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

Supporting Information: DNA Capping Agent Control of Electron Transfer from Silver Nanoparticles

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Chemical Reagents

DNA (low molecular weight (approximately 2000 bp) from salmon sperm, Sigma Aldrich), silver nanoparticles (nominally 50 nm in diameter, Nanocomposix, San Diego, USA), sodium nitrate ($\geq$ 99.0 %, Sigma Aldrich), and hydrochloric acid (reagent grade, 37%, Sigma Aldrich) were used as received. Where water is referred to, ultrapure water from Millipore with resistivity not less than 18.2 M Ωcm at 25 °C was used.

Nanoparticle Modification

A stock solution of DNA was prepared by dissolving 3.4 mg of solid in 1 mL of water. 20 μL of this solution was then combined with 200 μL of commercially sourced (from Nanocomposix, Dan Diego) citrate nanoparticles, shaken, and left overnight. Once the nanoparticles were successfully recapped (as evidenced by UV-Vis spectrophotometry, as detailed below), they were washed twice by being placed in a centrifuge at 14,000 rpm for one hour, whereby the supernatant was removed and replaced with fresh deionised water.

Transmission Electron Microscopy

Silver nanoparticle characterisation was performed by Transmission Electron Microscopy (TEM), using a JEOL JEM-3000F instrument with an accelerating voltage of 300 kV. Sample preparation consisted of drop casting silver NP suspensions on holey carbon grids (Agar Scientific) and allowing to dry. A total of 100 nanoparticles of each capping agent material were then sized using ImageJ software. The data analysis to gain the size distributions was performed in Origin 2015.

Dynamic Light Scattering

DLS measurements were undertaken using a Malvern Zetasizer Nano ZS (Malvern, Herrenberg, Germany) instrument, which was equipped with a 633 nm He-Ne laser and operated at an angle of 173 degrees. The software used for data analysis and correlation function fitting was the Zetasizer Software from Malvern. 500 μL of each sample was transferred to single-use polystyrene half-microcuvettes with a specified path length of 10 mm. The measurements were made under thermostated conditions at 25 °C and an equilibration time of 120 seconds prior to the beginning of the measurements. Runs of 10 s were performed, with three repeats. The Z-average diameter (Z-ave), and the polydispersity index (PdI) were obtained from the autocorrelation function using the general purpose mode algorithm. In this work we used General Purpose non-negative

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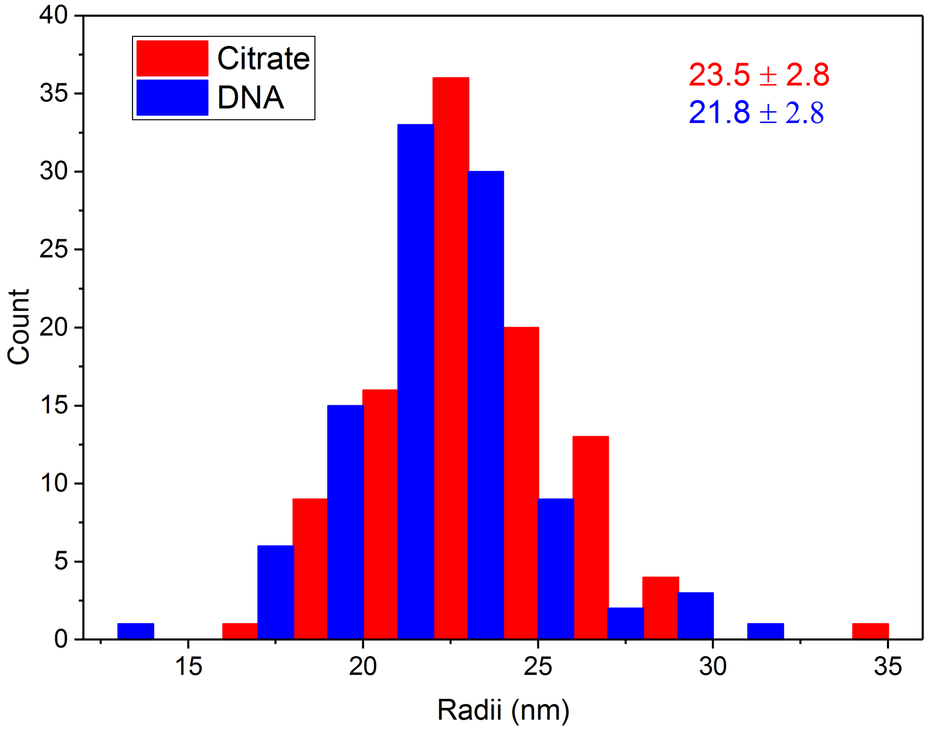

Figure S1: Sizing histrogram of the radii of citrate capped (red) and DNA capped (blue) silver nanoparticles from TEM.

least-squares (NNLS) analysis in order to gain the size distributions as it is widely available and commonly used for sizing purposes.

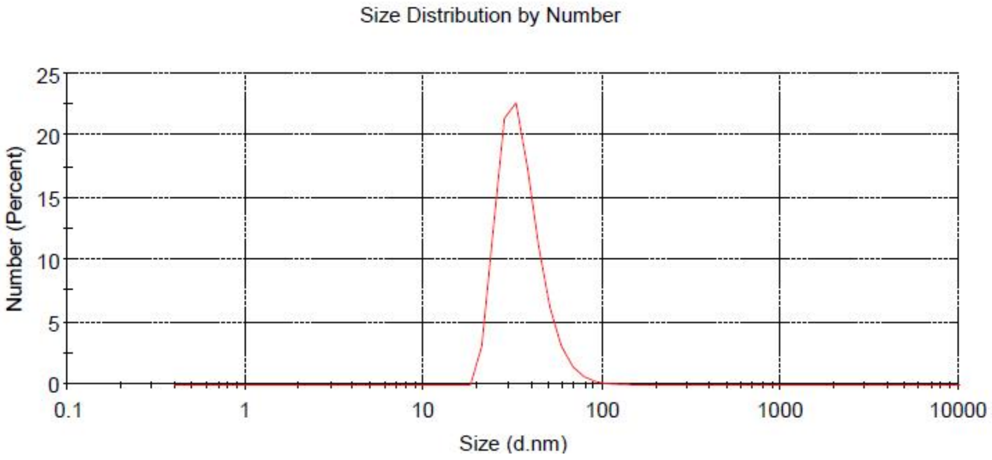

Figure S2: Size distribution for citrate capped nanoparticles from DLS.

Measurement	Z-average (nm)
1	60.49
2	59.99
3	59.88

Table 1: Z-averages of the hydrodynamic diameter of the citrate capped nanoparticles from DLS.

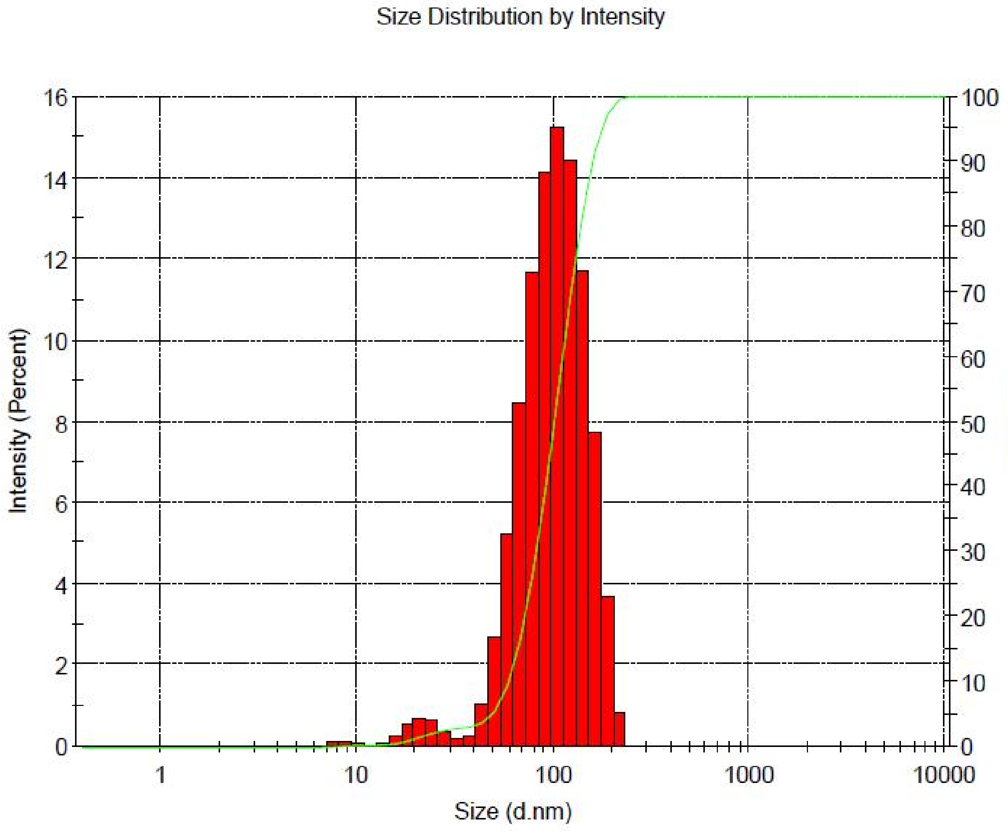

Figure S3: Size distribution for DNA modified nanoparticles from DLS.

Measurement	Z-average (nm)
1	160.4
2	163.4
3	159.2

Table 2: Z-averages of the hydrodynamic diameter of the DNA modified nanoparticles from DLS.

Zeta Potential

Zeta potential measurements were performed using a Malvern Zetasizer Nano ZS system with an irradiation wavelength of 633 nm laser source. The samples were filled in folded capillary cells and measured. The measurements were repeated six times and an average value reported.

For data processing ‘general purpose (normal resolution)’ option was selected and used for all measurements using Malvern Zetasizer software.

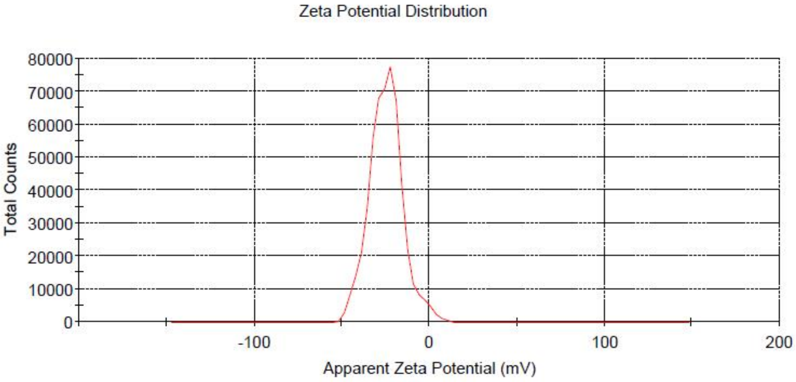

Figure S4: Representative zeta potential distribution of citrate capped nanoparticles

Measurement	Zeta potential (mV)
1	-22.0
2	-24.6
3	-22.3

Table 3: Zeta potentials measuring the charge on the citrate capped nanoparticles.

Measurement	Zeta potential (mV)
1	-19.6
2	-12.9
3	-14.1
4	-19.6
5	-18.2
6	-16.7

Table 4: Zeta potentials measuring the charge on the DNA modified nanoparticles.

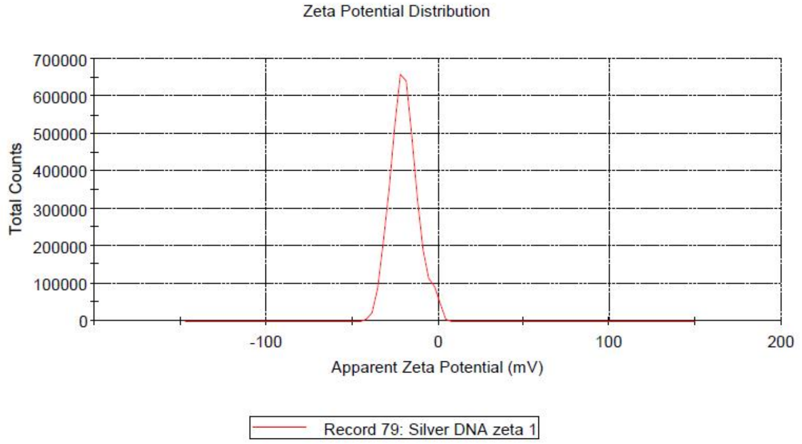

Figure S5: Representative zeta potential distribution of DNA capped nanoparticles

UV-Vis Spectroscopy

UV-Vis spectrophotometry was recorded on a Shimadzu UV-1800 using 50 μL High Precision Quartz Cells (Hellma Analytics, Germany). In all cases, a baseline correction was performed with empty cells inside the instrument prior to measurement, and the absorbance was recorded from 800 – 250 nm. Each sample was diluted prior to analysis by combining 25 μL of the nanoparticle solution with 50 μL of water, and water was used as the reference solvent. For the acid degradation experiments, 2 μL of 0.1M HCl was added, and measurements were recorded immediately afterwards, and then at various time points up until the disappearance of the peak at *ca.* 420 nm.

Electrochemical Apparatus

Cyclic voltammetry was undertaken using a μ-Autolab potentiostat (Eco-Chemie, Netherlands), whilst the chronoamperograms were conducted using a low noise potentiostat that was built in-house and has been described in full previously.[1, 2] Note that the analogue filters used within a potentiostat alter the original signal, and the transfer function of the circuitry may alter both shape and charge of the spikes output, making deliberate choice of the type of filter used essential. Both Bessel and Butterworth filters have been shown to accurately conserve the charge passed despite an alteration in the spike shape,[3, 4] and thus in this work the potentiostat used makes use of a low bandwidth Bessel filter. All experiments were conducted inside a temperature controlled Faraday cage.[5] For the dropcasting and solution phase experiments, the working electrode, a glassy carbon macroelectrode (1.5 x 10^{-3} m radius, BASi Analytical, USA), was polished prior to use on white lapping pads with diamond spray (3.0, 1.0, 0.1 μm, three minutes on each size from Kemet, Kent, UK). An Ag wire was used as a pseudo-reference electrode, and a 0.5 mm platinum wire was used as a counter electrode, and all three electrodes were immersed in a 20 mM sodium nitrate solution. For the nano-impact experiments, the working carbon microdisc electrode (IJ Cambria Scientific Ltd, UK), 33 μm, was polished prior to use using a water-alumina slurry (1, 0.3, 0.05 μm, five minutes on each grade) on soft lapping pads (Buehler, Illinois).[6] A 0.5 mm silver wire was used both as a counter and a quasi-reference electrode in all of the impact experiments. The electrodes were immersed into a 10 mM sodium nitrate solution with 2.4 ×

10^{-8} mol m^{-3} Ag NPs (blank shown below).

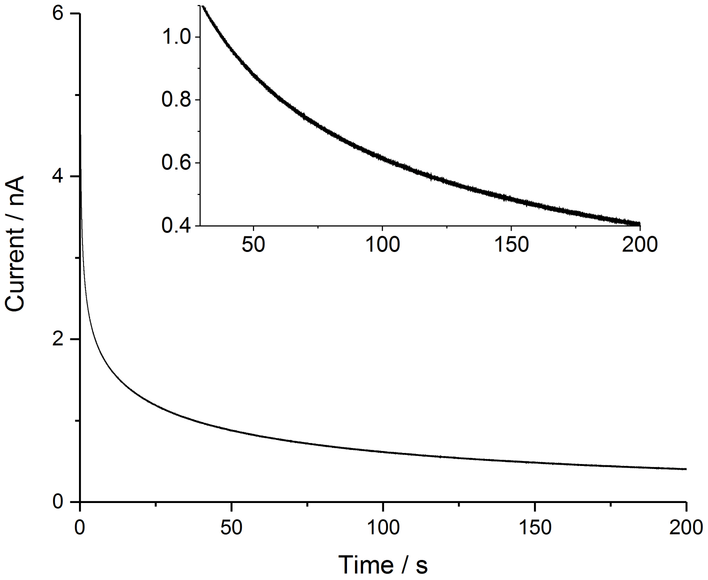

Figure S6: Chronoamperogram recorded in 20 mM sodium nitrate at 1.1 V vs Ag in the absence of nanoparticles.

References

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