Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Experimental

Chemicals

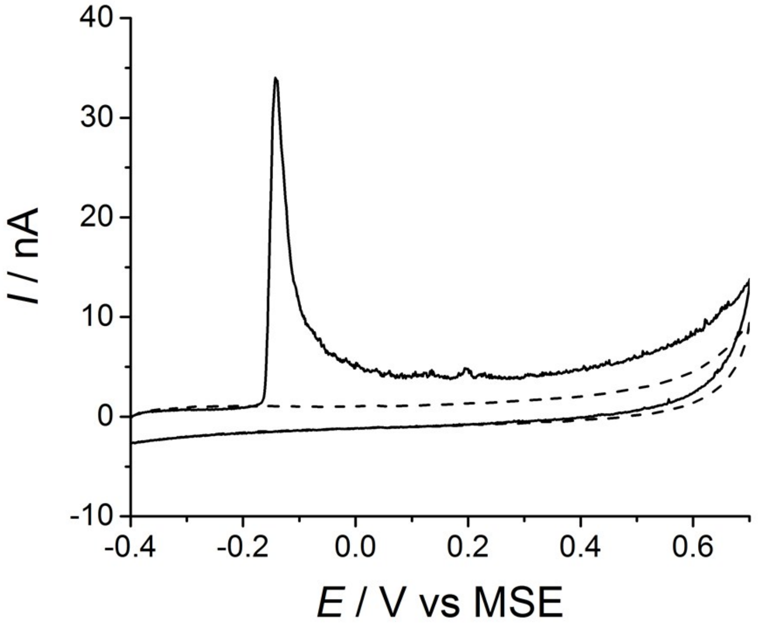
For nanoparticle (NP) synthesis, nanopure water from Alfa Aesar (ultrapure, spectrometric grade) was used for all dilutions. Sodium borohydride ($NaBH_4$, general purpose grade) was purchased from Fisher and tri sodium citrate (analR grade, 99.0 %) was obtained from BDH Chemicals Sigma Aldrich supplied silver nitrate ($AgNO_3$, ≥99.0 %) and bis (p-sulfonatophenyl) phenylphosphine dehydrate dipotassium (BSPP, 97 %) for synthesis and potassium nitrate (KNO_3, anal grade) for electrochemical experiments. For electrolyte dilutions, Millipore water of resistivity 18.2 MΩ.cm was used.

Analytical Equipment and Methods

UV-Vis studies were performed in 2 mm width quartz cells using a UV-1800 SHIMADZU UV spectrophotometer. Bulb transition was set to 300 nm, with 1 nm sampling frequency. Samples for TEM were drop-casted on to holey carbon TEM grids. Imaging was performed using a 300 kV JEOL 3000F microscope.

Nano-impact voltammetry was conducted using a three-electrode system consisting of a carbon fibre microelectrode encased in glass (BASi, USA) as the working electrode, a mercury-mercury sulphate reference electrode (MSE, equiv. to +0.64 V vs normal hydrogen electrode) (BASi, USA) and a platinum wire (Goodfellow Ltd., UK) as the counter electrode. Stripping voltammetry was conducted using the same reference and counter, however with a carbon fibre wire electrode, prepared as previously reported[1]. The potential was controlled by an in-house built low noise potentiostat[2] to allow low noise measurements. The measured electrical noise of the potentiostat was 2 pA. Due to the inherent noise a minimum charge of 3 fC per particle could be detected corresponding to a spherical particle of approximately 7 nm diameter; smaller particles are not visible. All electrochemical experiments were performed without degassing as this was found to induce aggregation of the prisms. The temperature was maintained at 25 ^{o}C through use of a thermo-regulated Faraday cage.

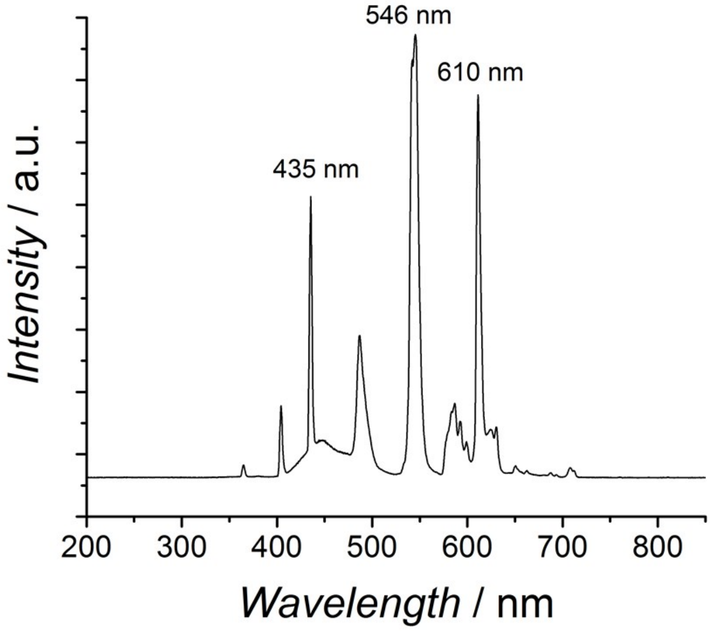
The potential for nano-impact voltammetry was determined by absorptive stripping voltammetry of the seed silver particles. A carbon fibre wire electrode was immersed into a suspension of 20 times diluted NP stock solution in 40 mM KNO_3 for 15 mins. This was then placed into a fresh solution of 40 mm KNO_3 and the adsorbed Ag stripped voltammetrically at 250 mVs^{-1}. The resultant voltammetry can be seen in SI 1. A clear silver stripping peak can be observed at -0.14 V vs MSE. Therefore, to ensure oxidation of the nano-prisms during nano-impact analysis, an overpotential of +0.40 V vs MSE was used throughout.



SI 1. Cyclic voltammetry on carbon fibre wire electrode in 40 mM KNO_3 at 250 mVs^{-1}. (Solid line) After 15 min immersion in 20 times diluted NP stock in 40 mM KNO_3. (Dashed line) Bare electrode.

Nano-prism Synthesis

The method used for prism synthesis was as previously reported[3], but with a 18 Watt fluorescent tube light source. The emission spectrum was measured using an Ocean Optics 2000 UV-Vis spectrometer, and is shown in SI 2.

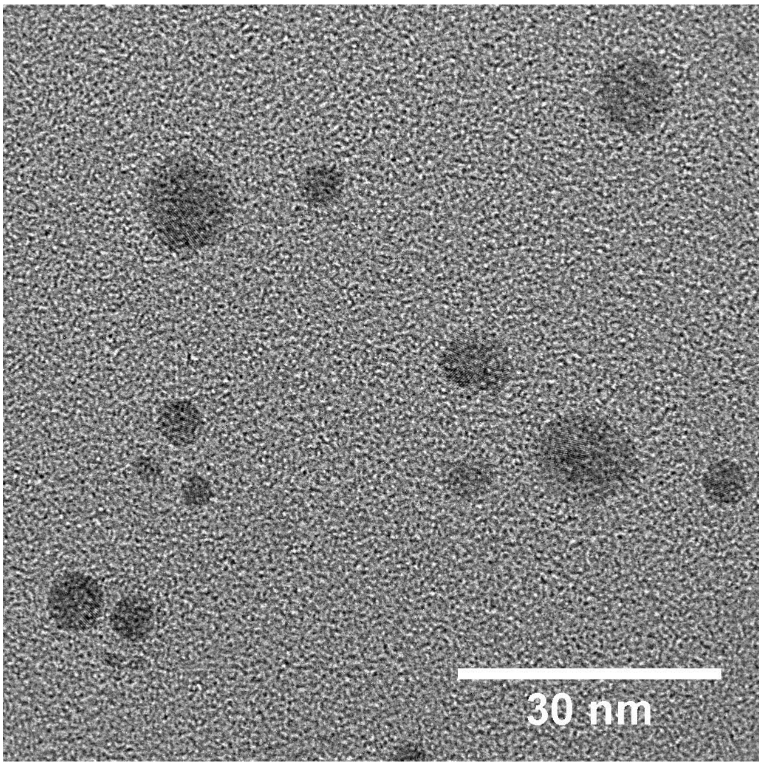


SI 2. Emission spectrum of fluorescent tube light source.

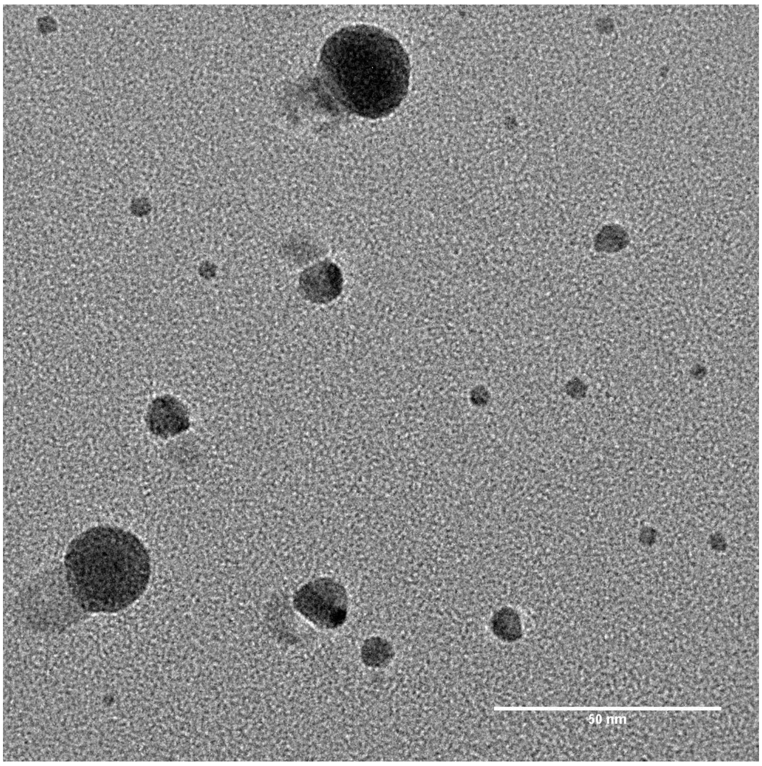
A 250 mL conical flask containing 95 mL nanopure water, 1 mL 30 mM trisodium citrate and 2 mL 5 mM $AgNO_3$ was emerged in an ice bath and bubbled with N_2 for 30 mins. After this, 1 mL 50 mM $NaBH_4$ was added under vigorous stirring, induced by magnetic stirrer, to begin the initial reduction. Over the next 16 mins, 4 drops of the $NaBH_4$ solution were added every 2 mins to ensure $AgNO_3$ reduction reached completion. Next, 1 mL 5 mM BSPP and 0.5 mL 50 mM $NaBH_4$ were simultaneously added dropwise over 5 mins. The reaction was left vigorously stirring overnight in the dark.

The next day, the photochemical conversion was initiated by positioning the flask at 135 mm from the light source described. The reaction mixture was not stirred during conversion. Samples were taken at 24 hour intervals and stored in the dark at (5.0 ± 0.2) ^{o}C.

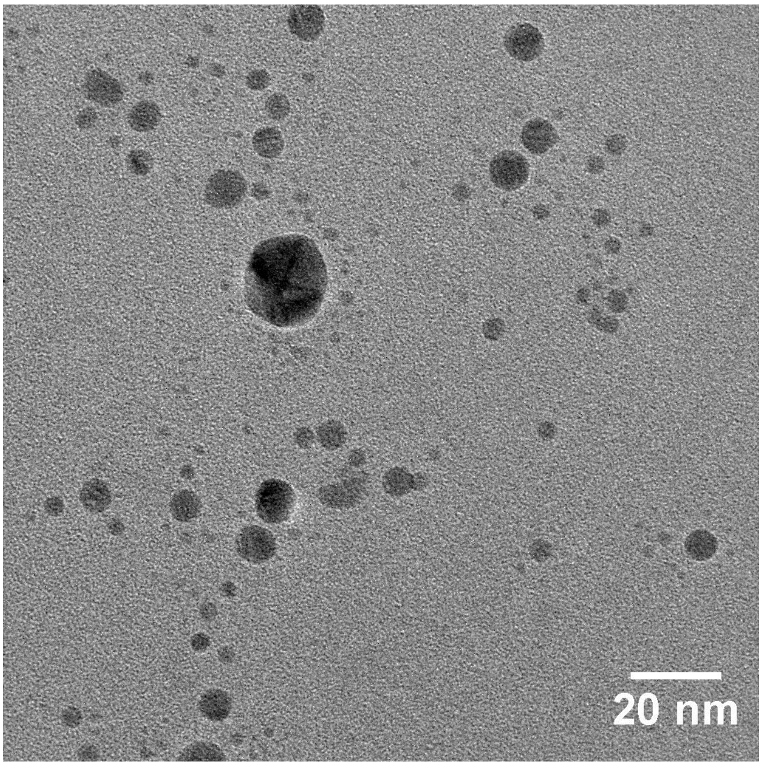
Additional TEM Images



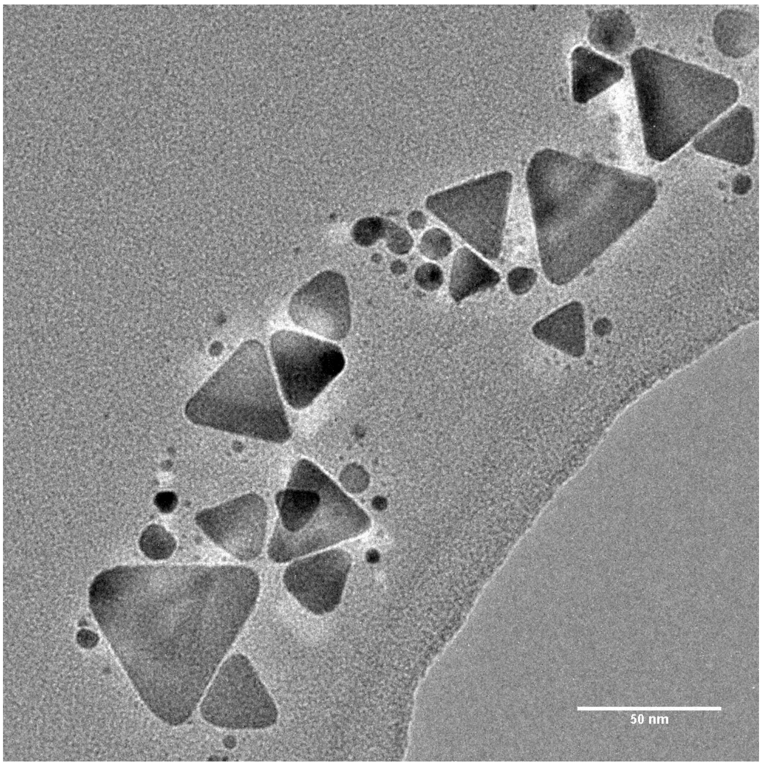
SI 3 (i). Example TEM Image on Day 0



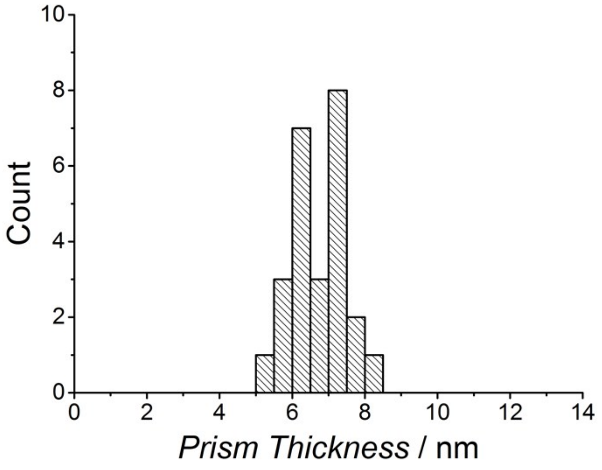
SI 3 (ii). Example TEM Image on Day 3



SI 3 (iii). Example TEM Image on Day 5

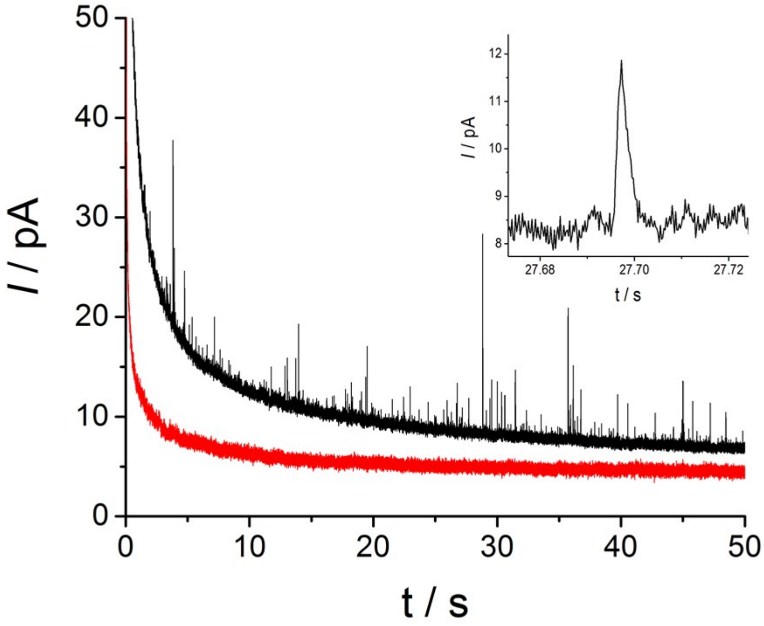


SI 3 (iv). Example TEM Image on Day 10



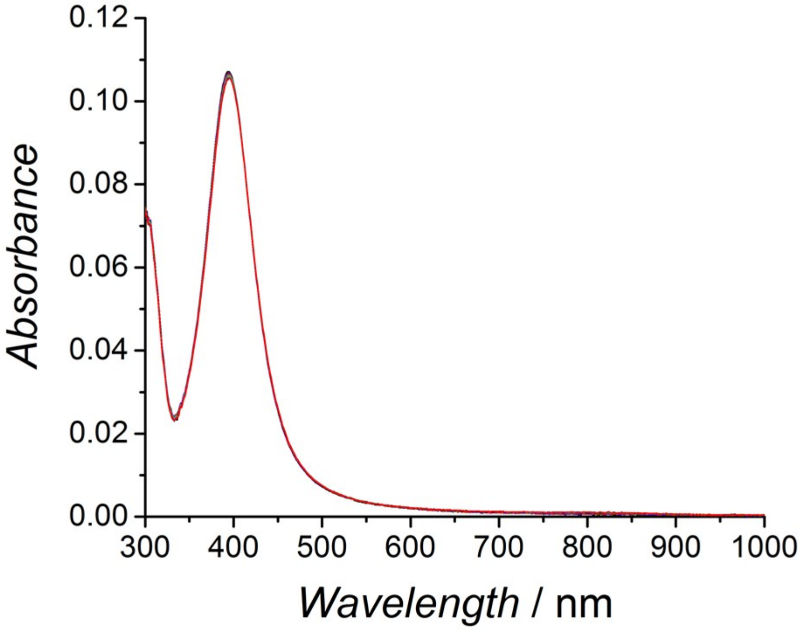
SI 3 (v). Distribution of prism thickness.

Nano-impact Current-time Transient Response Example

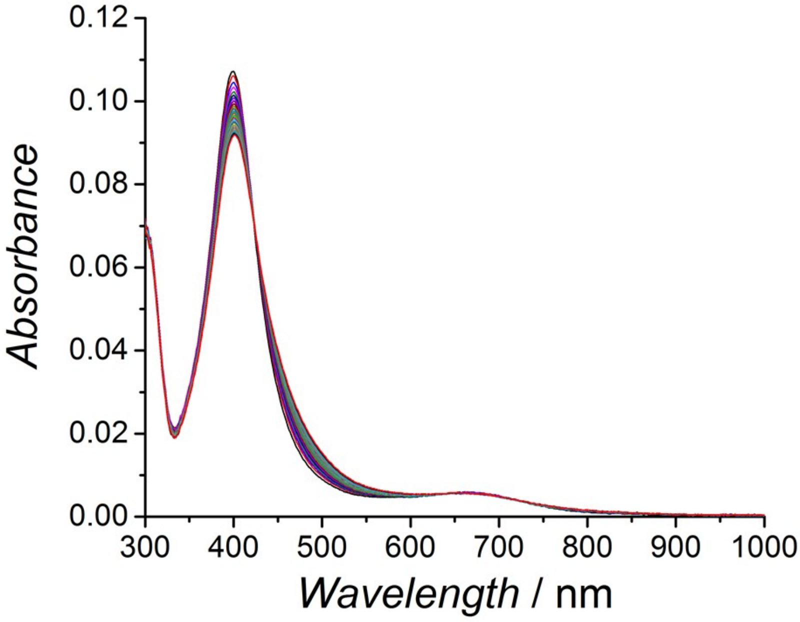


SI 4. Example of typical nano-impact current-time transient response at +0.40 V vs MSE. (Black) 20 times diluted day 5 nanoparticle stock in 40 mM KNO_3. (Red) Blank 40 mM KNO_3. Insert shows zoomed in image of a single nanoparticle impact spike.

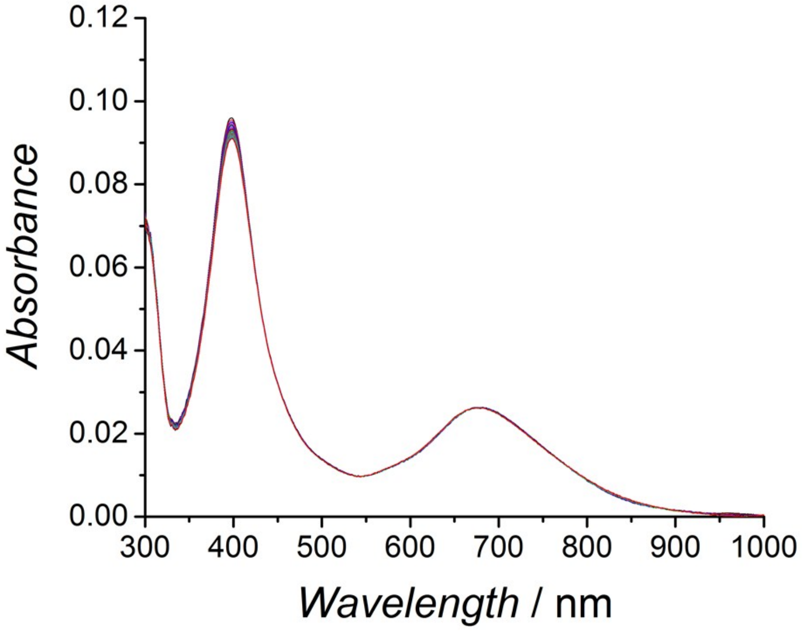
UV-Vis Stability of Nanoparticles During Conversion



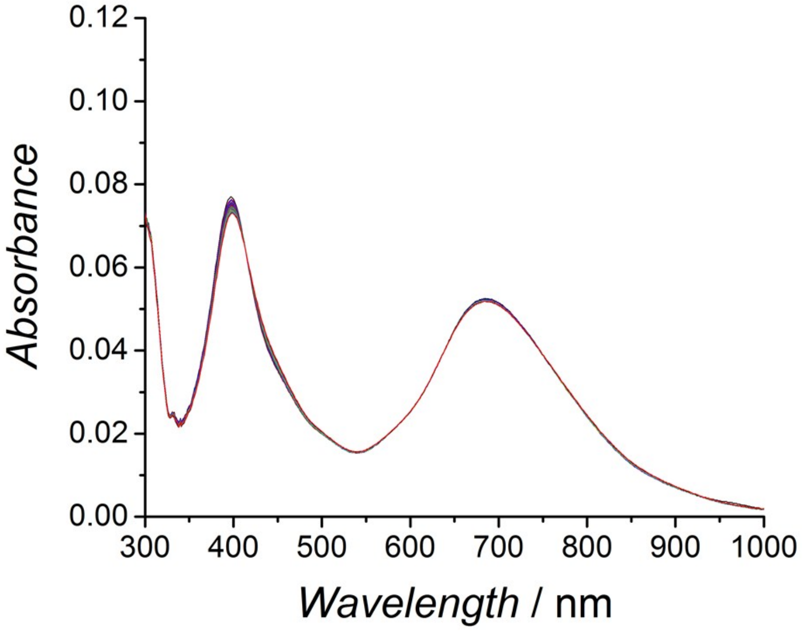
SI 5. a) Day 0 UV-Vis stability study of nanoparticle stock over 2 hours with 5 min scan intervals.



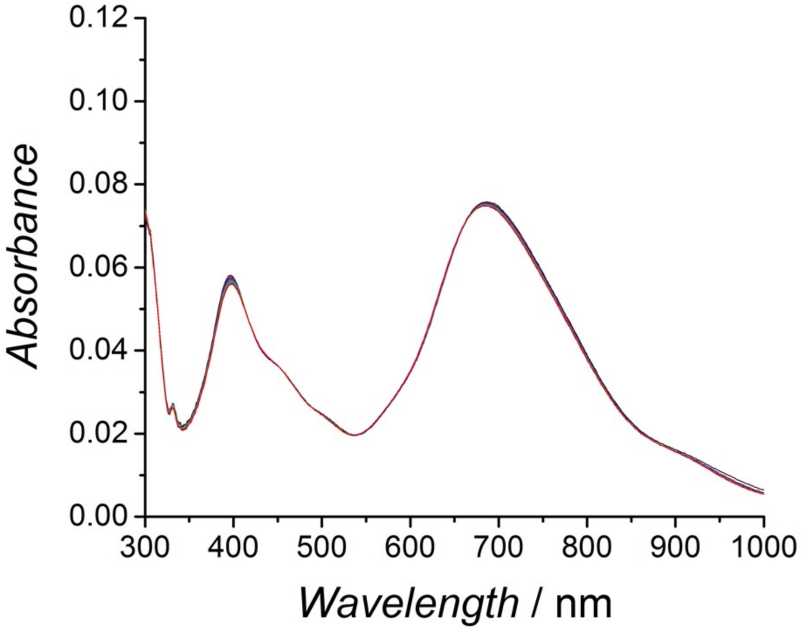
SI 5. b) Day 2 UV-Vis stability study of nanoparticle stock over 2 hours with 5 min scan intervals



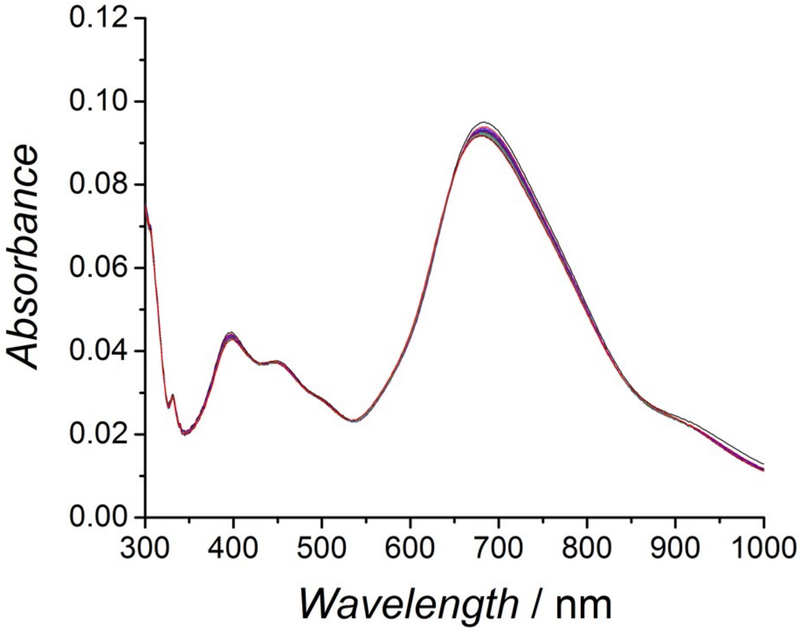
SI 5. c) Day 3 UV-Vis stability study of nanoparticle stock over 2 hours with 5 min scan intervals



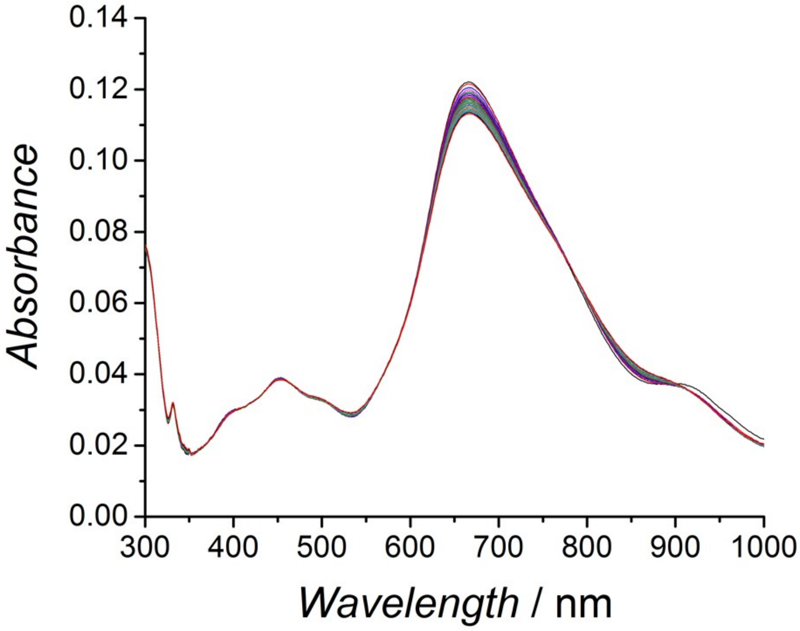
SI 5. d) Day 4 UV-Vis stability study of nanoparticle stock over 2 hours with 5 min scan intervals



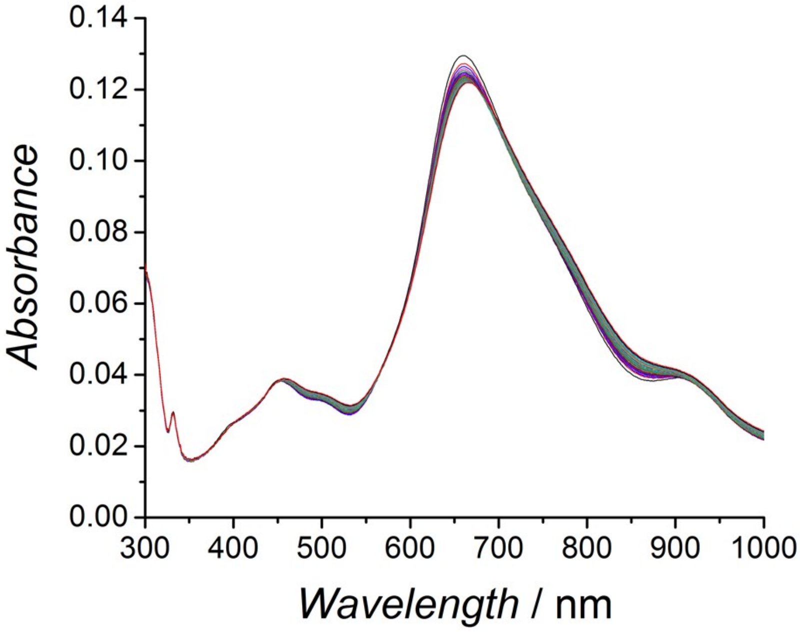
SI 5. e) Day 5 UV-Vis stability study of nanoparticle stock over 2 hours with 5 min scan intervals



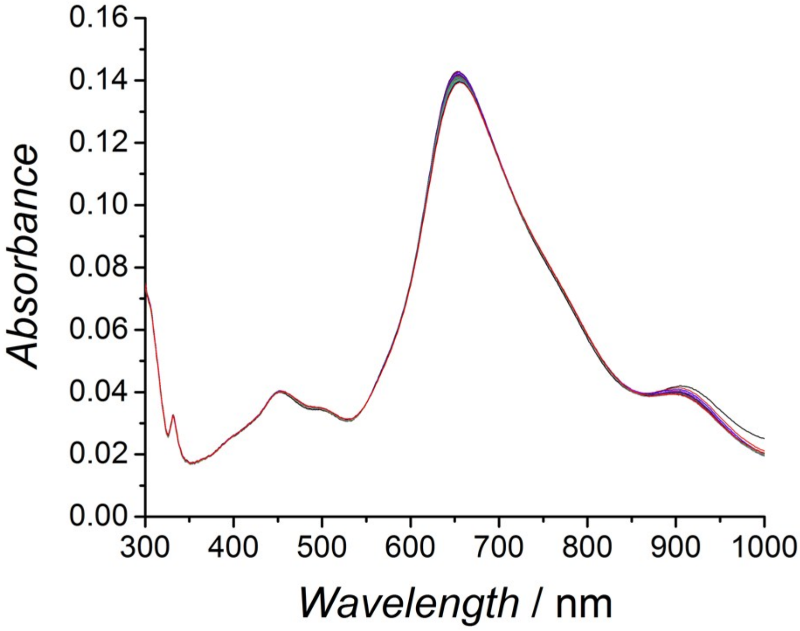
SI 5. f) Day 6 UV-Vis stability study of nanoparticle stock over 2 hours with 5 min scan intervals



SI 5. g) Day 8 UV-Vis stability study of nanoparticle stock over 2 hours with 5 min scan intervals



SI 5. h) Day 9 UV-Vis stability study of nanoparticle stock over 2 hours with 5 min scan intervals



SI 5. i) Day 10 UV-Vis stability study of nanoparticle stock over 2 hours with 5 min scan intervals

References

1. J. Ellison, C. Batchelor-McAuley, K. Tschulik and R. G. Compton, *Sens. Actuators, B*, 2014, **200**, 47-52.
2. C. Batchelor-McAuley, J. Ellison, K. Tschulik, P. L. Hurst, R. Boldt and R. G. Compton, *Analyst*, 2015, **140**, 5048-5054.
3. R. Jin, Y. C. Cao, E. Hao, G. S. Metraux, G. C. Schatz and C. A. Mirkin, *Nature*, 2003, **425**, 487-490.