

Supporting Information - Laser induced SERS switching using plasmonic heating of PNIPAM coated HGNs

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Experimental Section

Synthesis of PNIPAM coated HGNs with LSPRs at 690, 785 and 860 nm. The synthesis of PNIPAM-HGNs was carried out under inert conditions using a standard Schlenk line to prevent the cobalt nanoparticles from prematurely oxidising. In a typical synthesis, cobalt chloride hexahydrate (100 μ L, 0.4M; Fisher Scientific, 99.99%) and trisodium citrate dihydrate (550 μ L, 0.1 M; Sigma-Aldrich, >99%) were added into deionised water (100 mL) and degassed several times (10 mins vacuum and 15 mins argon). Sodium borohydride (1 mL, 0.1 M; Fisher Scientific, 99%) was injected into the solution and allowed to react for a further 20 minutes (under constant argon flow) until hydrogen evolution ceased, indicating complete hydrolysis of the reductant. The solution was degassed again (8 min vacuum and 10 min argon) before 33 mL of different concentrations ranging from 260 μ M (PNIPAM-690) to 235 μ M (PNIPAM-860) of chloroauric acid trihydrate (Fisher Scientific, ACS reagent grade) was injected. This mixture was allowed to react for an additional 10 minutes under argon with vigorous stirring. Before being exposed to air, were an obvious colour change from brown to green was observed. Trisodium citrate (500 μ L, 0.1 M) was added to stabilise the hollow gold nanoshell solution and allowed to stir for a further 1 hour before PNIPAM-NH₂ (300 μ L, 0.5% (w/v); Sigma-Aldrich) was added. This mixture was then left to stir gently for another hour. Post synthesis, the HGN solution was concentrated through centrifugation (5000 x g) and the precipitate was re-dispersed in deionised water to give final concentrations of 4.91 nM (PNIPAM-690; 2.96×10^{15} particles per L), 4.78 nM (PNIPAM-785; 2.88×10^{15} particles per L) and 4.94 nM (PNIPAM-860; 2.97×10^{15} particles per L).

A Nanosight LM10 was used initially to obtain concentrations in particles per L and following this the molar concentrations were calculated.

Synthesis of citrate capped HGNs resonant at 785 nm

The HGN synthesis was carried out under inert conditions using a standard Schlenk line to prevent the cobalt nanoparticles from prematurely oxidising. The method described was modified slightly from previous reports.¹⁻³ In a typical synthesis, cobalt chloride hexahydrate (100 μ L, 0.4 M; Fisher Scientific, 99.99%) and trisodium citrate dihydrate (550 μ L, 0.1 M; Sigma-Aldrich, >99%) were added into deionised water (100 mL) and degassed several times (10 mins vacuum and 15 mins argon). Sodium borohydride (1 mL, 0.1 M; Fisher Scientific, 99%) was injected into the solution and allowed to react for a further 20 minutes (under constant argon flow) until hydrogen evolution ceased, indicating complete hydrolysis of the reductant. The solution was degassed again (8 min vacuum and 10 min argon) before chloroauric acid trihydrate (33 mL, 130 μ M; Fisher Scientific, ACS reagent grade) was injected. This mixture was allowed to react for an additional 10 minutes under argon with vigorous stirring before being exposed to air, where an obvious colour change from brown to green was observed. Finally, trisodium citrate (500 μ L, 0.1 M) was added to stabilise the hollow gold nanoshell solution. Post synthesis, the HGN solution was concentrated through centrifugation (5000 x rpm) and the precipitate was re-dispersed in trisodium citrate solution (2mM) to give a final concentration of 4.86 nM (2.93×10^{15} particles per L).

Characterisation of HGNs

Before SERS and photothermal measurements, the concentrations of the hollow gold nanoparticle solutions were adjusted to the same level with the aid of a Nanosight LM10 via the procedure described in the instrument technical notes. Briefly, the original concentrated solutions were diluted with deionised water until 5 to 30 nanoparticles per CCD frame were obtained. The imaging videos were recorded for 90 seconds and analysed using the provided software (NTA 2.1). The required dilution factor was then applied to the samples so that each nanoparticle solution had a concentration of 4.7 nM (2.8×10^{15} particles per L).

The photothermal and SERS measurements were carried out by mixing 'as prepared' HGN solution (2025 μ L) with 225 μ L, 0.1 mM of the Raman reporter BPE ((1,2-bis(4-pyridyl)ethylene), Sigma-Aldrich >98 %) The instrumental design was based on an in-house set-up previously described by Xie et al.² Briefly, a 785 nm fibre coupled laser (B&W Tek Inc.) was used as the 'incident laser' for inducing plasmonic heating. The laser, with a power

of 346.5 mW at the sample was focused into a plastic cuvette using a standard $f=100$ mm UV fused silica plano-convex lens (1" diameter). A thermocouple from a heating mantle was inserted into the solution perpendicular to the path of the incident laser light, ~ 1.5 cm above the focus point. A portable 785 nm spectrometer (Deltanu Reporter R spectrometer) with a 'point and shoot' attachment was incorporated into the set-up to obtain the SERS spectra. This diode laser had a power of 100 mW at the sample and was held at an angle of 90 degrees and 1cm above the incident laser beam to minimise the interference between the two lasers. The cuvette contained 2.25 mL of the HGN suspension and a magnetic stirrer to ensure uniform heating of the sample. Additionally, a plastic stopper sealed with parafilm was used to cover the top of the cuvette in order to minimise heat loss to the environment. Initially the samples were left to stabilise for 3 minutes at room temperature with stirring, before the laser block was removed and the solution illuminated. The samples were illuminated for ~ 30 minutes; until the solution had equilibrated at its' maximum temperature. The laser block was then applied and the solutions allowed to cool back to room temperature and again the samples were left until the temperature had stabilised indicating the solution had equilibrated. This process was repeated over two cycles of heating and cooling. The SERS spectra and temperature readings were taken every 5 minutes. For the SERS measurements an exposure time of 5 seconds was employed and 5 scans at each time interval were recorded. All spectra have been background corrected and the peak intensity values shown in the bar charts are from the C-C stretch of BPE at 1603 cm^{-1} . Error bars represent one standard deviation resulting from 5 scans at each time interval. It should be noted, that all experimental parameters such as HGN concentration (number of nanoparticles per L), sampling geometries and instrumental parameters including depth of focus, laser power and acquisition times were kept constant for all the hollow gold nanoparticle solutions analysed.

A Varian Cary 300 Bio UV-Visible Spectrophotometer was used to acquire all the extinction spectra. For monitoring the stability of the resonant PNIPAM and citrate HGNs over two cycles of heating and cooling; 300 μL of concentrated HGN solution was added to 800 μL of deionised water and changes in extinction at 785 nm were monitored over the temperature range 20-90-20 $^{\circ}\text{C}$. Note a rate of 3.5 $^{\circ}\text{C}$ per minute was applied with 5 minute holds at each stage of the cycle being incorporated to allow the solution to equilibrate (at each stage) in order to replicate the SERS experiments. For monitoring the LSPR, average particle size and Zeta potential during each stage of the SERS experiments; 50 μL of the as prepared ' HGN + BPE solution' was added to 450 μL of deionized water and analysed. The extinction spectra

were recorded on the Varian Cary 300 Bio Uv-Visible Spectrometer, while a separate sample was analysed on a Malvern nanosizer for obtaining the zeta potential and particle size measurements.

Scanning electron microscope (SEM) images were obtained using a FEI Sirion 200 ultra-high resolution Schottky field emission scanning electron microscope with FEI software. From the SEM image, the particle size was confirmed using image-J software. The SEM samples were prepared on polyelectrolyte functionalised silicon wafers as previously reported.^{4, 5} Briefly, silica wafer substrates (5 x 5 mm) were washed with methanol wipes and placed in an oxygen plasma cleaner for 90 seconds. Immediately after, they were treated with poly(diallyldimethylammonium chloride) (PDDA ; Sigma Aldrich) solution to create a positive charge on the wafer surface. PDDA solution (10 μ L) was dissolved in sodium chloride (1 mL, 1 mM; Sigma Aldrich, 99%) and then this solution (15 μ L) was added dropwise onto the wafer surface. The wafers were left for 20 minutes in a petri dish, before being washed off with water and dried under a stream of nitrogen. Each wafer was then treated with concentrated HGN solution (50 μ L) and left for a further 10 minutes before being removed and rinsed with water and dried under nitrogen again. This spotting and removal process of the HGN solution was repeated a further twice.

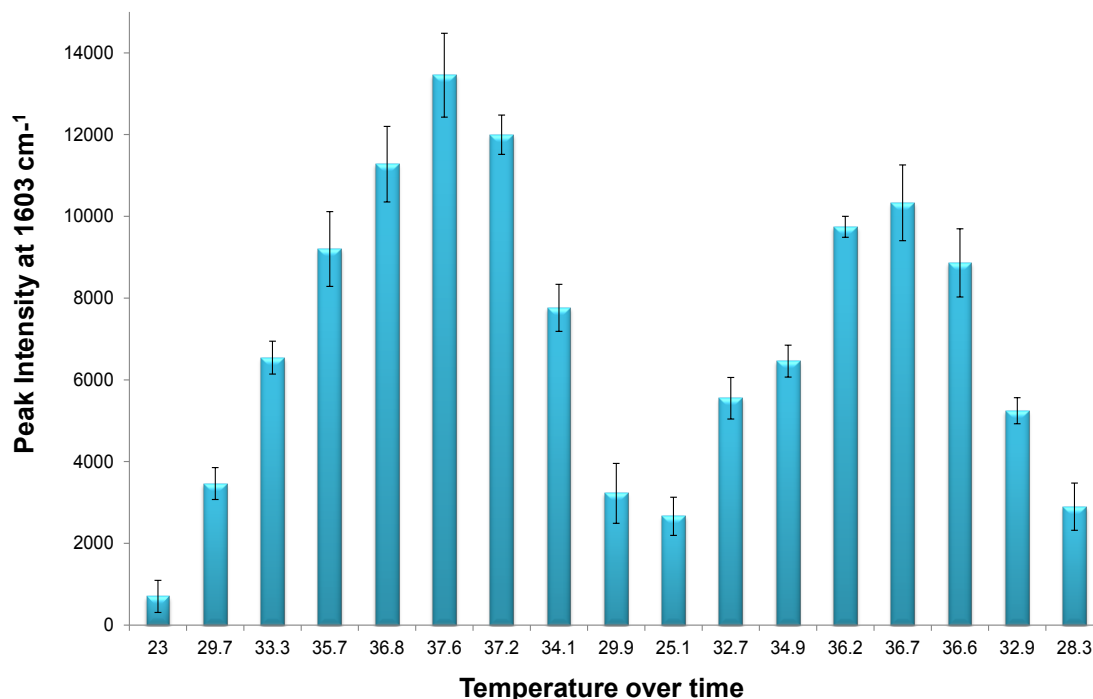


Figure S1. Bar chart showing the change in SERS signal of PNIPAM coated HGNs + BPE (0.1 mM) resonant at 785 nm over two cycles of heating and cooling past the LCST of 32 °C. The SERS spectra and temperature readings were taken every 5 minutes. A laser excitation of 785 nm was used to induce plasmonic heating of the HGNs and a secondary portable Deltanu 785 nm spectrometer was used to collect the SERS data. The peak intensity values shown in the bar chart are from the C-C stretch of BPE at 1603 cm⁻¹ and the error bars represent one standard deviation resulting from 5 scans at each time interval. The heating and cooling cycles were over the temperature ranges 23 °C to 40 °C, with the largest temperature increase being 14.6 °C.

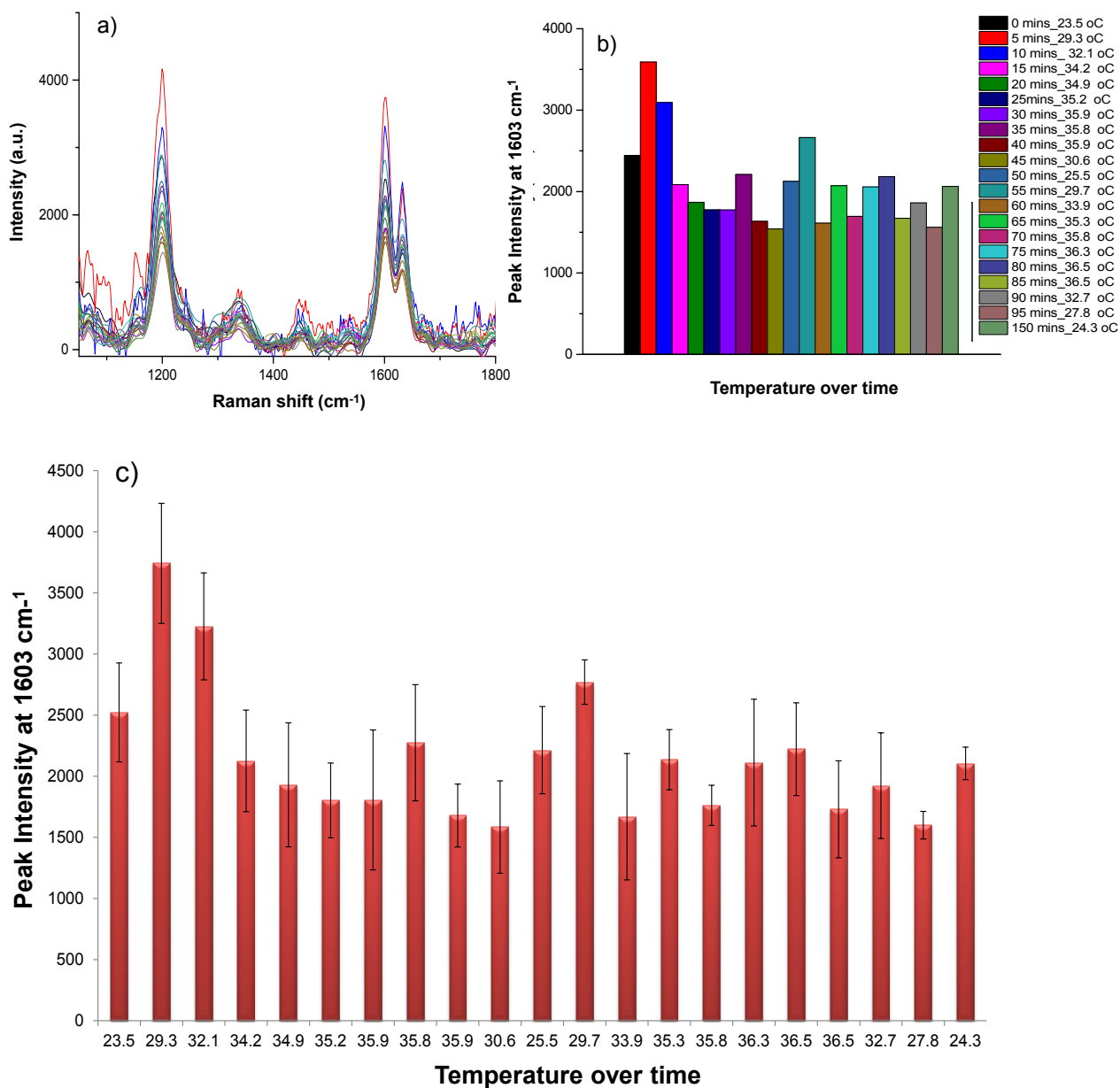


Figure S2. SERS spectrum (a), bar chart (b) and bar chart containing error bars (c) showing the change in SERS signal of citrate capped HGNs + BPE (0.1 mM) resonant at 785 nm over two cycles of heating and cooling past the LCST of 32 °C. The SERS spectra and temperature readings were taken every 5 minutes. A laser excitation of 785 nm was used to induce plasmonic heating of the HGNs and a secondary portable Deltanu 785 nm spectrometer was used to collect the SERS data. An accumulation time of 5 seconds was employed and 5 scans at each time interval were recorded. All spectra have been background corrected and the peak intensity values shown in the bar charts are from the C-C stretch of BPE at 1603 cm⁻¹. Error

bars represent one standard deviation resulting from 5 scans at each time interval. The heating and cooling cycles were over the temperature ranges 23.5 °C to 36.5 °C, with the largest temperature increase being 13 °C.

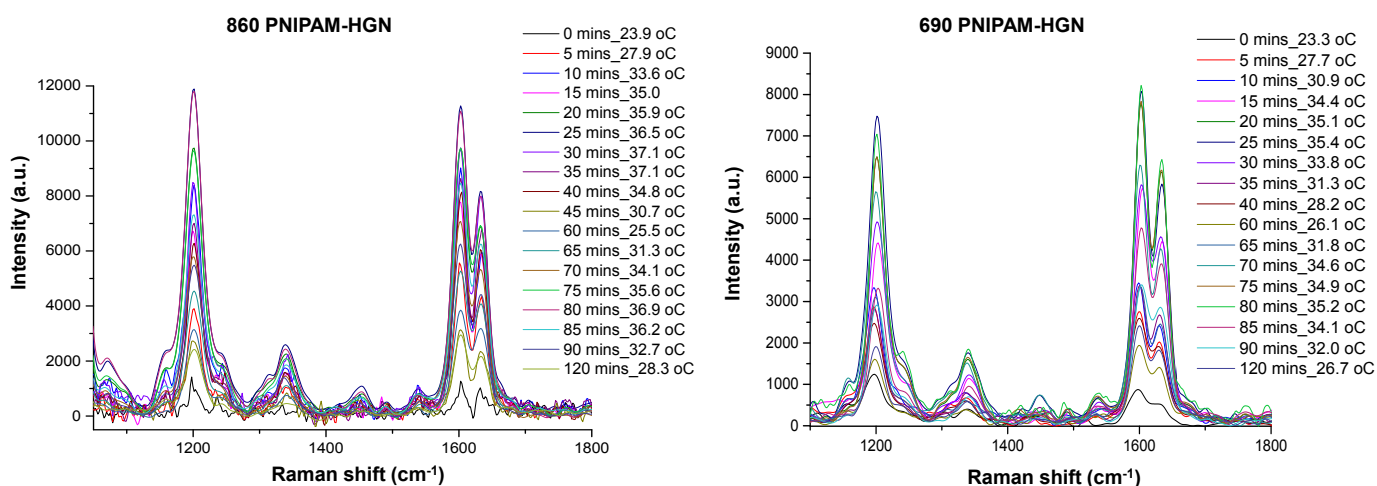
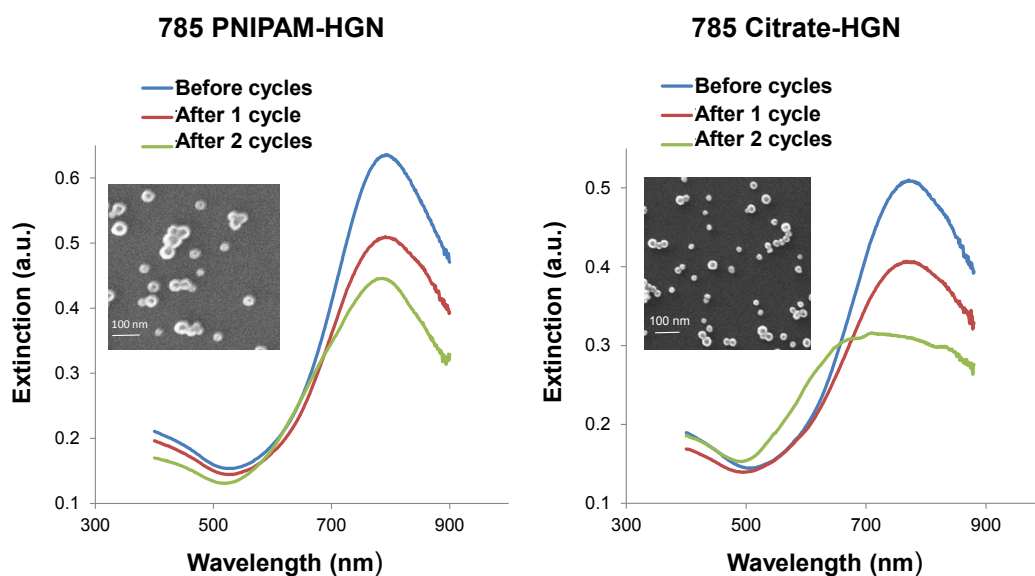


Figure S3. SERS spectra showing the change in SERS response for a range of PNIPAM coated HGNS + BPE (0.1 mM) over two cycles of heating and cooling past the LCST of 32 °C. The two batches of PNIPAM-HGNs have LSPRs at 860 and 690 nm with temperature increases of 13.2 °C and 12.1 °C respectively. Furthermore, the 860-PNIPAM nanotags have an average particle size of 156.3 ± 24.1 nm and a zeta potential value of -28.4 ± 6.82 mV; while the 690-PNIPAM nanotags have an average particle size of 114.8 ± 18.3 nm and zeta potential value of -30.9 ± 7.05 mV. The SERS spectra and temperature readings were taken every 5 minutes. A laser excitation of 785 nm was used to induce plasmonic heating of the HGNS and a secondary portable Deltanu 785 nm spectrometer was used to collect the SERS data. An accumulation time of 5 seconds was employed and 5 scans at each time interval were recorded. All spectra have been background corrected.



785-PNIPAM

785-Citrate

	Average Particle Size (nm)	Zeta Potential (mV)	Average Particle Size (nm)	Zeta Potential (mV)
Before cycles:	130.1 ± 15.2	-32.4 ± 9.38	70.26 ± 12.8	-51.1 ± 9.50
After 1 cycle:	136.6 ± 10.7	-24.7 ± 6.41	83.46 ± 14.4	-40.2 ± 21.1
After 2 cycles:	137.6 ± 17.5	-21.7 ± 8.11	286.5 ± 26.8	-8.24 ± 5.28

Figure S4 and table S1. Characterisation measurements taken during the SERS experiments for PNIPAM- HGNs and citrate-HGNs. Figure S4 - extinction spectra taken during SERS experiments, showing how the LSPR and stability changes over two cycles of heating and cooling past the LCST of 32 °C for PNIPAM coated HGNs and citrate capped HGNs resonant at 785 nm. Blue line highlights the extinction spectra for the bulk solutions before any heating and cooling occurs, red line is after 1 cycle of the heating and cooling process and the green line is after 2 cycles. Inserts are SEM images showing unaggregated solutions before the heating and cooling process, with an average size of 128.3 nm and 67.13 nm for the PNIPAM-HGNs and citrate-HGNs respectively. Table S1 highlights the average particle size and zeta potential values also recorded at each cycle of the SERS experiments.

References

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