Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Understanding and Improving Aggregated Gold Nanoparticles/dsDNA Interactions by Molecular Spectroscopy and Deconvolution Methods

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Determination of the concentration of AuNPs.

The mean number of Au atoms in a particle, *n*, can be calculated using Eq. 1:[1]

$$n = \frac{0.5\pi N_A d_m}{3V_m} \quad (1)$$

In the above equation, which assumes a spherical particle shape, N_A is Avogadro's number, d_m is the diameter of the nanoparticle expressed in cm and V_m is the molar volume of bulk gold (10.215 cm^3).[1] As the concentration of Au atoms is known from the reaction conditions, nanoparticle concentration can be easily obtained. Taking the average diameter of the AuNPs obtained from TEM measurements as 14.8 nm and considering that the reduction from gold (III) to gold atom was 100% complete, the AuNPs concentration was estimated at 3.3 $x10^{-9}$ M.

Estimation of dsDNA molecular weight.

According to bibliography, a solution of dsDNA with a concentration of 50 μg/ml has an absorbance of 1.[2] On the other hand, the absorption coefficient for *calf thymus* DNA is 6600 $M^{-1}\cdot cm^{-1}$ at 258 nm (concentration expressed in phosphate groups); when converted to DNA base pairs, the average molar absorption coefficient is 13200 $M^{-1}\cdot cm^{-1}$ at 258 nm. If these data are introduced in Lambert-Beer's law, it is possible to obtain the estimated molecular weight of *calf thymus* DNA: ~ 662 $g\cdot mol^{-1}$.

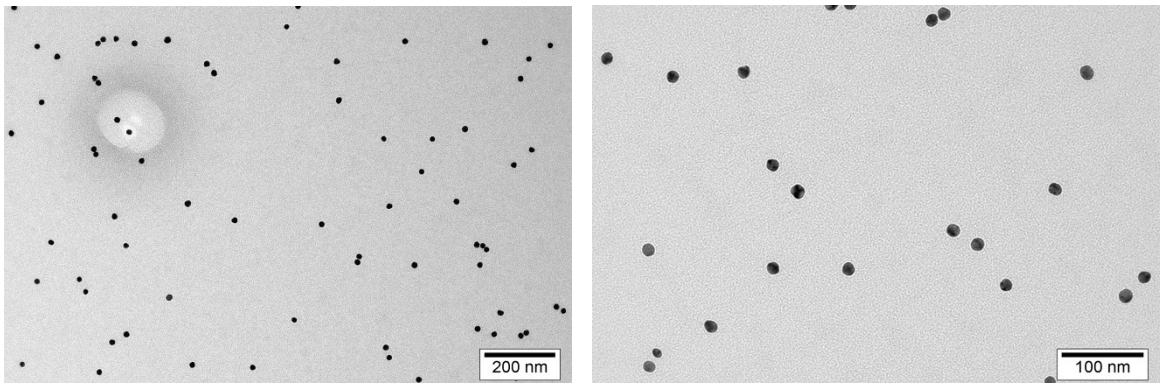


Figure S1. Examples of TEM images of AuNPs in water ([AuNPs] = 3.3×10^{-10} M) for the calculation of the average size of the colloidal system.

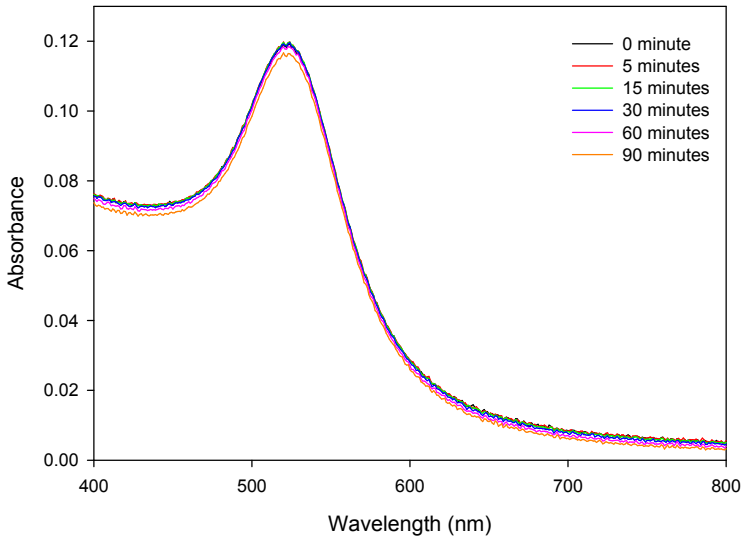


Figure S2. Time stability of UV-Vis absorption spectra of AuNPs at [DNA] = 10^{-3} M and [AuNPs] = 3.3×10^{-10} M, which corresponds to a ratio [AuNPs]/[DNA] = 3.3×10^{-7}. The same behavior is observed for the other samples with lower DNA concentrations.

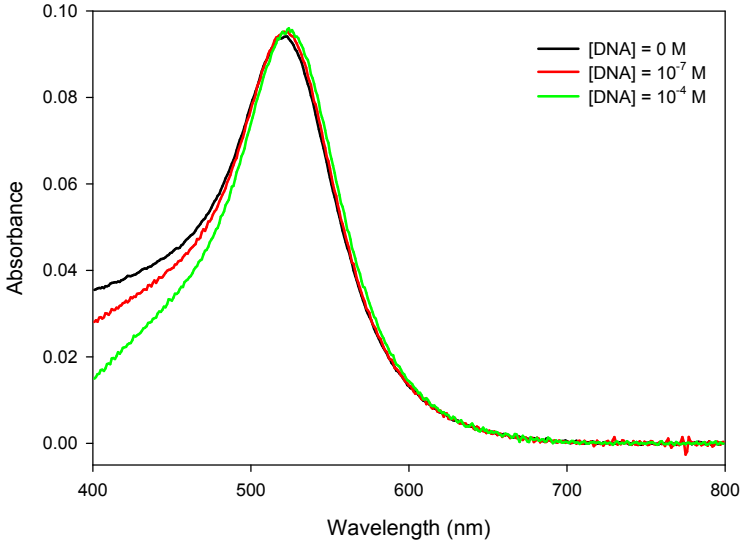


Figure S3. Absorbance spectra of AuNPs in presence of different dsDNA concentrations. Light scattering contribution has been corrected according to Leach and Scheraga's method.[3] [AuNPs] = 3.3 x 10^{-10} M.

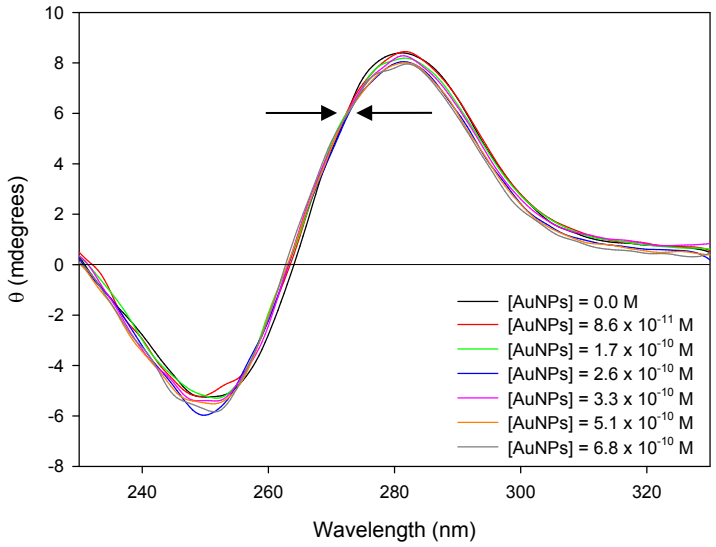


Figure S4. CD spectra of calf thymus dsDNA at different concentrations of AuNPs. The arrows mark the isosbestic point at 272 nm. [DNA] = 10^{-4} M. [AuNPs] = 0.0 – 6.8 x 10^{-10} M.

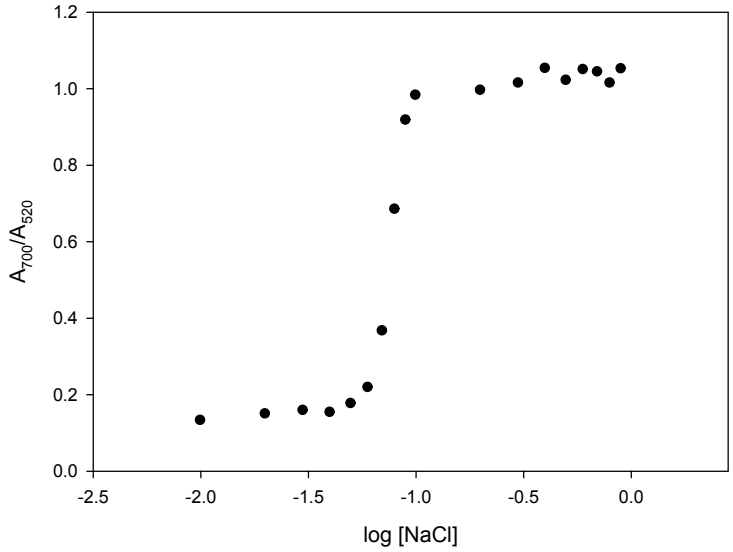


Figure S5. Evolution of aggregation degree (A_{700}/A_{520}) with increasing NaCl concentration at [AuNPs] = 3.3 x 10^{-10} M. The absorption data (A_{700} and A_{520}) are taken 10 minutes after the addition of salt to the gold colloids.

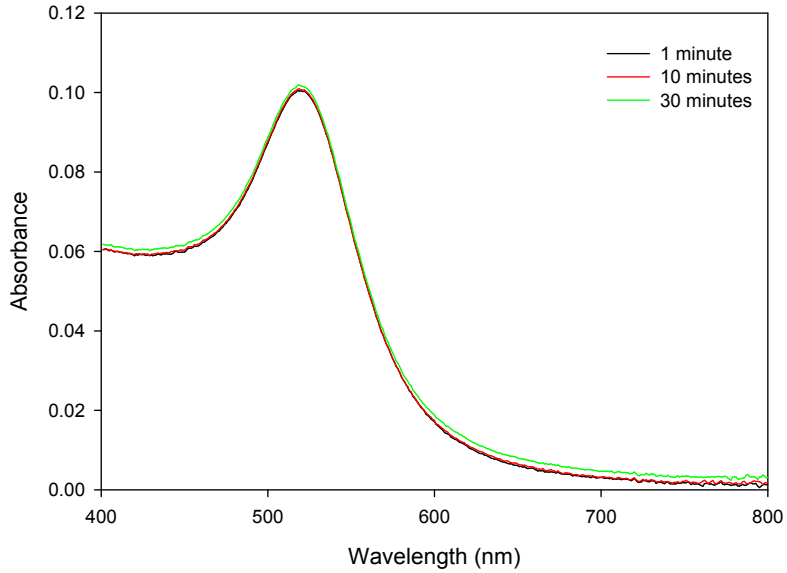


Figure S6. Evolution of the absorption spectrum of AuNPs in a mixture of cacodylate buffer (0.001 M) and NaCl (0.01 M) with time. [AuNPs] = 3.3 x 10^{-10} M.

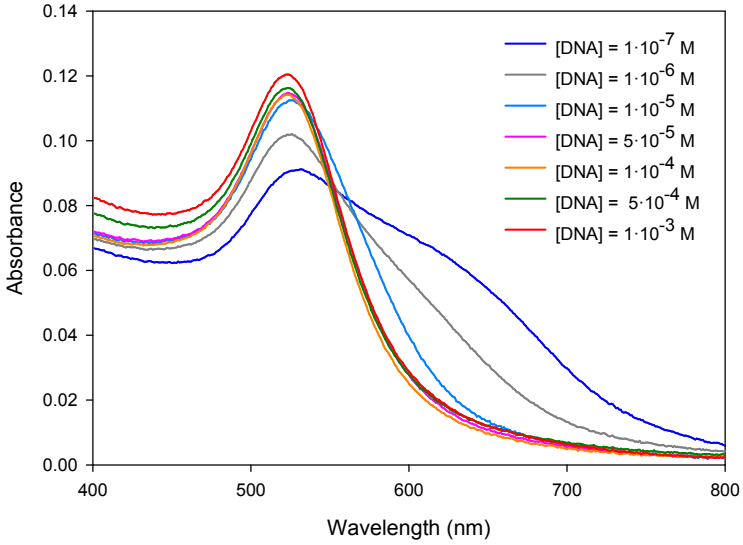


Figure S7. UV-Vis absorption spectra of AuNPs (3.3 x 10^{-10} M) in the presence of different dsDNA concentrations with [Na^+] = 0.075 M. The spectra have been obtained 30 minutes after adding the salt to the AuNPs-DNA solution.

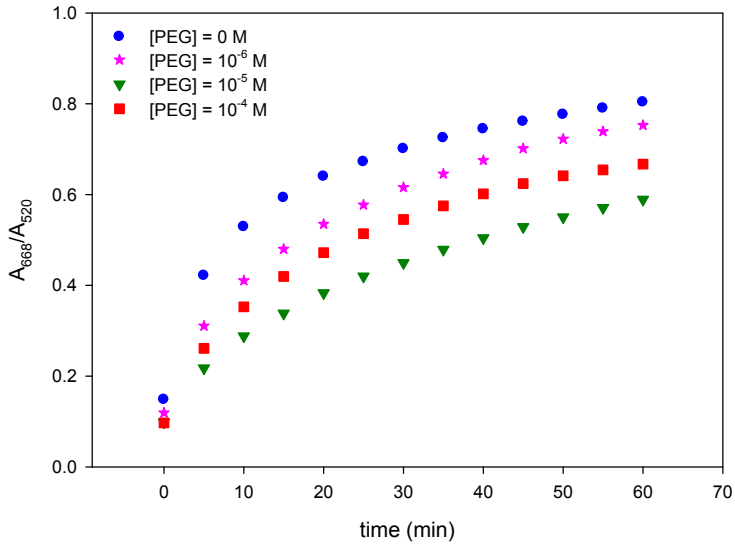


Figure S8. Evolution of A_{668}/A_{520} ratios with the time, where A_{668} is the absorption data at 668 nm and A_{520} at 520 nm. The blue circles correspond to [PEG] = 0 M; pink stars correspond to [PEG] = 10^{-6} M; inverted green triangles correspond to [PEG] = 10^{-5} M; and red squares correspond to [PEG] = 10^{-4} M.

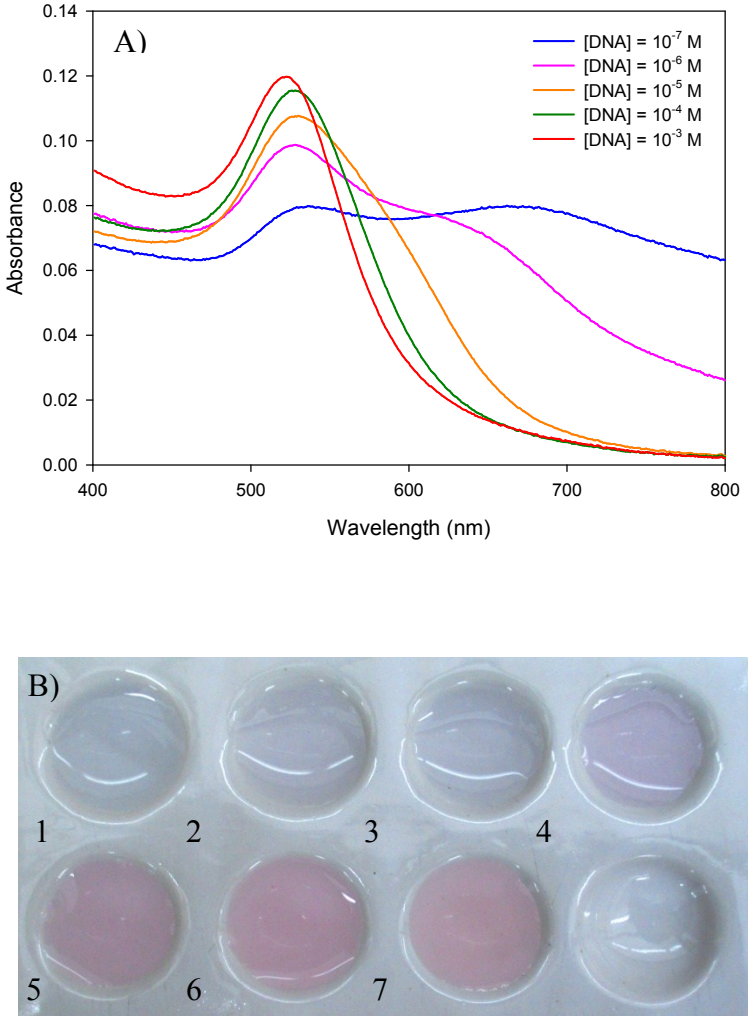
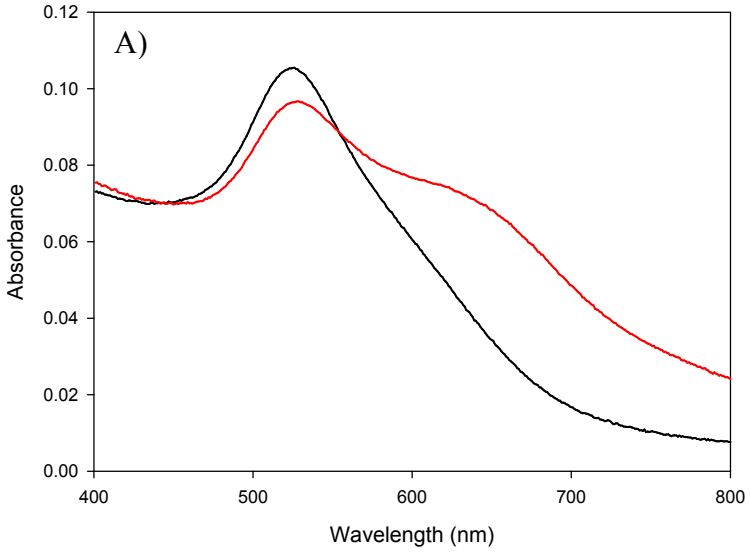
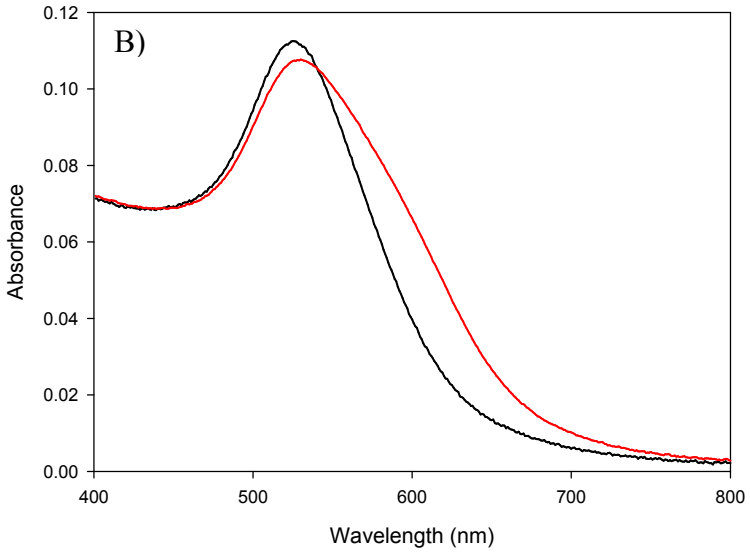
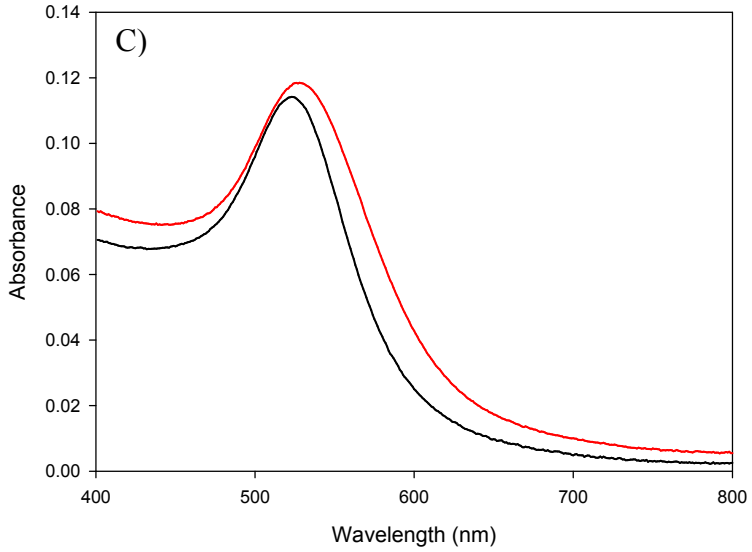


Figure S9. A) UV-Vis absorption spectra of AuNPs (3.3 x 10^{-10} M) obtained for solutions of DNA and NaCl, at [Na^+] = 0.075 M and varying concentrations of DNA. The spectra have been obtained 30 minutes after salt addition to the AuNPs-DNA solutions. B) Photographs of the different samples obtained by following Method C for [AuNPs] = 3.3 x 10^{-10} M. Each square except number 7 has [Na^+] = 0.075 M and different DNA concentrations: 1) [DNA] = 0 M; 2) [DNA] = 10^{-7} M; 3) [DNA] = 10^{-6} M; 4) [DNA] = 10^{-5} M; 5) [DNA] = 10^{-4} M; 6) [DNA] = 10^{-3} M; 7) [DNA] = 0 M, [Na^+] = 0 M.


A)
Absorbance
Wavelength (nm)
0.00
0.02
0.04
0.06
0.08
0.10
0.12
400
500
600
700
800


B)
Absorbance
Wavelength (nm)
0.00
0.02
0.04
0.06
0.08
0.10
0.12
400
500
600
700
800



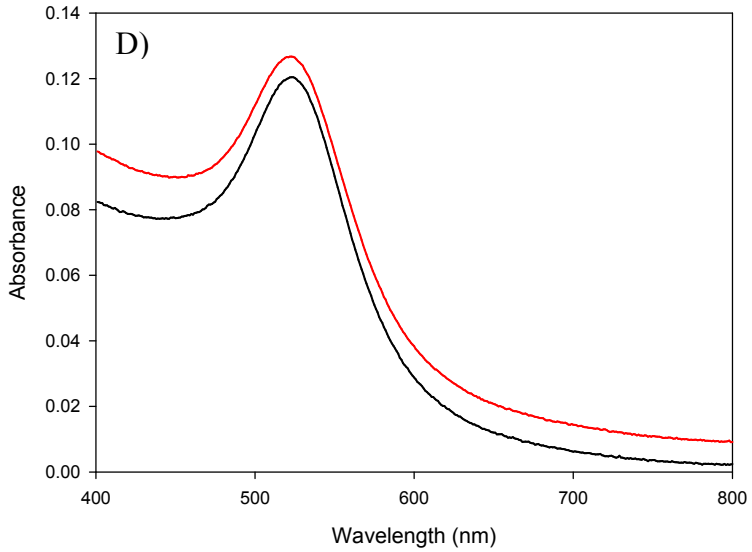


Figure S10. Comparative of the absorption spectra obtained by the Method A (black line) and the Method C (red line) for [AuNP] = 3.3 x 10^{-10} M, [Na^+] = 0.075 M. The DNA concentrations are: A) 10^{-6} M; B) 10^{-5} M; C) 10^{-4} M; D) 10^{-3} M. All spectra are obtained 30 minutes after mixing.

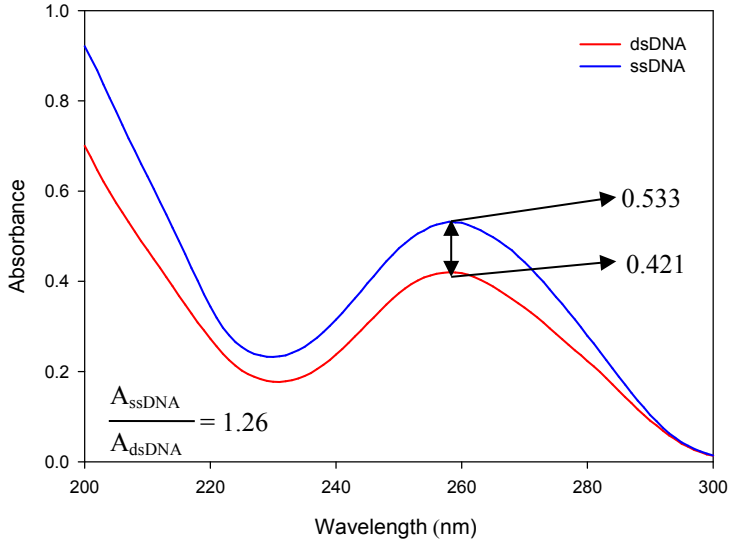


Figure S11. UV absorption spectra of dsDNA (red line) and of ssDNA (blue line), both with the same concentration. This comparative shows that ssDNA was obtained from dsDNA, since single stranded DNA has a higher absorption coefficient than double stranded DNA. A solution of dsDNA with a concentration of 50 μg/ml has an absorbance of 1, while a solution of ssDNA with a concentration of 40 μg/ml also shows an absorbance of 1.[2] Therefore, the ssDNA/dsDNA ratio of absorbance at the maximum wavelength is 1.25. Absorbance from experimental measurements shows a 1.26 ratio, confirming the presence of ssDNA.

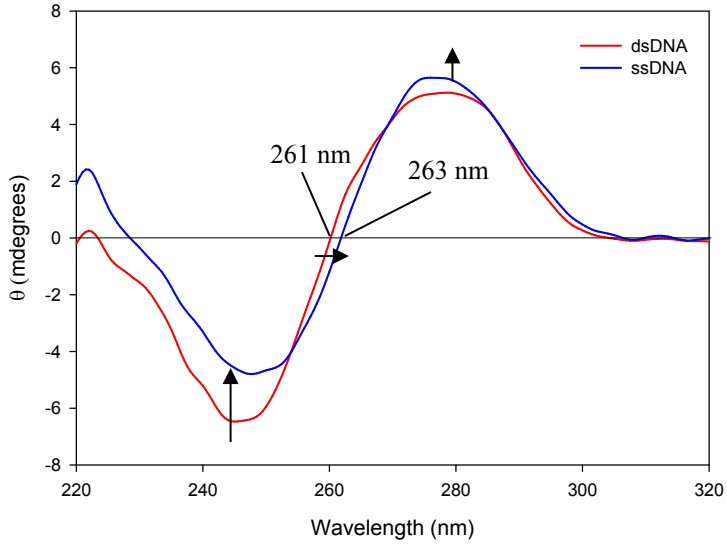
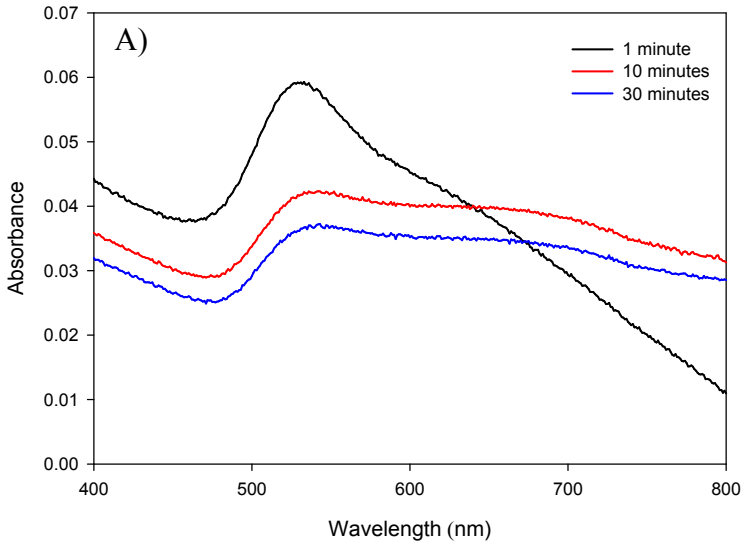
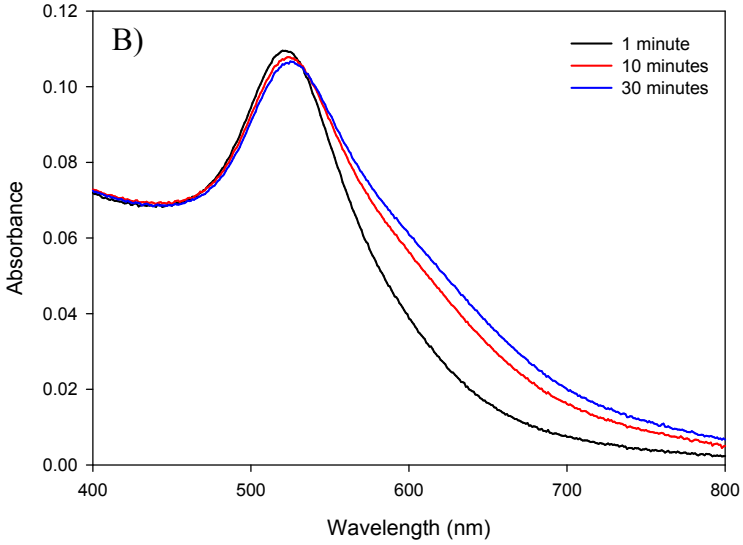
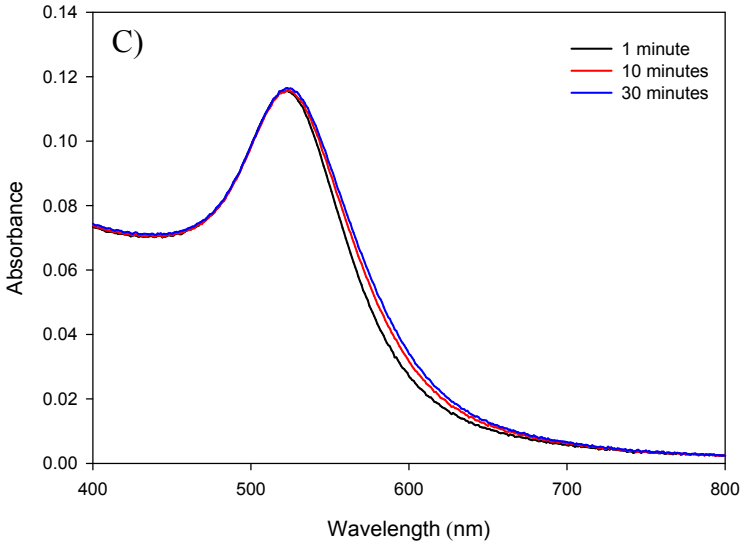


Figure S12. CD spectra of dsDNA (red line) and ssDNA (blue line), both with the same concentration. Dias and colleagues observed shifts in CD spectra when the dsDNA became single stranded: the negative band decreases while the positive band grows, and the crossover point advances 3 nm.[4] In our case, with different experimental conditions, the displacement was 2 nm.




B)
1 minute
10 minutes
30 minutes
Absorbance
Wavelength (nm)
0.12
0.10
0.08
0.06
0.04
0.02
0.00
400
500
600
700
800


C)
1 minute
10 minutes
30 minutes
Absorbance
Wavelength (nm)
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0.12
0.10
0.08
0.06
0.04
0.02
0.00
400
500
600
700
800

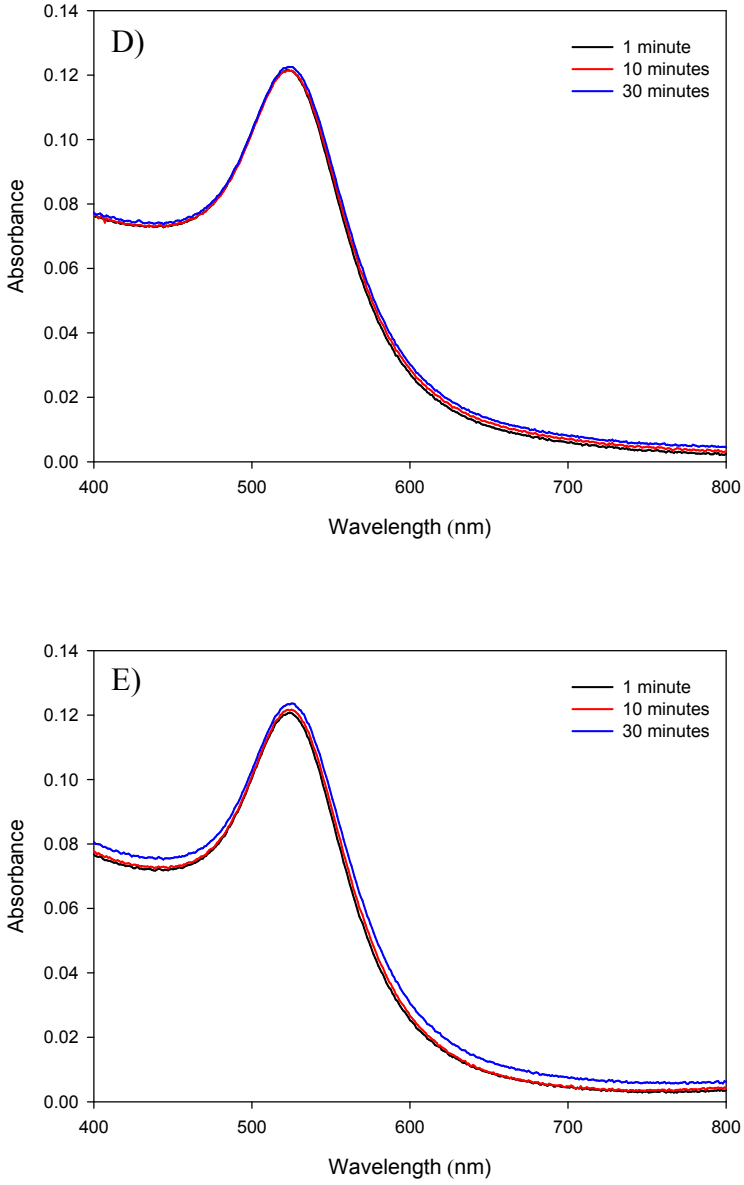

Figure S13. Time evolution of UV-Vis absorption spectra of AuNPs at [AuNPs] = 3.3 x 10^{-10} M, [Na^+] = 0.075 M. The ssDNA concentrations are: A) 10^{-7} M; B) 10^{-6} M; C) 10^{-5} M; D) 10^{-4} M; D) 10^{-3} M. Solutions were prepared following method A.

References

(1) Cumberland, S. L.; Strouse, G. F. Analysis of the Nature of Oxyanion Adsorption on Gold Nanomaterial Surfaces. *Langmuir* **2002**, *18* (1), 269–276.

(2) Sambrook, J.; Fritsch, E. F. F.; Maniatis, T. *Molecular Cloning: A Laboratory Manual*; Cold Spring Harbor Laboratory Press: New York, 1989.

(3) Leach, S. J.; Scheraga, H. A. Effect of Light Scattering on Ultraviolet Difference Spectral. *J. Am. Chem. Soc. Soc* **1960**, *82* (6), 4790–4792.

(4) Rosa, M.; Dias, R.; da Graça Miguel, M.; Lindman, B. DNA - Cationic Surfactant Interactions Are Different for Double- and Single-Stranded DNA. *Biomacromolecules* **2005**, *6*, 2164–2171.