



Figure S5. SERS spectra of pA on AgSp, AgHX (pH 7.3) either aggregated with MgSO₄ or SpCl₄, and AgHX (pH 3.5) aggregated with MgSO₄. Final pA concentration in the samples 1 μ M. Inset: molecular structure of the Adenine base (R= H) and its corresponding pKa.³



Figure S6. SERS spectra of single and double-stranded DNAs on silver colloids. For the sake of comparison, the spectra were normalized to the PO_2^- stretching at ca. 1089 cm⁻¹. The final ssDNA and dsDNA concentrations were kept constant to 1 μ M.

References

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