

## Electronic Supplementary Information

# One-Pot Polyol Synthesis of Highly Monodisperse Short Green Silver Nanorods

Javier Patarroyo, Aziz Genç, Jordi Arbiol, Neus G. Bastús, and Victor Puntes.

### Chemicals.

Ethylene glycol anhydrous, 99.8% (EG, C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>), silver trifluoroacetate (CF<sub>3</sub>COOAg), silver nitrate (AgNO<sub>3</sub>), hydrochloric acid (HCl), poly(vinyl pyrrolidone) (PVP, MW 1,300,000; 350,000), tannic acid (TA, C<sub>76</sub>H<sub>52</sub>O<sub>46</sub>), gold (III) chloride trihydrate >99.9% (HAuCl<sub>4</sub> · 3H<sub>2</sub>O) and cetyltrimethylammonium bromide ≥ 99% (CTAB) were purchased from Sigma-Aldrich. All chemicals were used as received without further purification. Distilled water passed through a Millipore system ( $\rho = 18.2 \text{ M}\Omega$ ) was used in all experiments.

### Methods

#### Synthesis of Ag nanorods. (Ag NRs)

In a typical procedure, 5 mL of EG were added into a 100 mL three necked round bottom flask, and heated under magnetic stirring in an oil bath pre-set to 170°C. After 10 min 60  $\mu\text{L}$  of TA (30 mM in EG to a final concentration 0.25mM) was injected into the flask. After, 0.5 mL of HCl solution (3 mM in EG) was injected into the reaction solution., followed by the addition 1.25 mL PVP, (20 mg mL<sup>-1</sup>) into the reaction solution. Finally 0.4 mL of CF<sub>3</sub>COOAg (282 mM in EG) was added into the mixture. After 20 min the reaction was stopped by placing the reaction flask in an ice-water bath.

Resultant Ag NPs were purified by centrifugation (8000g) in order to remove the EG the excess of TA and PVP, and further redispersed in Milli-Q-water before sample characterization.

As previously reported,<sup>1-3</sup> the addition of small amounts of HCl has an outstanding impact on the control of the final structure of Ag NRs, which can be associated to its Ag surface adsorption, its ability to act as a complexing agent, and its role as surfactant micelle controller among others. Thus, the presence of Cl<sup>-</sup> assists the anisotropic growth of the Ag NRs via the stabilization of certain facets to direct the synthesis toward a precise crystallographic structure.

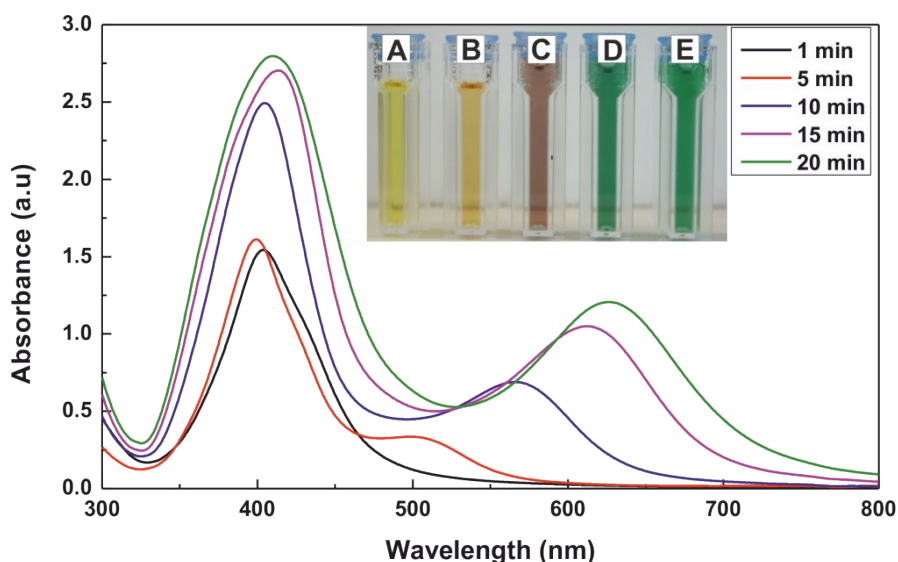
### Synthesis of AgAu hollow alloy nanorods.

In a typical procedure, 0.25 mL of Ag NRs ( $10^{12}$  NPs/mL) were dispersed in 2 mL of MilliQ water, then 1 mL of CTAB (20 mM) and 10  $\mu$ L of ascorbic acid (15 mM) were added. 0.3 mL of a solution of H<sub>2</sub>AuCl<sub>4</sub> (1 mM) was injected at a rate of 25  $\mu$ L/min using a syringe pump. The reaction was stirred for 30 min and the product were collected by centrifugation (8000g for 10 min) and then suspended in water for further characterization.

### Characterization.

Absorption spectra of the as synthesized nanoparticles were acquired with a Shimadzu UV-2401 PC spectrophotometer. An aliquot of the nanoparticles solution was placed in a cell, and spectral analysis was performed in the 300–800 nm range at room temperature.

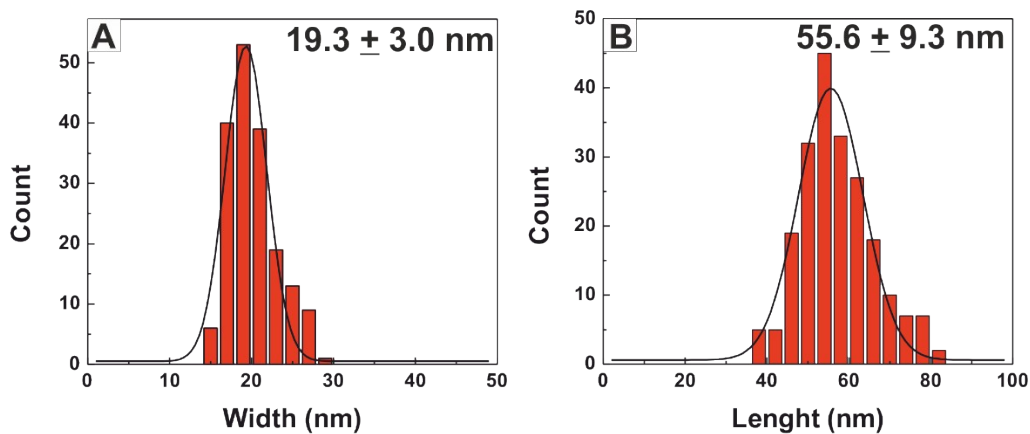
The morphology and size of the nanoparticles were visualized using FEI Magellan 400L XHR SEM, in scanning mode operated at 1kV and in transmission mode operated at 20 kV. STEM/HAADF images were obtained in a FEI Tecnai G2 F20 S-TWIN HR(S) TEM, operated at an accelerated voltage of 200 kV. A droplet of the sample was drop cast onto a piece of ultrathin carbon-coated 200-mesh copper grid (Ted-pella, Inc.) and left to dry in air. XRD data were collected on a PANalytical X'Pert diffractometer using a Cu K $\alpha$  radiation source.



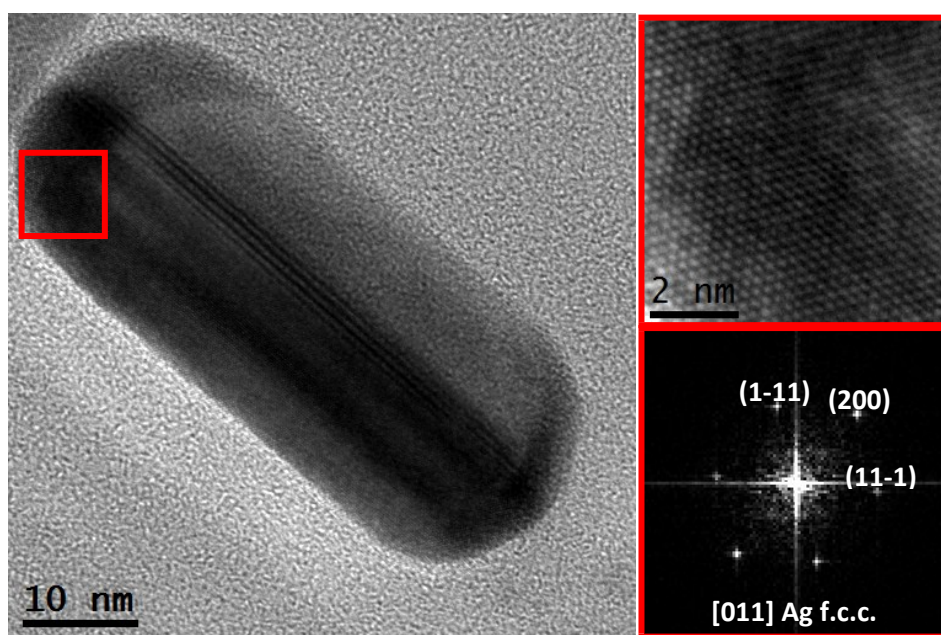
**Figure S1:** Time-dependent UV-vis spectra and photographs of aqueous dispersion of AgNR at different times: **A.** 1 min, **B.** 5 min, **C.** 10 min, **D.** 15 min, **E.** 20 min.

Different sets of experiments suggest us the possibility to control (to some extent) the aspect ratio of the final Ag NRs by carefully adjusting synthetic conditions, in particular the reaction time. Thus, by decreasing the reaction time, the aspect ratio of the observed Ag NRs is lower.

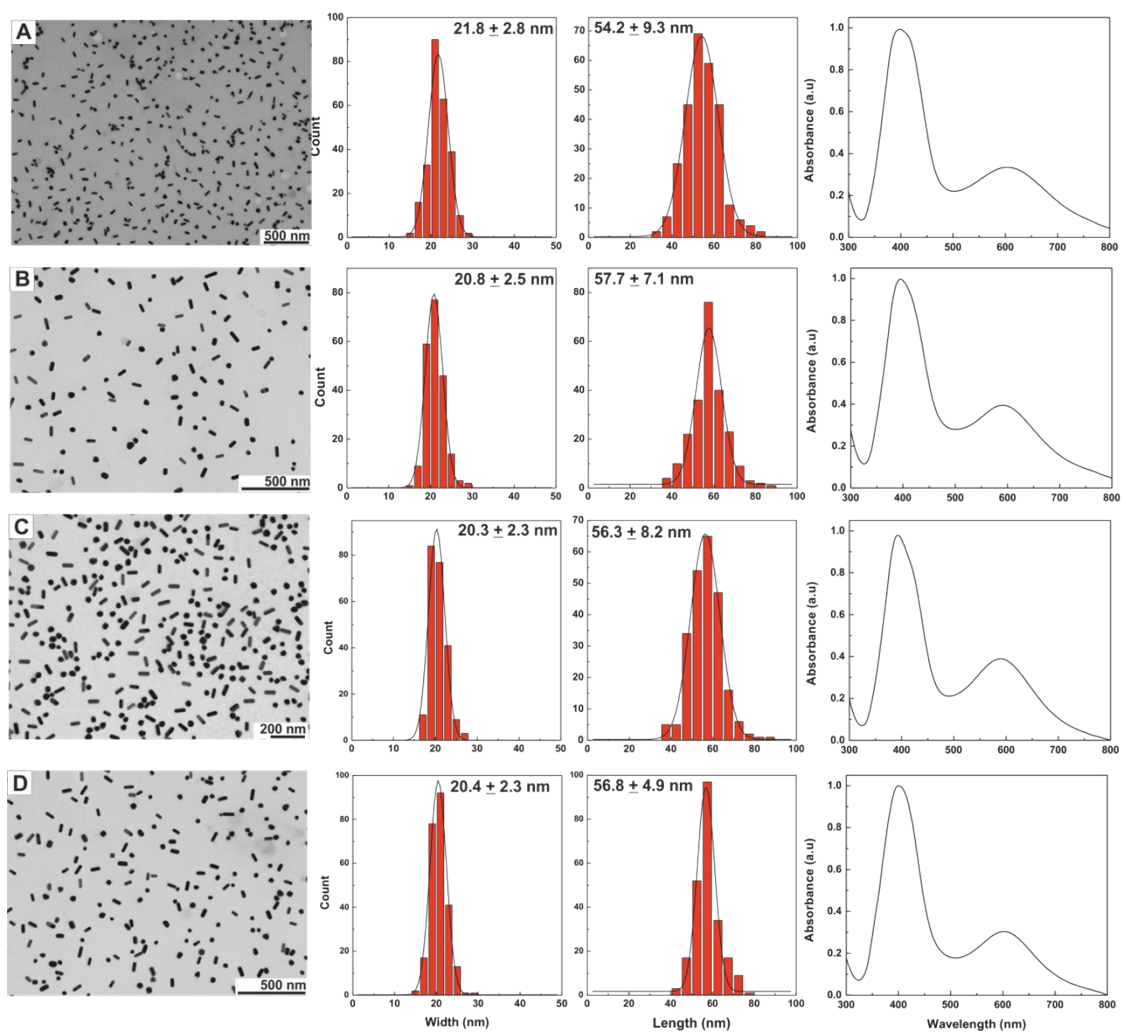
However, this is associated to a decrease of the reaction yield, which suggests that Ag NRs growth by incorporation Ag precursor from solution. Time-dependent UV-vis spectra show a systematic red-shift of longitudinal and transversal plasmonic bands, which can be univocally associated to an increase of the aspect ratio of Ag NRs.



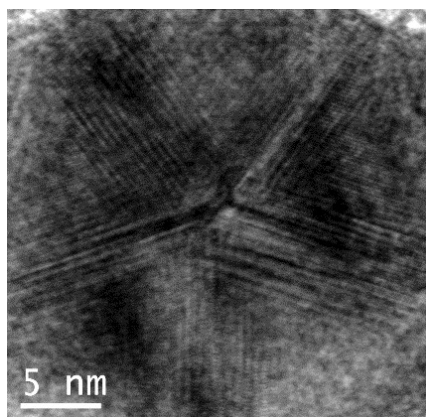
**Figure S2:** Particle size distribution of Ag NRs. A. Width and B. Length (nm)



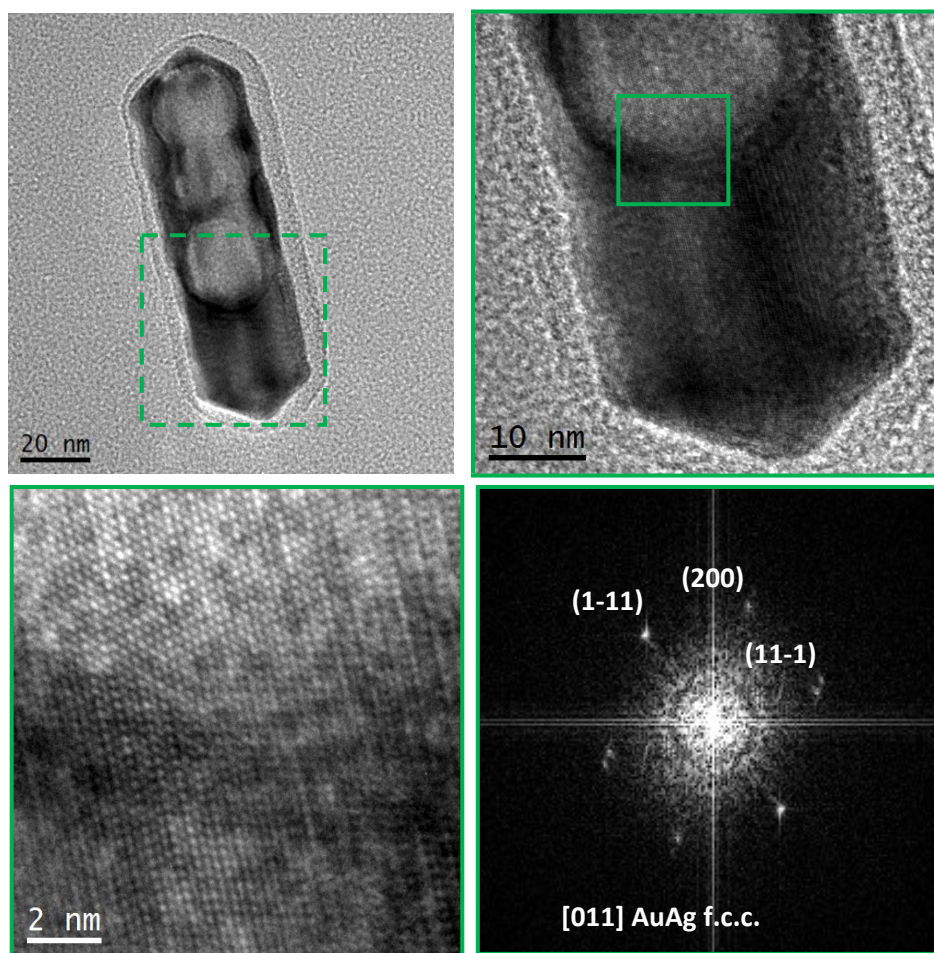
**Figure S3.** HRTEM images of AgNR showing details of the red squared area and its corresponding FFT pattern.



**Figure S4:** TEM images, particle size distribution and UV-vis spectra of 4 (A-D) independent syntheses of Ag NRs.



**Figure S5:** HR-TEM of the decahedral seeds obtained in the presence of TA.



**Figure S6.** TEM and HRTEM images of a single AgAu hollow alloy NR showing details of the indicated areas in HRTEM images along with its FFT pattern.

## References

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