SUPPORTING INFORMATION

1. Experimental section

Synthesis of ultra-long silver nanowires

In a 100 ml three neck bottom flask, 37 ml of 1,2-propanediol is heated at 140 °C (oil bath temperature) for 45 minutes. Then, 5 ml of a solution of HCl diluted in 1,2-propanediol (3 mM) is quickly added. After 10 min, 15 ml of $AgNO_3$ dissolved in 1,2-propanediol (94 mM) and 15 ml of PVP-1300K dissolved in 1,2-propanediol (147 mM) are simultaneously injected drop-by-drop (45 ml/h) into the solution. The resulting silver concentration is then 19.6 mM. The silver concentration can be tuned by varying the overall volume of the reaction medium. The stirring rate was set at 100 rpm during the entire process and the reaction time was set at 1 h. Once the reaction is completed, the flask is cooled down to room temperature with an ice bath. Finally, a purification step consisting of the precipitation of the NWs with the addition of 40 ml of acetone and the removal of the supernatant is applied to the final solution. This step is repeated three times and the product is redispersed in 20 ml of ethanol.

Mass concentration of the AgNWs solution

The calculation of the yield of nanowires vs nanoparticles was performed by measuring the concentration of Ag^+ in the batches by using inductively couple plasma (ICP) spectrometry. 10 ml of the solution is mixed with 45 ml of acetone. Once the silver nanowires precipitates, the supernatant is removed. The solid phase is then redispersed in a mixture of water/acetone (v/v 10/35) and centrifuged for 10 minutes at 4000 rpm. This step is repeated three times and the silver nanowires are finally redispersed in 20 ml of ultra-pure water. A few millilitres of the previous solution are then redispersed in a mixture of HNO_3 and water for analysis.

Nuclear magnetic resonance (NMR) investigation

The active species derived from the oxidation of 1,2 propanediol were investigated by heating the solvent at 140°C overnight in the presence of silver nitrate (19.3 mM) under inert atmosphere (Ar bubbling). In order to maximize the signal of oxidized species against the polyol, the volatile species were trapped in a cold trap before NMR analysis, similar to the process developed by Takahashi et al.[1]

^1H (300 MHz) and ^{13}C-{^1H} (75 MHz) NMR spectra were recorded on a Bruker DPX-300 spectrometer. ^1H and ^{13}C assignments were confirmed when necessary with the use of two dimensional ^1H-^1H COSY, ^1H-^{13}C-HSQC and ^1H-^{13}C-HMBC NMR experiments. All spectra were referenced internally to residual protio-solvent (^1H) or solvent (^{13}C) resonances and are reported relative to trimethylsilane (δ = 0 ppm). Chemical shifts are quoted in δ(ppm).

AgNW network deposition

Two sets of electrodes were performed on Roth glass (2.4 cm x 3.2 cm and thickness of 0.17 mm). One set of electrodes was performed by Mayer rod coating. 4 coatings steps of 50 µl of AgNW suspension (2 mg·ml^{-1}) were spread over the substrates in 4 orthogonal directions with a rod (RDS 10). Finally, a thermal treatment of 1 hour at 200 °C was applied. The second set of electrodes were performed by spray coating using the commercial spray coater Airbrush Infinity by Harder & Steenbeck (Norderstedt, Germany) integrated in an automated x-y moving system. The glass substrates are placed on a metallic plate that is heated constantly at 95 °C for direct evaporation of the solvents. The distance between the spray head and the substrate was fixed at 4.5 cm, the AgNW suspension concentration was 0.5 mg.ml^{-1}, the flow rate was 4 droplets per 20 seconds, the nitrogen gas pressure during spraying was 3 bar and the aperture of the airbrush nozzle was 0.4 mm. Depending on the sheet resistance desired, 2 cycles of 2 crossed passing (CP) to 4 CP were applied to deposit the solution.

One set of electrodes were fabricated on Corning glass substrates (2 cm x 2 cm and thickness of 1.1 mm) for in-situ thermal annealing analysis: the electrodes were deposited by Mayer rod coating. 4 coatings steps of 35 µl of AgNW suspension were spread over the substrates in 4 orthogonal directions with a rod (RDS 10). Finally, no thermal treatment was applied, and the electrodes were dried at room temperature.

Structural, electrical and optical characterization of the AgNW networks

200 µl of silver nanowire solution was mixed with 1.5 ml of ethanol and a few drops of this mixture were deposited onto a glass substrate that was subsequently dried in an oven set at 70 °C for 10 minutes. The substrate was then observed using SEM to visualize the configuration of the network. One drop of the same solution was deposited onto a carbon-coated copper grid, and TEM images were collected on a JEOL JEM-1400 Plus electron microscope operating at 120 kV.

The sheet resistance was measured using a four-point probe using a Lucas Labo Pro4 apparatus, with a device head composed of in-line mounted tungsten probe pins, separated by 1 mm, with a pin radius of 40 µm.

The transparency of the AgNW networks was measured using a UV-Vis-NIR spectrophotometer (Perkin Elmer Lambda 950) equipped with an integrating sphere. The beam of photons illuminated the specimens at normal incidence.

In-situ thermal annealing

The as-deposited transparent electrodes associated with different AgNW network densities were placed on a hot plate connected to a temperature controller (Eurotherm 3504). The electrical resistance was measured in situ by two probes connected to a Keithley 2400 source meter. Using LabVIEW software, the temperature of the hot plate was controlled and recorded as well as the electrical resistance. The electrical resistance was measured while the temperature was varied: a ramp of 5 °C/min from room temperature (~20 °C) to 400 °C was applied.

2. AgNW morphology characterization

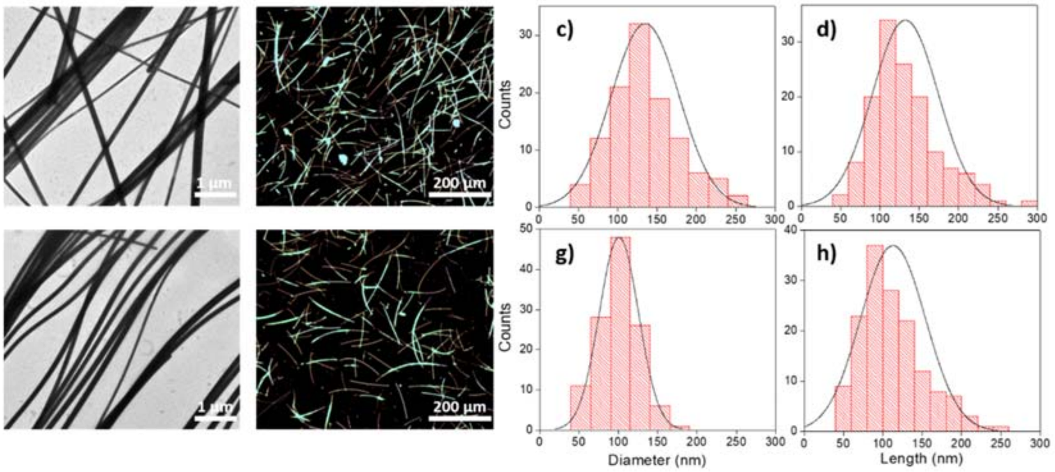

Fig. S1. TEM (first column) and optical (second column) dark field images of AgNWs synthesized with a silver concentration of 20.4 mM (a, b) and 19.3 mM (e, f) and their respective diameter and length distributions (c, d) and (g, h). Their average diameter and length values are d=135 ± 51 nm, L = 135 ± 43 µm (c, d) and d=114 ± 43 nm, L = 101 ± 25 µm (g, h).

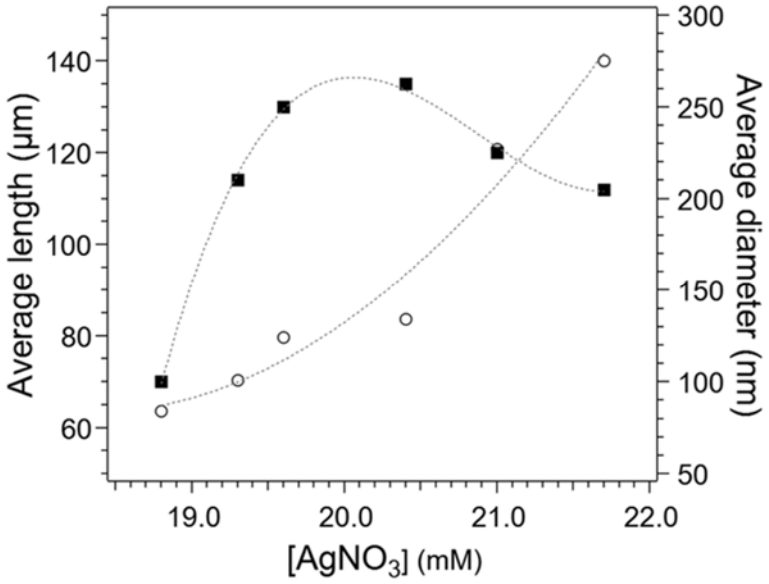

Fig.S2. Average length and diameter obtained as a function of the silver nitrate concentration used in the synthesis.

3. Insights into the growth mechanism of Ag nanowires in 1,2-propanediol

1D and 2D ^{1}H and ^{13}C NMR experiments confirmed the formation of acetone, characterized by a singlet at 2.2 ppm (C$\underline{H_3}$) in ^{1}H NMR and resonances at 207.0 ppm ($\underline{C}$=O) and 30.9 ppm ($\underline{C}$H$_3$C=O) in ^{13}C NMR, and of 2,2,4-trimethyl-dioxolane, characterized in ^{1}H NMR by a doublet at 1.27 ppm (-CH(C$\underline{H_3}$)), two singlets at 1.36 and 1.41 ppm (-C(C$\underline{H_3}$)$_2$)), two doublet of doublets around 3.92 and 4.05 ppm (C$\underline{H_2}$) and a multiplet at 4.22 ppm (C$\underline{H}$). Moreover, the ^{13}C NMR spectrum showed typical resonances detected at 27.2 and 25.9 ppm ((-C($\underline{C}$H$_3$)$_2$)), 18.6 ppm (-CH($\underline{C}$H$_3$)), 72.0 ppm (-$\underline{C}$H(CH$_3$)-O), 70.8 ppm (-$\underline{C}$H$_2$O) and 108.7 ppm (-O-$\underline{C}$(CH$_3$)$_2$-O) which is fully consistent with the formation of 2,2,4-trimethyl-dioxolane.[2] The propanal, difficult to trap experimentally, likely reacts with the metallic precursor yielding silver seeds with a decahedral multi-twinned structure.[3] AgCl seeds are also formed in the experimental conditions adopted. Both seeds were observed in the first stage of the synthesis and favor the anisotropic growth of the metal (FigS3(b) and (c)).

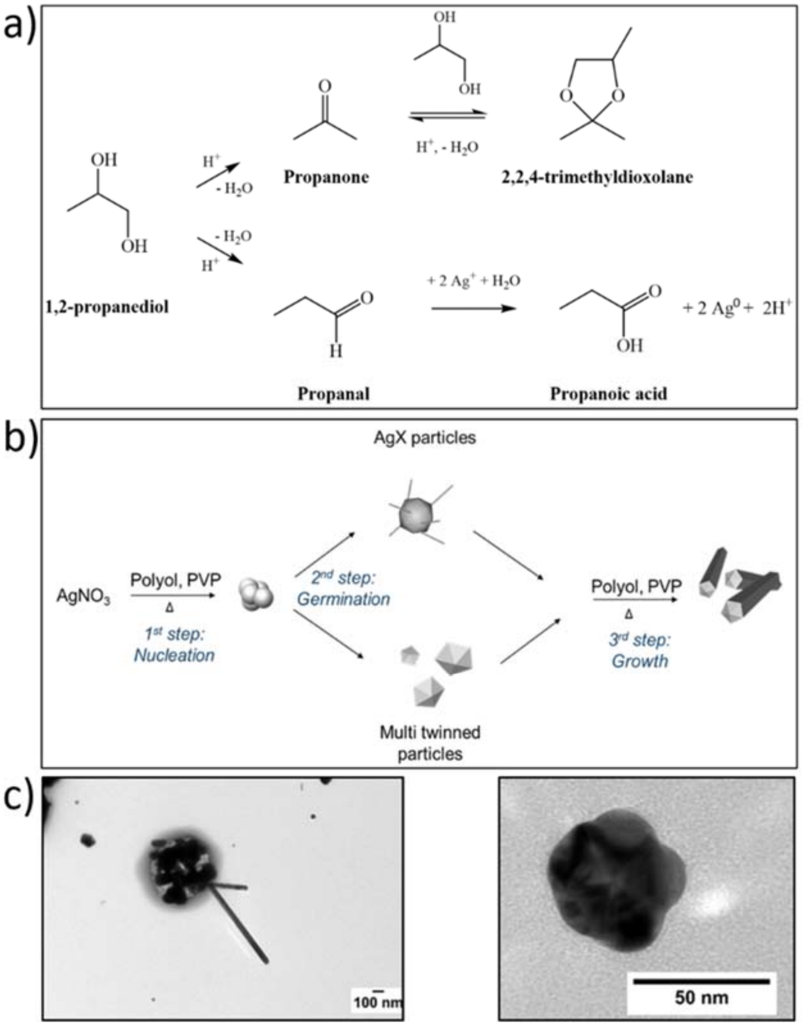

Fig. S3. a) Mechanism of 1,2 propanediol oxidation. b) Schematic of the possible pathways of silver nanowire growth. c) TEM images of AgCl (left) and Ag (right) seeds observed in the first stage of the synthesis.

4. Characterization and properties of AgNW networks

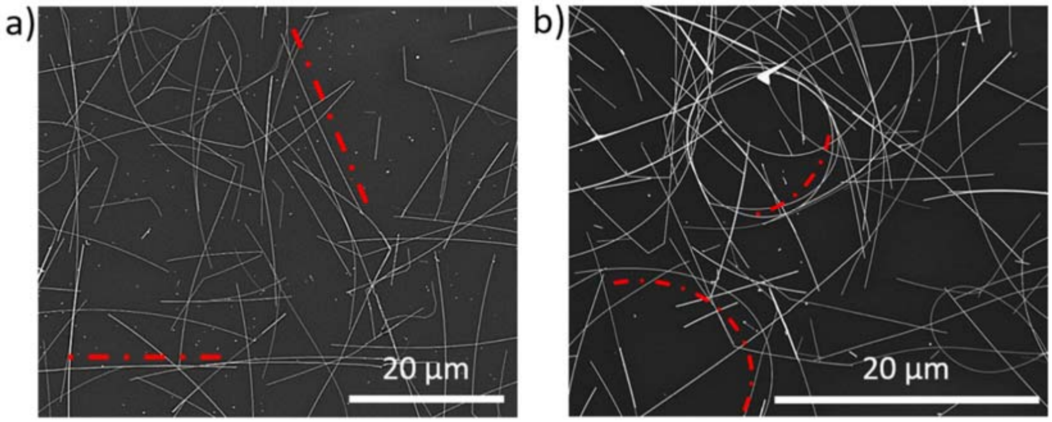

Fig. S4. Higher magnification SEM images of the AgNW networks deposited by (a) Mayer rod coating and (b) spray coating. The red lines highlight the curved and straight profile of the deposited nanowires.

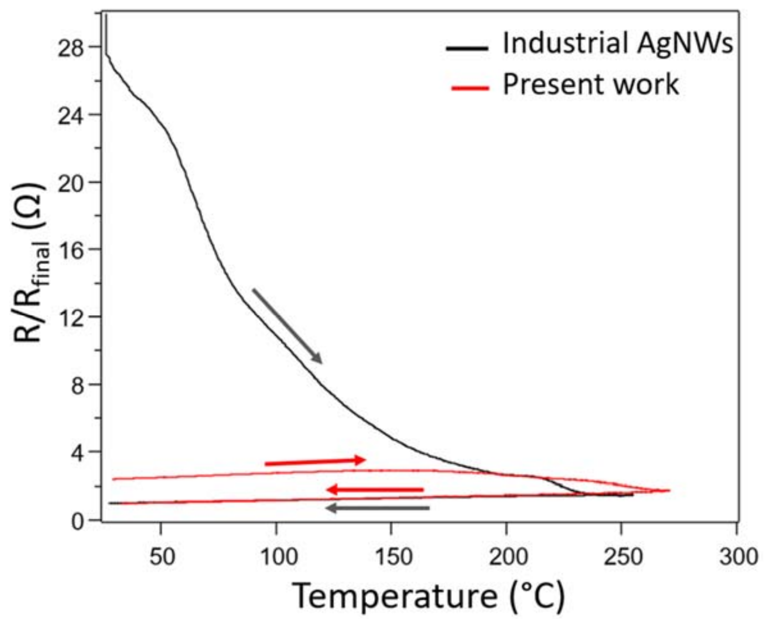

Fig. S5 Evolution of the relative electrical resistance (i.e. resistance divided by the final room temperature resistance) versus temperature of electrodes made with commercial AgNWs (black curve)[4] and with our as-synthesized 130 µm long AgNWs (red curve). An anneal up to the temperature at which the minimum resistance is reached was applied followed by a cool down to room temperature.

Fig. S6 shows how the thermal annealing profile of our networks depends on density and dimensions. The nanowires in Fig. S6(b) were synthesized using different $AgNO_3$ ratios. The shortest NWs (orange curve) have the highest resistance and the largest resistance drop with annealing. The longest NWs (green curve) have the lowest drop. Regarding the profile at temperatures greater than 300 °C, the largest diameter NWs (green curve) have the highest spheroidization temperature (350 °C), as would be expected. The spheroidization temperature also generally increases for sparser networks (Fig. S6(a)). Since silver has low emissivity, sparser networks, which have less silver, more effectively emit thermal radiation than denser networks. Thus films of sparser networks on top of a hotplate can radiate more heat away from the top surface and in turn have a lower steady state temperature.

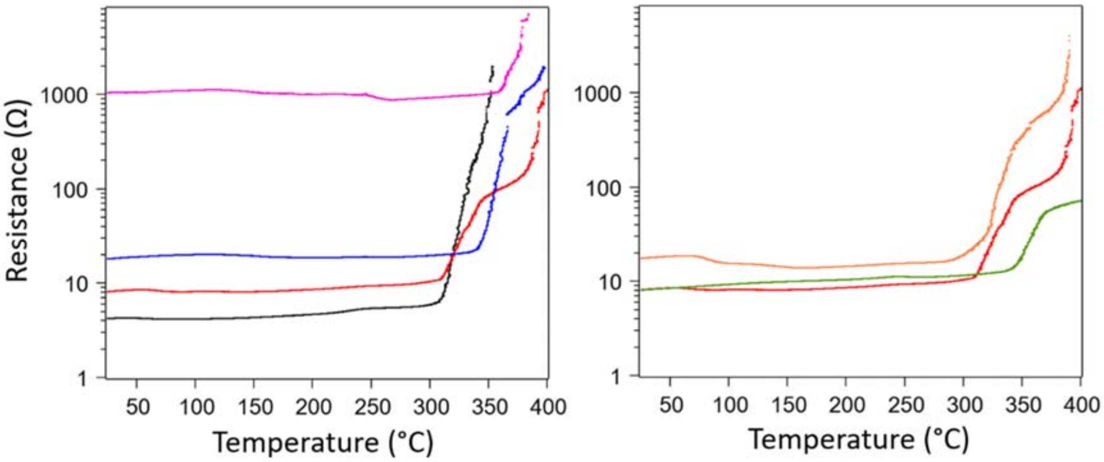

Fig.S6. Temperature evolution of the electrode resistance during a thermal ramp of 5 °C/min in air. a) The electrodes were made with 130 µm long nanowires with different network densities. The AgNW suspension was diluted to a concentration of 0.1 mg/ml (pink curve), 0.5 mg/ml (blue curve), 1 mg/ml (red curve) and 2 mg/ml (black curve). b) The electrodes were made with three types of nanowires: d=135 ± 51 nm, L = 135 ± 43 µm (green curve), d =124 ± 25 nm, L = 130 ± 36 µm (red curve), and d=114 ± 43 nm, L = 101 ± 25 µm (orange curve). All AgNW suspensions were diluted to a concentration of 1 mg/ml.

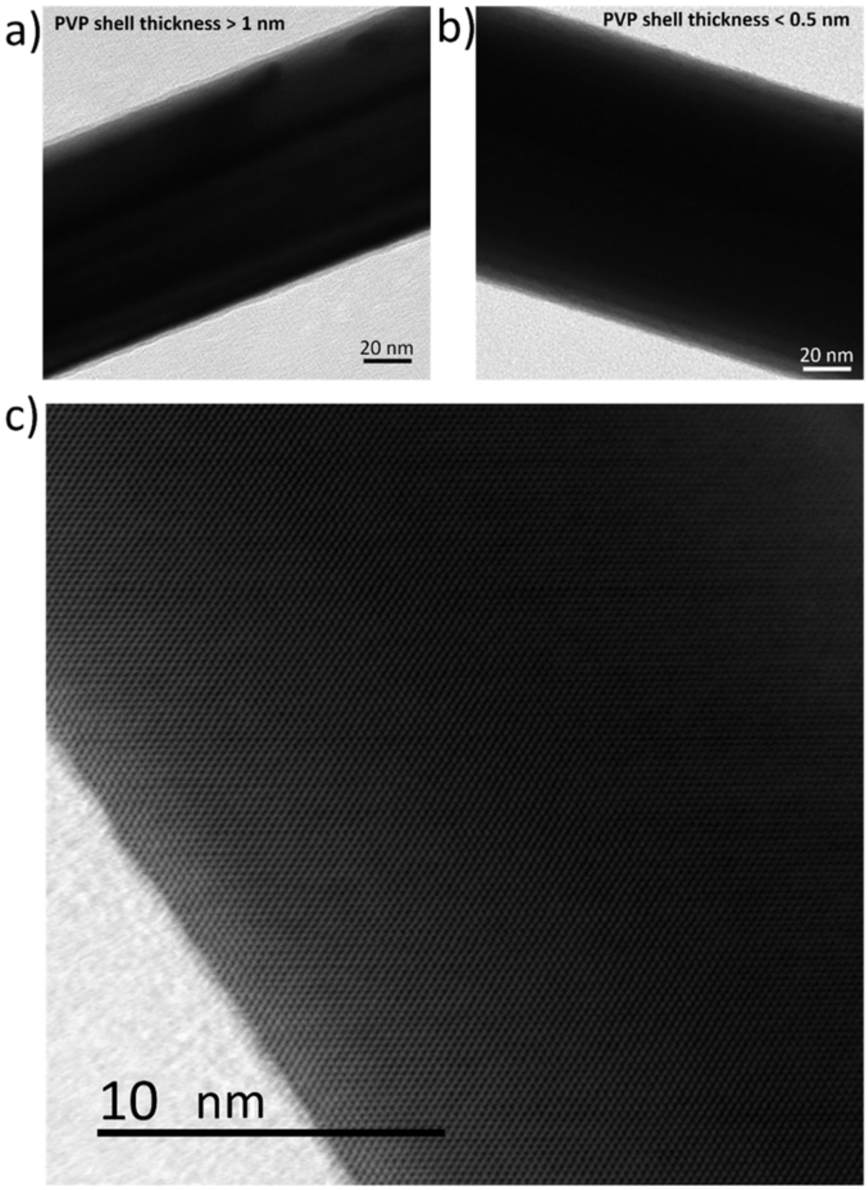

Fig. S7 TEM images evidencing the PVP shells on a) commercial AgNWs purchased from ACS Materials (Pasadena, CA) and b) our AgNWs. c) Atomic resolution microscopy (ARM) image of our nanowire shows minimal PVP on the surface.

References

1 K. Takahashi, S. Yokoyama, T. Matsumoto, J. L. Cuya Huaman, H. Kaneko, J.-Y. Piquemal, H. Miyamura and J. Balachandran, *New J. Chem.*, 2016, **40**, 8632–8642.
2 Y. Senda, J.-i. Ishiyama, S. Imaizumi, *Bull. Chem. Soc. Jpn*, 1977, **50**, 2813-2814.
3. V.S. Santosh, K. Kondeti, U. Gangal, S. Yatom, P. J. Bruggeman, *J. Vac. Sci. & Technol. A*, 2017, 35, 061302.
4. M. Lagrange, D. P. Langley, G. Giusti, C. Jiménez, Y. Bréchet and D. Bellet, *Nanoscale*, 2015, **7**, 17410–17423.