Supplementary Material (ESI) for Chemical Communications
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Supporting Information for:

A Seedless Approach to Continuous Flow Synthesis of Gold Nanorods

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Experimental details

Materials: All aqueous solutions were prepared using MilliQ water. $HAuCl_4$ was obtained from high gold wire (AGR Matthey, >99.9%), and aqua regia prepared from analytical grade HCl and HNO_3 (BDH). All other chemicals were used as received. Acetylacetone, sodium carbonate and sodium hydrogencarbonate were obtained from Ajax Fine Chemicals; technical grade CTAB was purchased from Lancaster Chemicals; and Silver Nitrate (99.5%) was from Aldrich.

Preparation of stock solutions: Two stock solutions were prepared as described below:

Solution 1 was comprised of 100 mM CTAB, 1 mM $HAuCl_4$, and 10 mM acetylacetone.
After dissolution of CTAB (36.4g/L) with stirring and gentle heating, 10 mL/L of 100 mM $HAuCl_4$ was added to produce an orange coloured solution with some fine orange precipitate. Solution 1 was warmed to *ca.* 30°C-35°C for 15 minutes to produce a transparent, deep orange solution. At this time acetylacetone (10 mM) was added with stirring at which point the solution colour changed to colourless indicating complexation of gold by acac. The low pH (*ca.* 3-3.5) kinetically retarded the formation of significant amounts of Au(0) until several weeks after solution preparation; with reliable results for AuNR synthesis achieved for up to 3 weeks from a given solution stored at room temperature in a cupboard. The solution temperature was maintained at 30±2°C during the RTP experiments using a hotplate-stirrer.

Solution 2 was comprised of 0.1 M CTAB, 0.1 mM and 0.025 mM, 0.05 mM or 0.1 mM $AgNO_3$.
The solution was buffered to pH 10 using 0.1 M $NaHCO_3/Na_2CO_3$. After complete dissolution of CTAB (36.4 g in 900 mL) at 30°C-35°C, 100 mL of buffer (0.5 M $NaHCO_3$/0.5 M Na_2CO_3) in 100 mM CTAB was added. Finally 0.25-1 mL/L of 100 mM $AgNO_3$ was added to the buffered CTAB solution. Solution 2 was found to be stable for AuNR synthesis for several weeks.

Description of rotating tube (RTP) system: The key features of the RTP is the hollow, thin-walled cylinder, as an interchangeable stainless steel tube 6 cm diameter and 30 cm in length which rotates about a horizontal axis at controllable speeds up to 2000 rpm.[1] A set flow of liquids were introduced from a conical inlet at one end of the tube, with the discharged liquid collected by a peripheral ring at the other end. Under typical operating conditions with flow rates of 30mL/minute and tube rotation rate of 1000 RPM, the average film thickness is *ca.* 300μm.

1. Fang, J.: Evans, C. W.; Willis, G. J.; Sherwood, D.; Guo, Y.; Lu, G.; Raston, C. L.; Iyer, K. S. *Lab Chip*, **2010**, *10*, 2579.

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AuNR synthesis using RTP/NCR: Separate beakers of Solution 1 and Solution 2 were connected to the two inlet flow lines of the RTP system. The RTP unit was thoroughly rinsed with MilliQ water, and was operated at a rotation rate speed of 1000 RPM. The pumps were set to the desired flow rates of between 20 mL/min and 160 mL/min, and were started simultaneously to give equal flow rates of each solution into the RTP.

In-line sampling of the output stream was achieved for the [Ag] switching experiment by manual insertion of a silicone tube directly into the output flow for a period of 5-10 seconds for each run . The samples were passed through a *ca.* 15-20 metre silicone tube (3 mm internal diameter) with the flow controlled by a Gilson Minipuls3 peristaltic pump set at 5-10 mL/min. The tubing and flow rate were selected to a provide sufficient time to complete the growth of AuNRs ($T_{growth,tubing}$= 38°C ±2°C) before UV-visible spectroscopy was performed at the end of the tube using a 2 mm path-length solution cell and Ocean Optics USB2000^{+} spectrometer. Where the Au/Ag ratio was varied, two stock solutions ('Solution 2') were prepared and the RTP feed was manually switched between the solutions.

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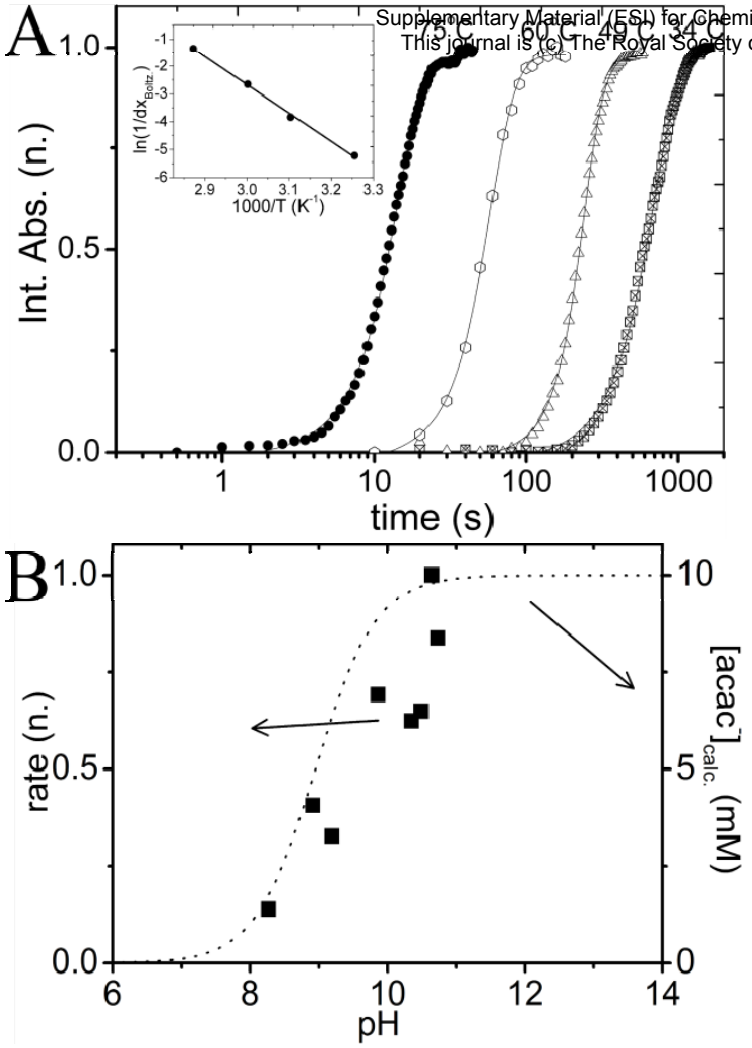
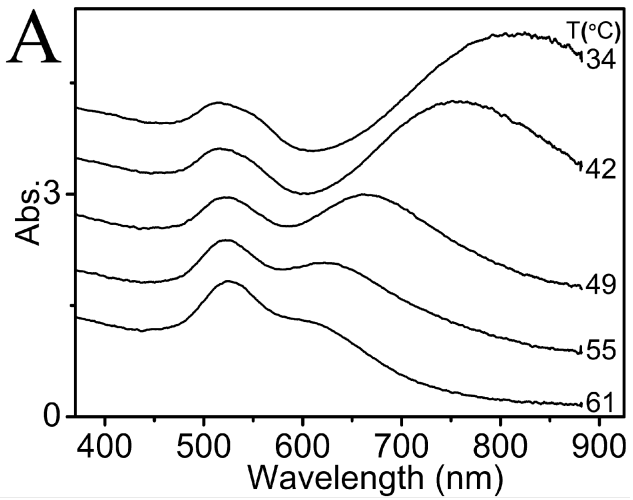


Figure S1 Effect of temperature and pH on the growth kinetics of AuNRs at pH 10 using acac reductant in batch experiments. A. Temperature dependent growth curves fitted with Boltzmann function and resultant Arrhenius plot (inset), with E_a = 85 ±3 kJ/mol. B. pH dependence of AuNR growth kinetics in carbonate buffer solutions. The dotted line corresponds to the calculated pH dependence of [$acac^-$] (pKa 8.95)



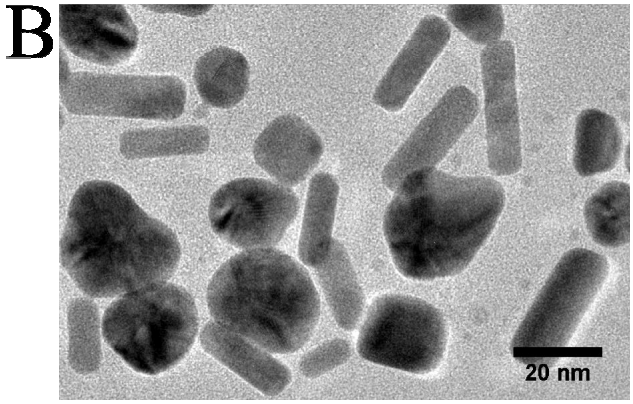


Figure S2 A. Absorbance spectra of AuNR solutions prepared using acac, at temperatures indicated. Spectra normalised offset for clarity, and samples were diluted three-fold. B. Representative HR-TEM image of the nanocrystals prepared at 61°C.

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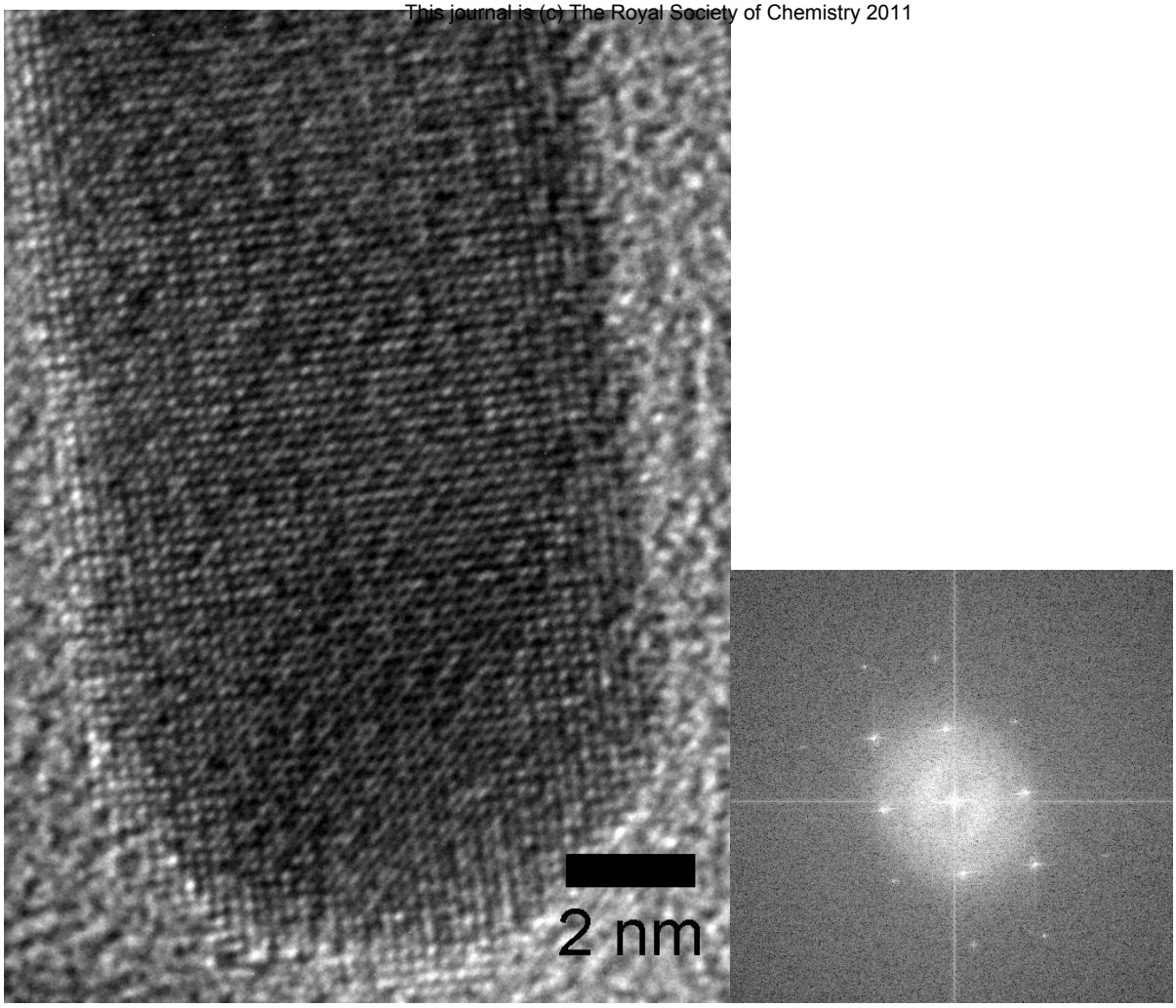

Figure S3. HR-TEM images and FFT image ([100] zone axis) of a typical AuNR prepared using the RTP-NCR system.