Supporting information

A simple and fast high-yield synthesis of silver nanowires

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Content

S1. Influence of the nature of AgCl

The first step in the growth of pentagonally twinned silver nanowires is the nucleation of pentagonally twinned silver nanoparticles. In our study we find that a key parameter to obtain a high yield of AgNWs is the use of freshly prepared AgCl. Silver chloride, in fact, is easily photoreduced under normal room illumination conditions into irregularly-shaped Ag nanoparticles[1] that lead to the formation of a high amount of by-products as indicated by a broadening of the transverse plasmon resonance of the wires at 377 nm and an increase in the overall extinction for $\lambda > 500$ nm (see Figure S1a).
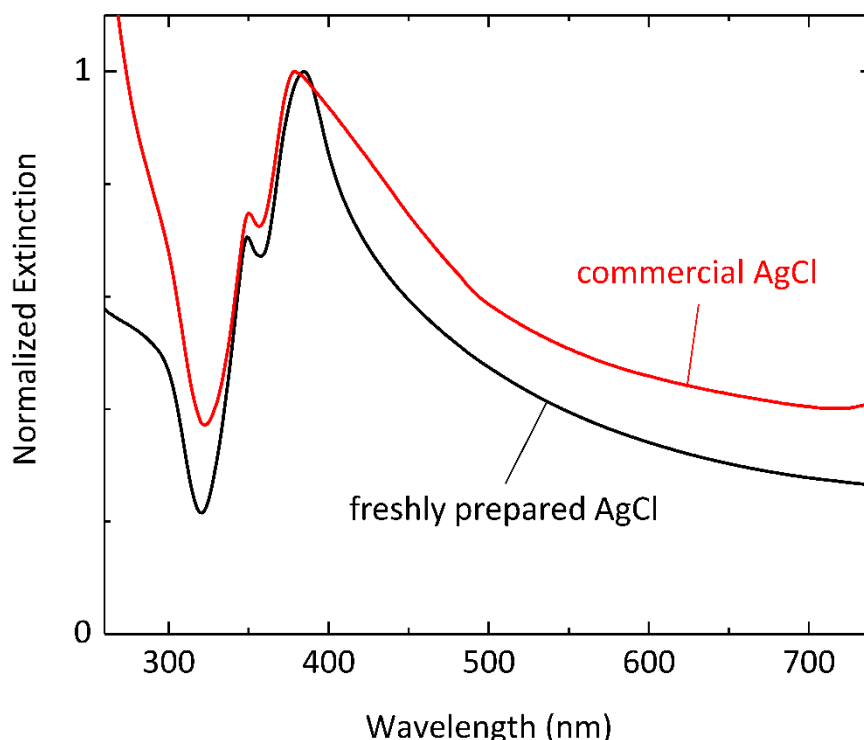

Figure S1a. Normalized extinction spectra of the product of two syntheses of AgNWs performed at 170 °C for 30 minutes using (black line) freshly prepared AgCl and (red line) stock AgCl (Alfa Aesar, 99.9%). Both syntheses have been performed in three-neck round bottom flasks closed with glass stoppers but not sealed.

To support our proposed correlation between the photoreduction of AgCl and the amount of by-products at the end of the process, we performed two syntheses of AgNWs by using freshly prepared AgCl and the same AgCl that has been aged for two days under ambient illumination. The used of aged AgCl, leads to an increase in the formation of by-products at the end of the synthesis, as highlighted by the increase in the FWHM of the peak as well as the residual extinction above 500 nm.
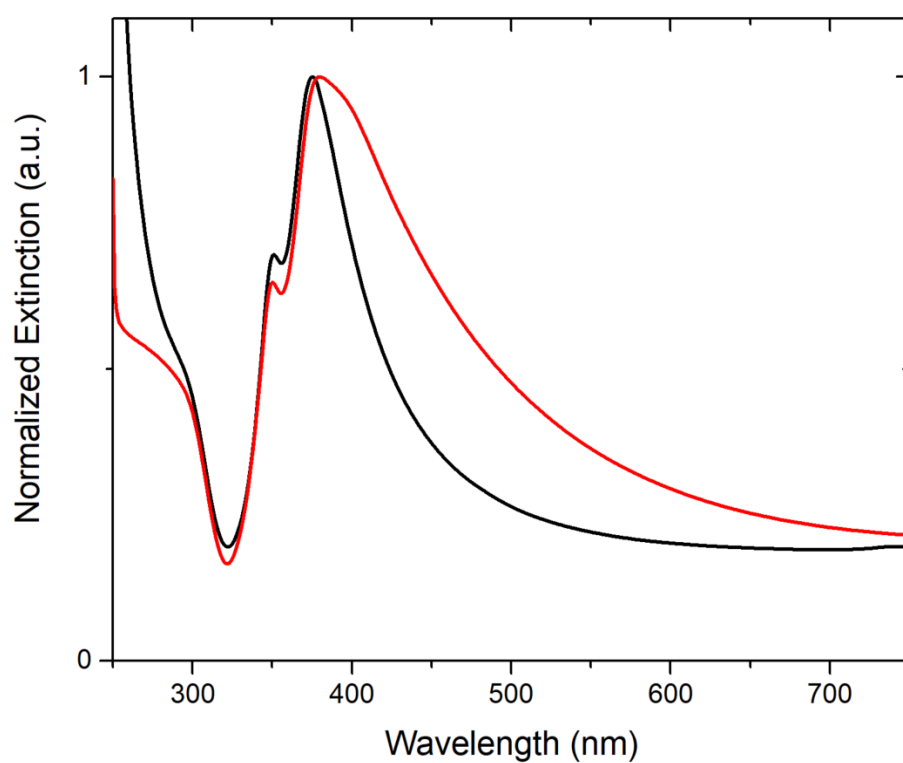
Figure S1b. Normalized extinction spectra of the product of two syntheses of AgNWs performed at 160 °C for 24 minutes using (black line) freshly prepared AgCl and (red line) same AgCl aged for 2 days under ambient light conditions.

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S2: Influence of the concentration of AgCl

Here we study how the concentration of AgCl influences the products in our synthesis. As can be seen in the supplementary video, a certain amount of unreacted AgCl sits at the bottom of the flask during the reaction, highlighting the fact that we are working in excess of this chemical. We therefore perform control experiments by decreasing the amount of AgCl used during the synthesis from the original 25 mg to 10, 5, and 0 mg (Figure S2). A lower AgCl amount results in an increase in the by-products at the end of the synthesis, as can be seen by the increase in the linewidth of the extinction peak and by the increase in the residual extinction above 500 nm.
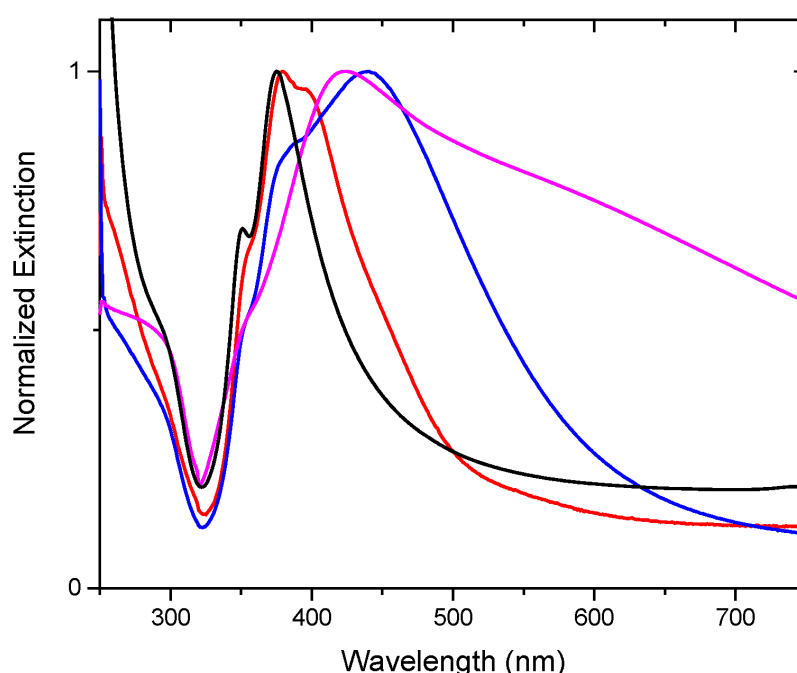

Figure S2. Normalized extinction spectra of the products of three syntheses performed at 160 °C for 24 minutes using (black) 25 mg of AgCl, (red) 10 mg AgCl, (blue) 5 mg AgCl, and (purple) 0 mg AgCl.

Interestingly, the spectra of the syntheses using 0, 5, and 10 mg of AgCl are qualitatively similar to the spectra of our standard synthesis after 16, 18, and 20 minutes, respectively (see Figure 1a of the main text), suggesting that a lower AgCl concentration slows down the reaction kinetics. A slower reaction rate at lower AgCl concentrations may be linked to the role of chloride anions in minimising the formation of irregularly shaped particles and promoting the directional transformation of twinned silver nanoparticles into 1-D nanowires[2].

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S3: Relationship between UV-Vis spectra and reaction yield

Here we show that if the relationship between the structural and optical properties of AgNWs is known, UV-Vis can provide statistical insights on the yield of a silver nanowires synthesis, whereas both SEM and TEM can be misleading.

We first performed 2D FDTD electromagnetic calculations of the optical extinction of an infinite silver nanowire with a width comparable to our experimentally synthesized ones. An important factor in modeling the optical properties of AgNWs is their pentagonally-twinned structure: the peak typically visible at ~350 nm can in fact only be reproduced assuming a (quasi) pentagonal cross-section. In our simulation, we have optimized the radius of curvature of the nanowire edges (see Figure S3a) to avoid spurious extinction peaks due to finite meshing and multipole resonances. Furthermore, the simulated wire has a PVP shell thickness[3] of 5 nm modeled as a dielectric with a refractive index of 1.56.
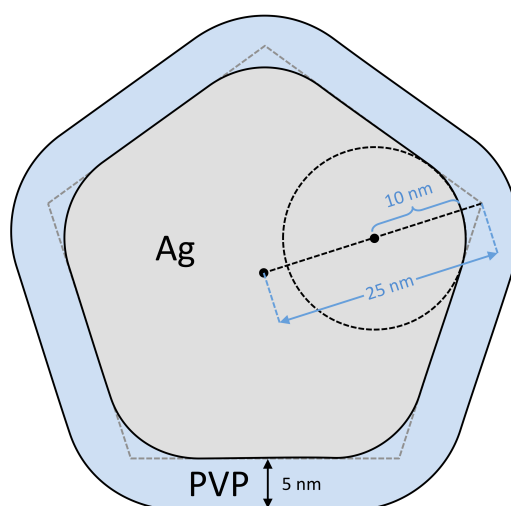

Figure S3a. Schematic of the nanowire cross-section used for the FDTD simulation.

The simulations show that the extinction of a single silver nanowire is ~3x10^{-13} m^2. Our final AgNW solution has an optical density of ~40 at the plasmon resonance of the silver nanowires (see Figure S4). Such a high value corresponds to the extinction of ~10^{12} nanowires. On the other hand, size distributions and yield analyses performed using SEM or TEM pictures are typically based on samples sizes smaller than ~100 nanowires[4–6]. This means that, if the spectral information can be correlated to the structure of the wires, a single UV-Vis spectrum measured on a 100x diluted silver nanowires solution, contains as much information as ~<u>10^{10}</u> SEM or TEM pictures.

Moreover, it is a well-known effect that metal nanoparticles tend to aggregate and self-assemble upon drying on SEM and TEM substrates, due to minimization of surface energy, as can be seen in Figure S3b.
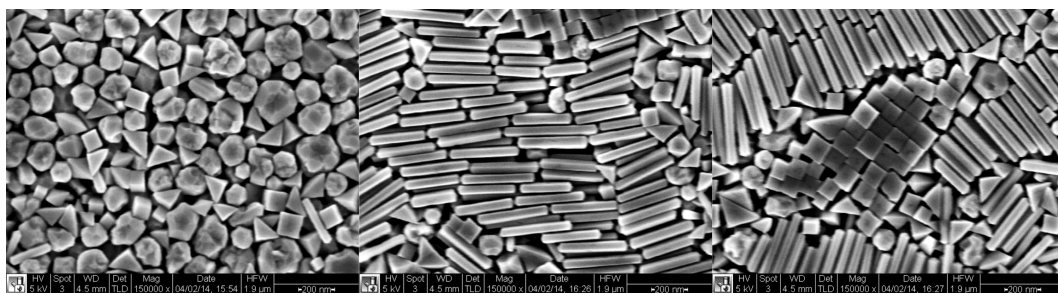
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Figure S3b. SEM images of palladium nanoparticles imaged over different areas of the same SEM sample.

These problems of undersampling and shape selection in metal nanoparticles dried on SEM or TEM substrates are particularly worrying when only high magnification pictures are shown, as often happens in the literature. We therefore argue that, if a clear understanding of the optical properties of AgNWs can be obtained, our UV-Vis spectroscopy approach offers statistically more valuable information than electron microscopy.

The spectrum of our as-synthesized wires shows a FWHM and a residual extinction above 500 nm which are the closest to the simulated one, indicating a minimal level of by-products even in the absence of any purification step (see Figure 2 in the main text).

It is worth noting that our FDTD simulations accurately reproduce the measured extinction baseline throughout the 500-800 nm range at ~20% of the AgNWs peak, which cannot therefore be due to residual impurities in our synthesis.

To further prove the direct correlation between the presence of synthetic by-products and the width of the plasmon resonance peak of the silver nanowires, we performed an additional experiment in which we first synthesized AgNWs according to our procedure and then purified them via one step of centrifugation and redispersion in water. The comparison between the UV-Vis spectra of these two solutions is shown in Figure S3c below.
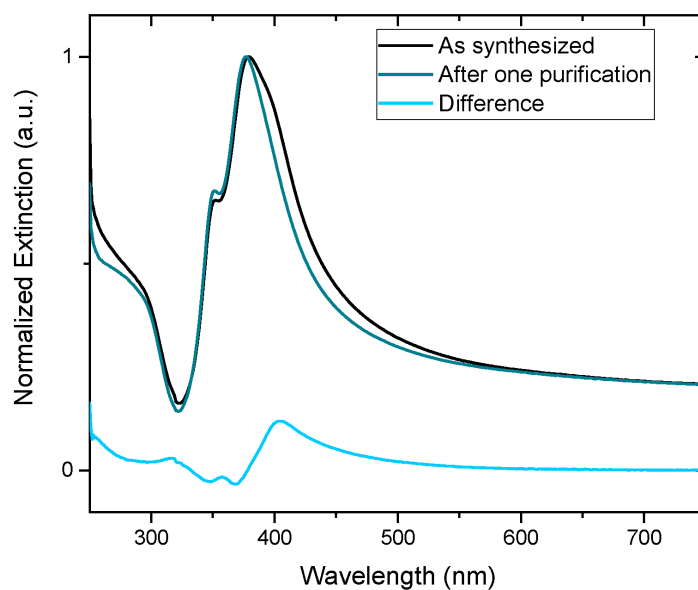
Figure S3c. Normalized extinction spectra of the as-synthesized product (black) and of the product after one cycle of purification (dark cyan). Extinction spectrum of the difference between the as-synthesized and the one time purified (light cyan).

After one cycle of purification, the FWHM of the resonance peak of the silver nanowires decreases and the shoulder at ~400 nm disappears due to the removal of by-products. Strikingly, the difference spectrum is similar to the one of the product of our synthesis after 6 minutes from the addition of $AgNO_3$ (see the first spectrum in Figure 1a of our manuscript), corresponding to spherical Ag nanoparticles (see SEM picture in Figure 3a of our manuscript). Silver nanoparticles, in fact, are known to show extinction spectra with maxima above ~400 nm.[7]

S4: Increase in optical density during the reaction

The formation of AgNWs is accompanied by a drastic increase in the optical density of the solution.
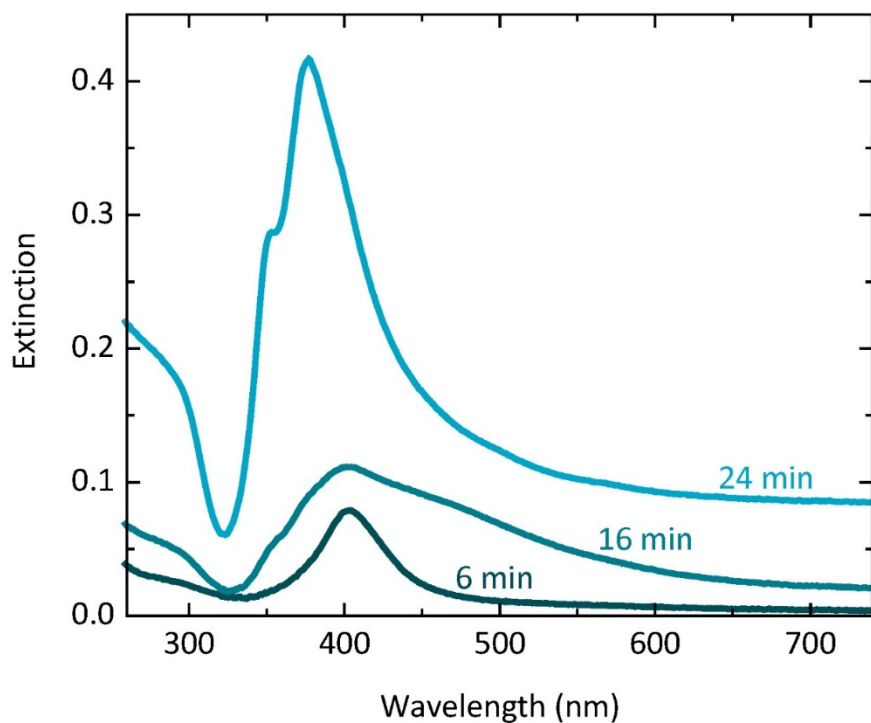

Figure S4. Non-normalized extinction spectra of the synthetic product during the AgNWs synthesis at 160 °C sampled at different times from the addition of $AgNO_3$. The spectra are measured over aliquots diluted 100x in water.

S5: Optical density: comparison with literature

The high yield of our synthesis is confirmed by comparing the optical density of our final solution with the one reported for the large-scale synthesis of nanowires of similar diameters by Sun et al. (Chem. Mater, 14, 4736-4745 (2002))[8]. Unfortunately, most synthetic papers do not report the optical density of the as-prepared AgNWs solutions before any purification step, therefore preventing any further quantitative comparison with the literature.
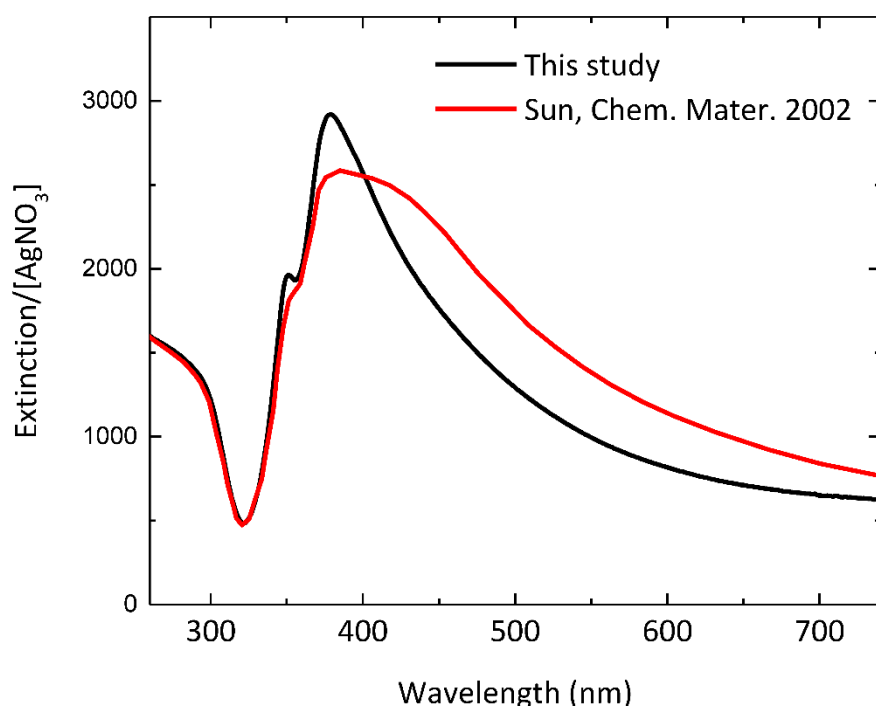

Figure S5. Extinction spectra normalized by the concentration of silver nitrate expressed in molarity of the initial products of two AgNWs syntheses: (black line) AgNWs synthesized in this study after 30 minutes of heating at 160 °C and (red line) AgNWs synthesized by Sun et al. (Chem. Mater, 14, 4736-4745 (2002))[8] after 60 minutes of heating at 160 °C. Both spectra are corrected for the dilution factors (100x in our case, 30x in the cited paper) and for the molarity of the $AgNO_3$ used (32 mM in our case, 23 mM in the cited paper).
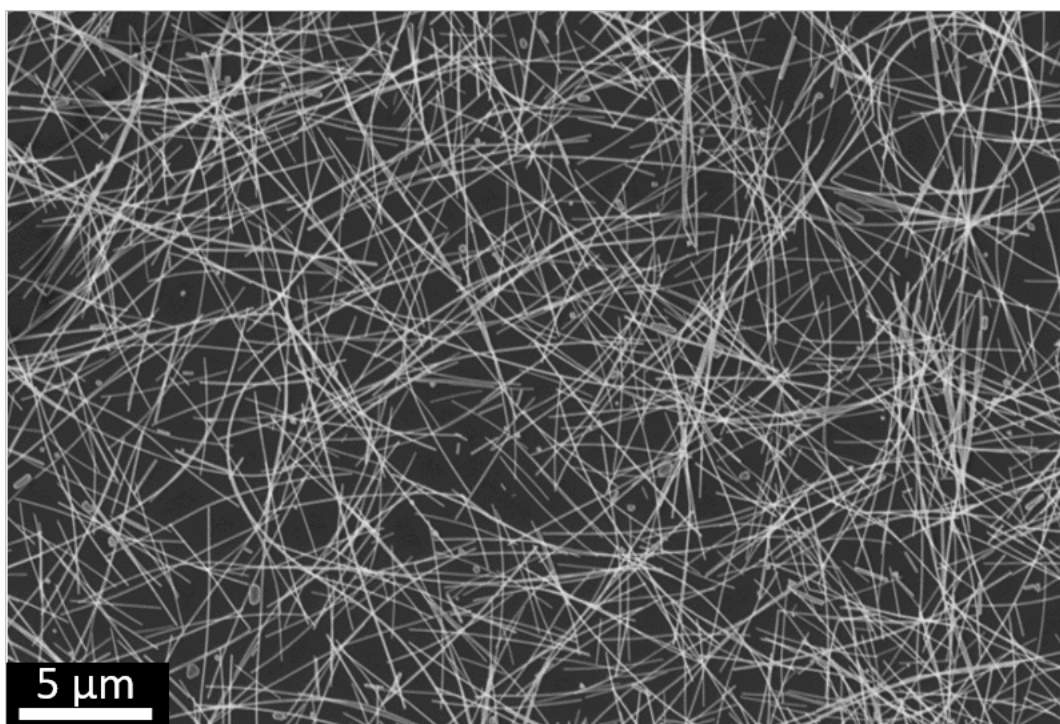
S6: Size distribution

Figure S6a. Representative SEM picture of silver nanowires obtained with our synthesis. The SEM sample has been prepared without any purification step and by diluting the final solution of AgNWs by 100x times.
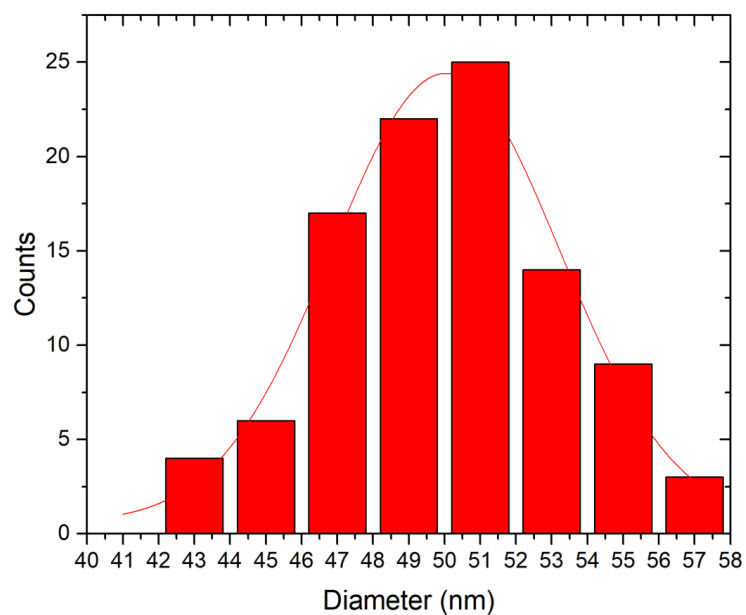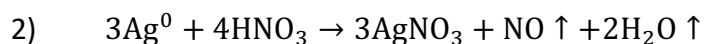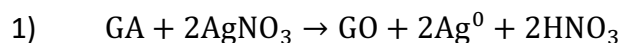

Figure S6b. Size distribution of the diameter of our AgNWs measured over 100 wires.

S7: Pressure build-up during the synthesis

To calculate the pressure buildup, we have to take into account the main chemical reactions that take place during the synthesis[9], as reported in the main text.

1) $GA + 2AgNO_3 \rightarrow GO + 2Ag^0 + 2HNO_3$

2) $3Ag^0 + 4HNO_3 \rightarrow 3AgNO_3 + NO \uparrow + 2H_2O \uparrow$

Where GA is glycolaldehyde and GO is glyoxal. These equations state that for each mole of $AgNO_3$ a maximum of 0.75 moles of gas can be developed. In our synthesis we use 110 mg (= 6.84×10^{-4} moles) of $AgNO_3$, which therefore correspond to 4.86×10^{-4} moles of gas.

We perform our synthesis in a 25 ml three-neck round bottom flask with a total volume of 47.5 mL when all the caps are inserted. As the volume of the ethylene glycol solution is 20 mL, 27.5 mL of dead volume are left for the development of the gasses. Assuming ideal gas behavior and negligible contributions from atmospheric H_2O and NO, 4.86×10^{-4} moles of gas in 27.5 mL give rise to an overpressure in our reaction vessel of ~0.64 bar. It is important to note that this pressure build-up is the maximum that can be reached in a sealed vessel, if all the nitric acid developed during the synthesis decomposes into gaseous products. A pressure increase of 0.64 bar is perfectly sustainable by our 25 ml three-neck round bottom flask, as most standard round bottom flasks can easily sustain 1 bar overpressure.

S8: Control of by-products by varying the reaction volume

Our standard synthesis is carried out in a nominal 25 mL three neck round bottom flask, which has a real volume of 47.5 mL when all the caps are inserted. We typically perform our synthesis in 20 mL ethylene glycol, which leaves 32.5 mL of dead volume for gas expansion. We performed our synthesis by varying the dead volume to 22.5 mL and to 32.5 mL.
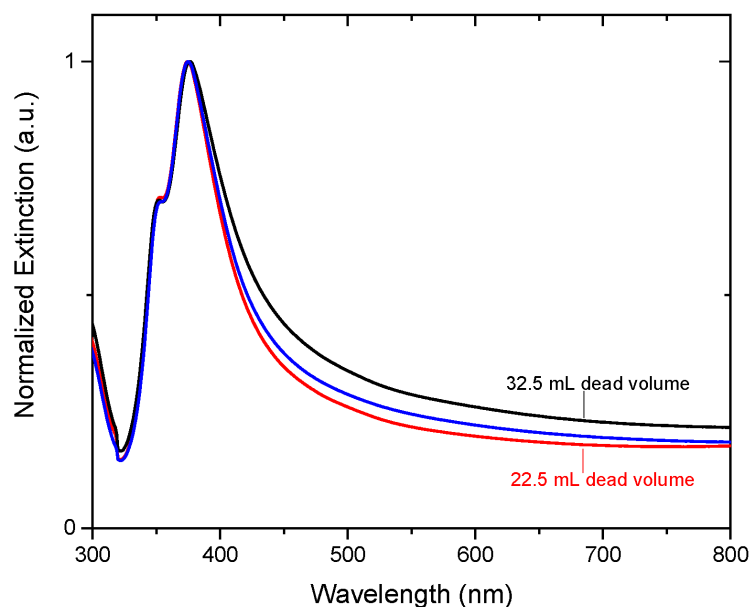

Figure S8. Normalized extinction spectra for the synthesis of AgNWs reported in our manuscript performed by varying the dead volume in the reaction vessel. (Black) 32.5 mL of dead volume. (Blue) Standard synthesis with 27.5 mL of dead volume. (Red) 22.5 mL of dead volume.

When we increase the dead volume in which gasses can expand, the reaction leads to an increased amount of by-products (black curve), i.e. and increase in the residual extinction above 500 nm and in the linewidth of the peak. When we perform the reaction by decreasing the amount of dead volume, we see a lower formation of by product, i.e. a decrease in the residual extinction above 500 nm and in the linewidth of the peak.
These finding are in agreement with our proposed reaction mechanism.

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