

Supplementary Material

Highly controlled synthesis of nanometric gold particles by citrate reduction using the short mixing, heating and quenching times achievable in a microfluidic device

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Experimental Section

Chemicals

All chemicals were used as received without any purification. Hydrogen tetrachloroaurate (III) trihydrate 99.99%; Au 49.5% (HAuCl_4) were purchased from Alfa Aesar, Sodium citrate tribasic dehydrate 99% ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) from Sigma Aldrich. All solutions were prepared from distilled water (filter system: AUTOSTILL 4000X). The experiments were carried under clean room conditions to prevent any contamination.

Preparation of Nano-Au in Batch mode

The preparation of the gold nanoparticles (nano-Au) was performed according to the original procedure reported by Enüstün and Turkevich [1, 2]. In a typical preparation, 212.5 mL of deionized water was heated with vigorous stirring under reflux. Then, 25 mL of a HAuCl_4 solution ($5.4 \times 10^{-3} \text{ M}$) was added to the boiling water. The obtained solution was left under mechanical stirring until boiling was reached again. Then 12.5 mL of a sodium citrate solution (10 mg.mL^{-1}) was added. The system was then left under reflux for 30 minutes. During this period the top of the flask was protected with aluminum paper to prevent any transformation induced by sunlight. Finally, the resultant colloid solution was slowly cooled down to room temperature.

Microfluidic device used for the gold particles solution generation

The microfluidic device used for the preparation of the Nano-Au solution was composed of two syringes (Hamilton glass syringes, Gastight, 1005C, 5.0 mL), containing the reactant solutions driven by a syringe pump (Harvard Apparatus – PHD ultra). The outlets of the syringes were connected to a T-mixer (Upchurch Scientific, Tee, Micro Static Mixing, 1/16 o. d., PEEK) which was acting as a static mixer. A fused silica capillary tubing (Polymicro capillaries; ID $200 \mu\text{m}$, OD $350 \mu\text{m}$) was connected to the outlet of the T-mixer and acted as the reactor. The capillary is rolled on a temperature regulated hot plate (Bioblock Scientific) The plate temperature was

checked with an infrared external temperature sensor (Oakton Temp Testr[®] IR Thermometer). Then all the system was covered with a sheet of aluminum paper.

Preparation of Nano-Au within the microfluidic device

Before starting the reaction, the capillary was heated to 100 °C with the regulated hot plate. One syringe was filled with the HAuCl₄ solution (5.4×10^{-3} mol.L⁻¹) and the other one contained the sodium citrate solution (0.5 g / 100 mL water) in order to keep the same HAuCl₄/sodium citrate ratio as in the classical batch mode protocol. The syringe pump was programmed to deliver a 40 μL.min⁻¹ flow rate for each syringe which gave a total 80 μL.min⁻¹ flow rate and corresponded to a 35 second residence time in the reactor.

Characterization

The samples were characterized directly after the end of the synthesis without any purification treatment like filtration or ultracentrifugation.

The UV-vis spectra of the nano-Au solution samples were measured using a PERKIN ELMER LAMBDA 650S spectrophotometer. For Dynamic Light Scattering (DLS) analysis a Zetasizer nano ZS from Malvern instrument (Malvern - UK) at 25 °C with a fixed scattering angle of 173 ° was used. The samples from microfluidic experiments for transmission electronic microscopy (TEM) were obtained from a fresh nano-Au solution drop, transferred directly from the outlet of the capillary onto a copper coated grid. The grid was dried for 5 hours at room temperature and then introduced with a grid holder into a TEM FEI Tecnai G2-20 twin, operated at 200 kV accelerating potential. For classical batch synthesis, a nano-Au solution drop was deposited on the grid with a Pasteur pipette.

TEM and DLS characterization of gold nanoparticles obtained in batch mode and microfluidic device

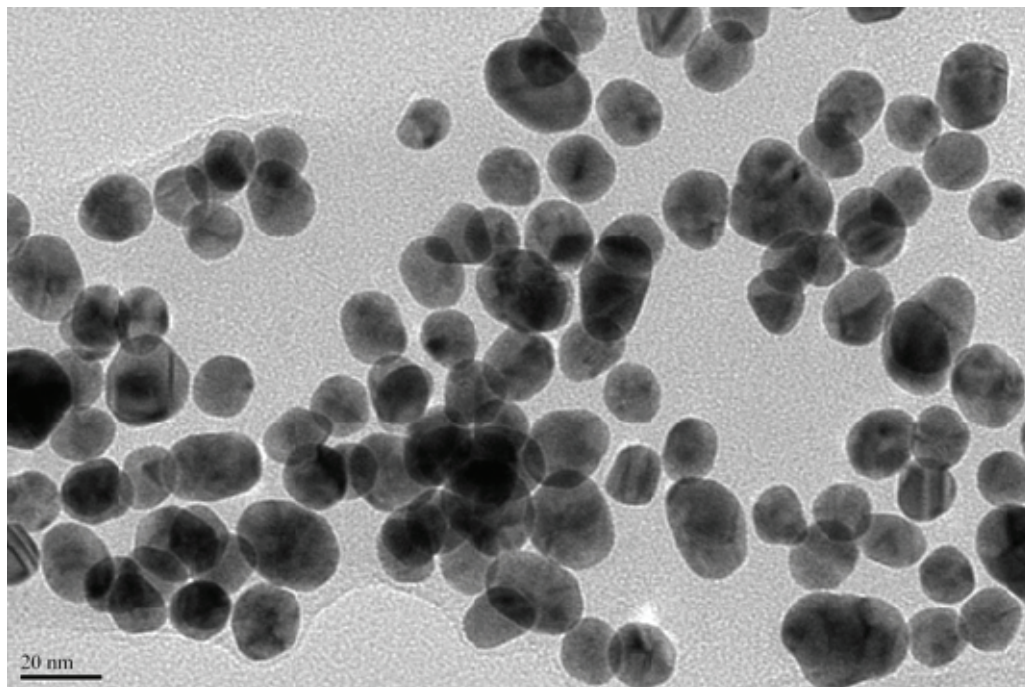


Figure S1. TEM image of nano-Au obtained in classical batch synthesis (scale bar 20 nm).

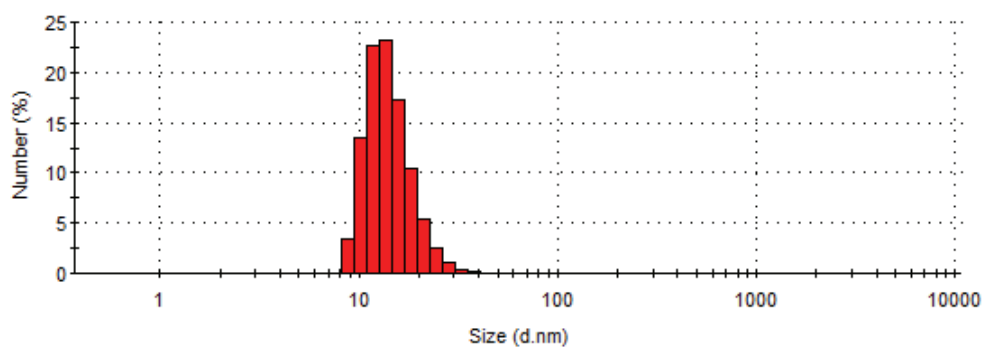


Figure S2. DLS size distribution of nano-Au obtained in classical batch synthesis (logarithmic scale).

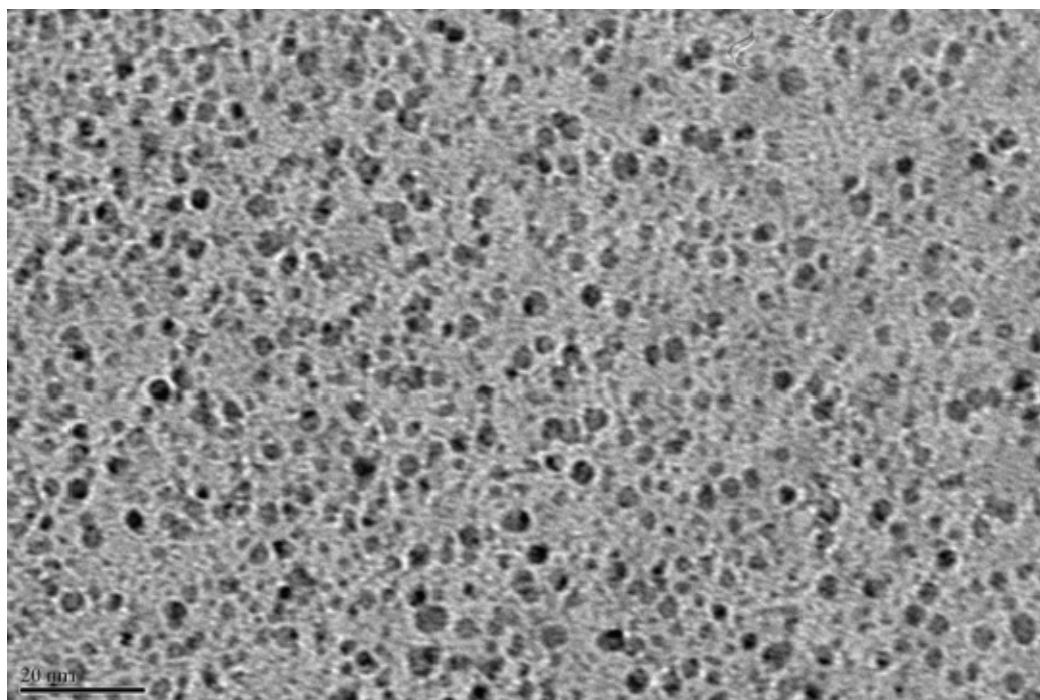


Figure S3. TEM image of nano-Au obtained in microfluidic device at $80 \mu\text{L}.\text{min}^{-1}$ flow-rate (scale bar 20 nm).

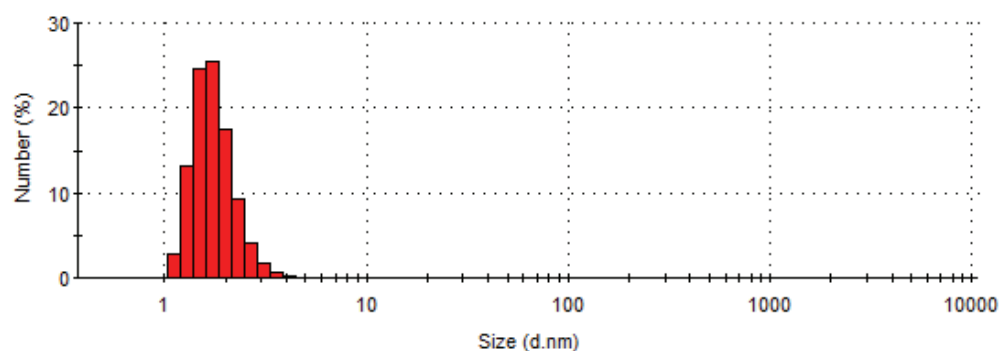


Figure S4. DLS size distribution of nano-Au obtained in microfluidic device at $80 \mu\text{L}.\text{min}^{-1}$ flow-rate (logarithmic scale).

1. Turkevich, J., P.C. Stevenson, and J. Hillier, *The nucleation and growth processes in the synthesis of colloidal gold*. Discuss. Faraday Soc., 1951. **11**: p. 55-75.
2. Turkevich, J., P.C. Stevenson, and J. Hillier, *The formation of colloidal gold*. J. Phys. Chem., 1953. **57**: p. 670-3.