Supporting information

Spray-assisted Alignment of Layer-by-Layer Assembled Silver Nanowires: A General Approach for the Preparation of Highly Anisotropic Nano-composite Films

Hebing Hu,[a] *Matthias Pauly,*[a,b*] *Olivier Felix,*[a] *and Gero Decher*[a,b,c,d*]

[a] Institut Charles Sadron, CNRS (UPR22), 23 rue du Loess, F-67034 Strasbourg, France

[b] Université de Strasbourg (Faculté de Chimie), 1 rue Blaise Pascal, F-67008 Strasbourg, France

[c] International Center for Frontier Research in Chemistry, 8 allée Gaspard Monge, F-67083 Strasbourg, France

[d] Excellence Cluster "Nanostructures in Interaction with their Environment" (LabEx NIE), 23 rue du Loess, F-67034 Strasbourg, France

Corresponding authors email: matthias.pauly@ics-cnrs.unistra.fr; decher@unistra.fr

S-I/ Experimental Section

Chemicals and Materials

Poly(ethyleneimine) (PEI, $\overline{M_n} \approx 60{,}000\ g/mol$), poly(sodium 4-styrenesulfonate) (PSS, $\overline{M_w} \approx 70{,}000\ g/mol$), poly(allylamine hydrochloride) (PAH, $\overline{M_w} \approx 15{,}000\ g/mol$), poly(vinylpyrrolidone) (PVP, $\overline{M_w} \approx 40{,}000\ g/mol$), silver nitrate and glycerol were purchased from Sigma-Aldrich (Saint Quentin Fallavier, France). Sodium chloride was purchased from Carl Roth GmbH (Karlsruhe, Germany). All the chemicals were used without further purification. The aqueous solutions were prepared with ultrapure water (resistivity = 18.2 MΩ.cm, Milli-Q Gradient system, Millipore, Molsheim, France).

PEI solutions were freshly prepared by direct dissolution of 2.5 mg/mL of the polymer in ultrapure water. PSS solutions were prepared in NaCl solution (0.5 M) at a concentration of 0.62 mg/mL. PAH solutions were prepared in NaCl solution (0.5 M) at a concentration of 0.29 mg/mL.

Synthesis of Silver nanowires.

Uniform Ag nanowires were prepared following a previously published method.[1,2] 1.76 g of PVP, $\overline{M_w} \approx 40{,}000\ g/mol$) were added into 57 mL of glycerol in a round bottom flask and the solution was kept at 90°C under stirring till a homogeneous solution was obtained. After cooling down to room temperature, 0.47 g of $AgNO_3$ was added to the solution. Then a NaCl solution (17.7 mg of NaCl dissolved in 0.15 mL of ultrapure water and 3 mL of glycerol) was added to the reaction mixture. The solution was heated from room temperature to 210°C in 20 minutes while stirring. When the temperature reached 210°C, the heating was stopped. 60 mL of ultrapure water was added and the solution left to return to room temperature. The solution was kept undisturbed for 1 week and the sediment at the bottom of the flask was collected carefully. The obtained Ag nanowires were carefully washed 10-15 times with Milli-Q water by centrifugation at 2000 rpm for 30 min. Finally, the products were suspended in 170 mL of water.

The concentration was found to be 1.20 mg/mL by freeze drying and weighing a known volume of suspension.

Film build-up by spraying.

Silicon wafers and glass slides were cleaned thoroughly with ethanol and Milli-Q water. Prior to use, each substrate was activated for 3 min by plasma treatment.

For film build-up, the substrates placed vertically were first orthogonally sprayed with the PEI solution for 10 seconds using spraying bottles followed by rinsing with pure water for 10 seconds.

An aqueous suspension of silver nanowires (0.12 mg/mL) were deposited on the PEI-coated substrates (either glass slides or silicon wafers) for 200 seconds (unless otherwise specified). We used a home-made spraying system, which includes a gas flow controller to adjust the air flow rate (model Red-Y, Voegtlin, Aesch, Switzerland), a liquid handling pump (model M50, VICI, Schenkon, Switzerland), and 2-fluid nozzles (internal diameter: 300 μm, Spraying Systems, Wheaton, Ill). The nozzle was held at a distance of 1 cm from the substrate. The liquid flow rate was set to 1 mL/min and the air flow to 30 L/min, which produces a cloud of droplets with a diameter in the range of 5 – 20 μm as determined by Phase Doppler Interferometry (PDI, data not shown here). The angle between the spray cone main axis and the receiver substrate was 15°. The deposition of AgNW was followed by a rinsing step with water for 100 seconds using an equivalent nozzle fed with air at 25 L/min and water at 10 mL/min. Finally, the substrate was dried using air flow.

Note that spray droplets may present a substantial health risk when inhaled or when brought in contact with skin, especially when spraying polymer solutions or nanoparticle suspensions. Spraying should only be carried out in well ventilated environments and any accidental exposure to any spray through the lung or through the skin should be strictly avoided.

For AgNW multilayer buildup, a polyelectrolyte multilayers spacer was deposited between each AgNW layer using air-pump spray cans (Roth, Lauterbourg, France). Each polyelectrolyte was sprayed for 10 seconds, followed by a rinsing step with water for 10 seconds. A PEI/$(PSS/PAH)_5$/PSS/PEI multilayer was deposited on the PEI/AgNW films, followed by grazing-incidence spraying of a subsequent AgNW layer in the same conditions as those used for the first layer, and the whole process can be repeated several times. The architecture of all multilayer samples discussed here can therefore be denoted as PEI/AgNW/$[PEI(PSS/PAH)_5PSS/PEI/AgNW]_{n-1}$, n indicating the number of individual nanowire layers.

Characterization of NWs and NW assemblies.

Transmission electron microscopy (TEM) was performed at 200 kV with a Tecnai G2 (FEI) microscope and an Eagle 2 k (FEI) ssCCD camera. Scanning electron microscopy (SEM) was performed with a JEOL 6700F equipped with a field emission gun operating at an accelerating voltage of 3 kV. The image analysis was performed using ImageJ. The orientation analysis was done with OrientationJ, a plugin developed for ImageJ, which is based on the analysis of the structure tensor in a local neighborhood (see Figure S2 for a detailed description of the orientation analysis procedure). UV-Vis spectra were recorded with a Cary5000 spectrophotometer equipped with a Glan-Taylor polarizer. The measurements were done through a 5-mm diameter circular hole in a cover mask centered on the area of the substrate where the orientation is the highest.

S-II/ Nanowire size distribution

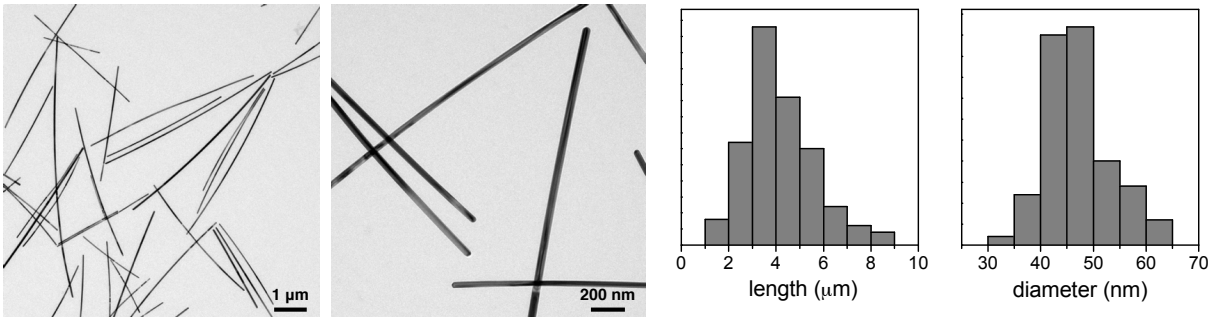

Figure S1. TEM images of silver nanowires and the corresponding length and diameter distribution.

The nanowires have been imaged by TEM in order to measure their size distribution. This distribution has been determined on more than 100 nanowires in order to get a representative statistic. Nanowires have a diameter of 47 ± 6 nm and a length of 4.2 ± 1.5 µm.

S-III/ Analysis of the nanowire orientation

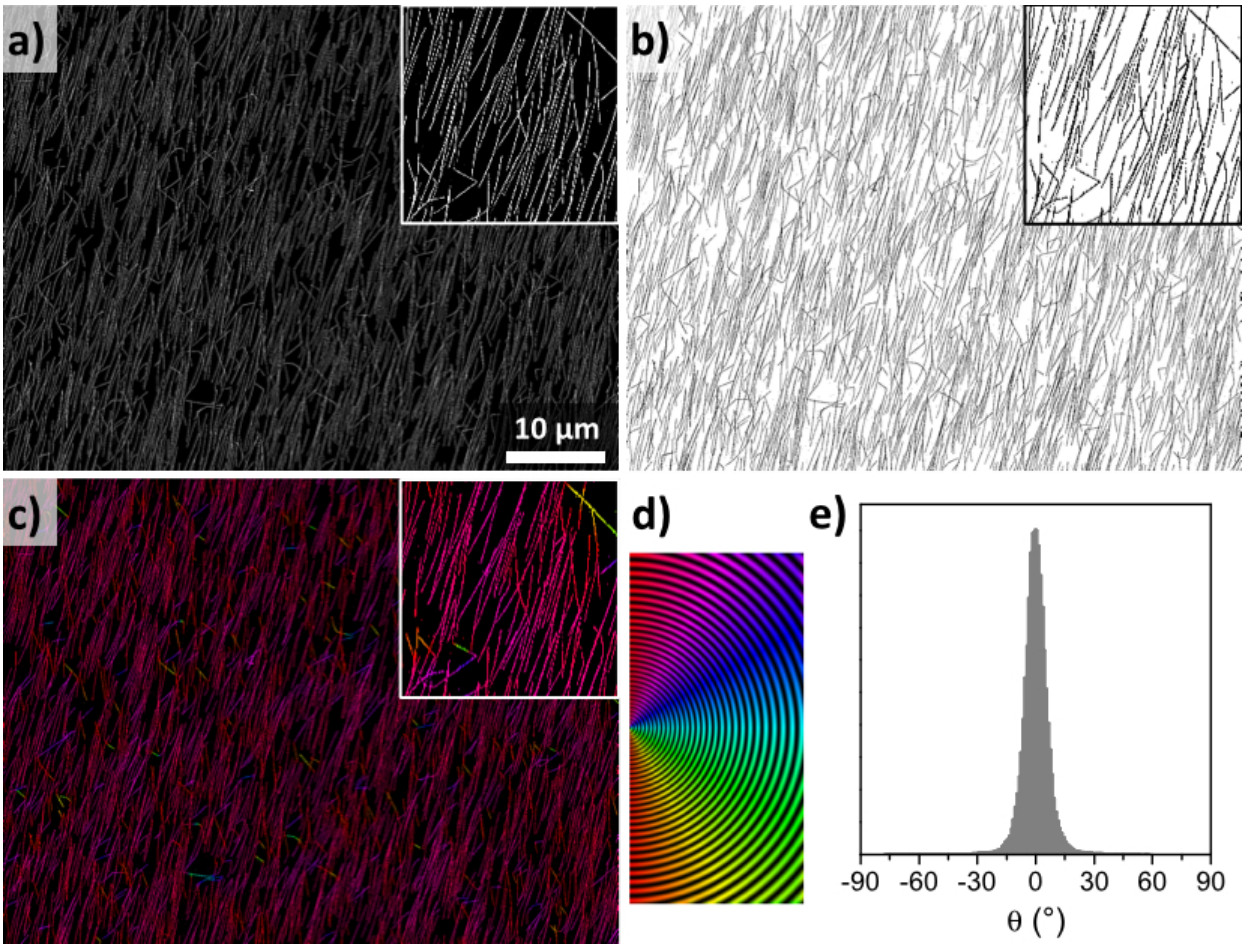

Figure S2. a) Original SEM picture. b) Same picture after binarization. c) Color-coded picture as given after applying the OrientationJ plugin. d) Color-code for the orientation. e) Angle distribution extracted from the image analysis. The insets are zooms of the corresponding main pictures.

In order to extract the distribution of orientation of the nanowires with respect to the spraying direction, the plugin OrientationJ for ImageJ has been used.[3] Although it has been originally developed for the analysis of optical micrographs of biological tissues or cells, this tool can be readily used for the analysis of electron microscopy pictures. The analysis, which is based on the computation of the local structure tensor in the local neighborhood of each pixel, is applied to the original SEM picture (Figure S2a) which had been previously binarized (Figure S2b). As a result, an orientation angle is given for each pixel, and a color-code which represents each angle

by a color (Figure S2d) is used to build Figure S2c. Finally, the angle distribution can be extracted (Figure S2e). The distribution is non-weighted (i.e. 1 pixel = 1 count), but the pixels for which the values of the coherency or the energy are lower than 20% have been ignored. Indeed, these pixels are often artifacts, for instance noisy pixels or located at edges and corners.

S-IV/ Optical properties of a disordered thin film

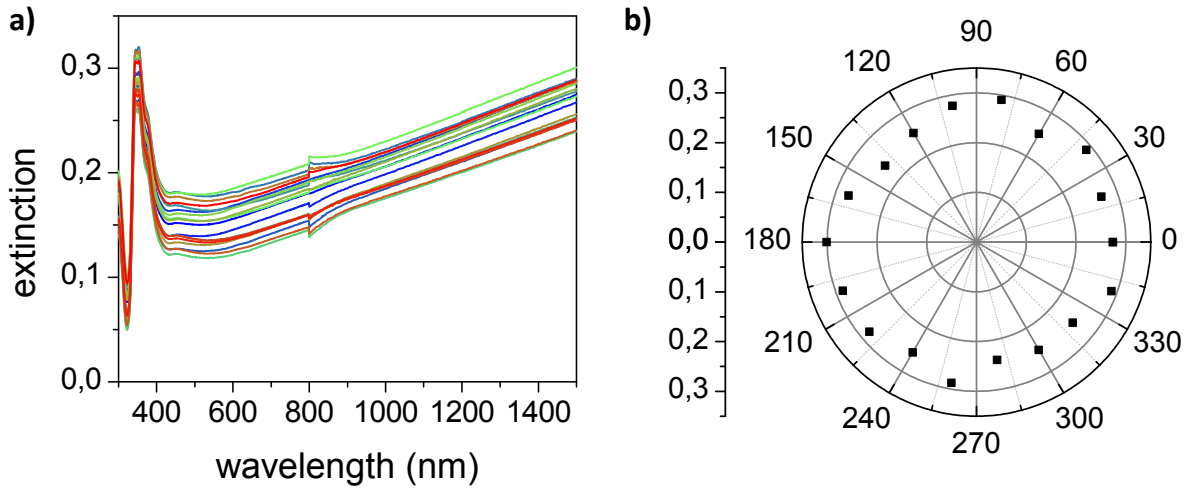

Figure S3. a) Extinction spectra for different light polarization angles ϕ measured on a nanowire thin film prepared by drop-casting in which the nanowires show no specific orientation. The polarization angle has been varied from 0° to 360° with a spectrum taken every 20°. b) Polar plot of the extinction at 1500 nm as function of the polarization angle ϕ.

The extinction spectra of the disordered thin film do not depend on the polarization angle, as it is expected for an isotropic nanoparticle assembly. This is reflected in the circular shape of the polar plot of the extinction in the NIR, in contrast to the typical shape observed for oriented samples (see Figure 3c in the main manuscript). The discontinuities in the spectra at 800 nm are artifacts due to the change of grating in the spectrometer.

S-V/ Reflected intensity on crossed-polarized optical micrographs

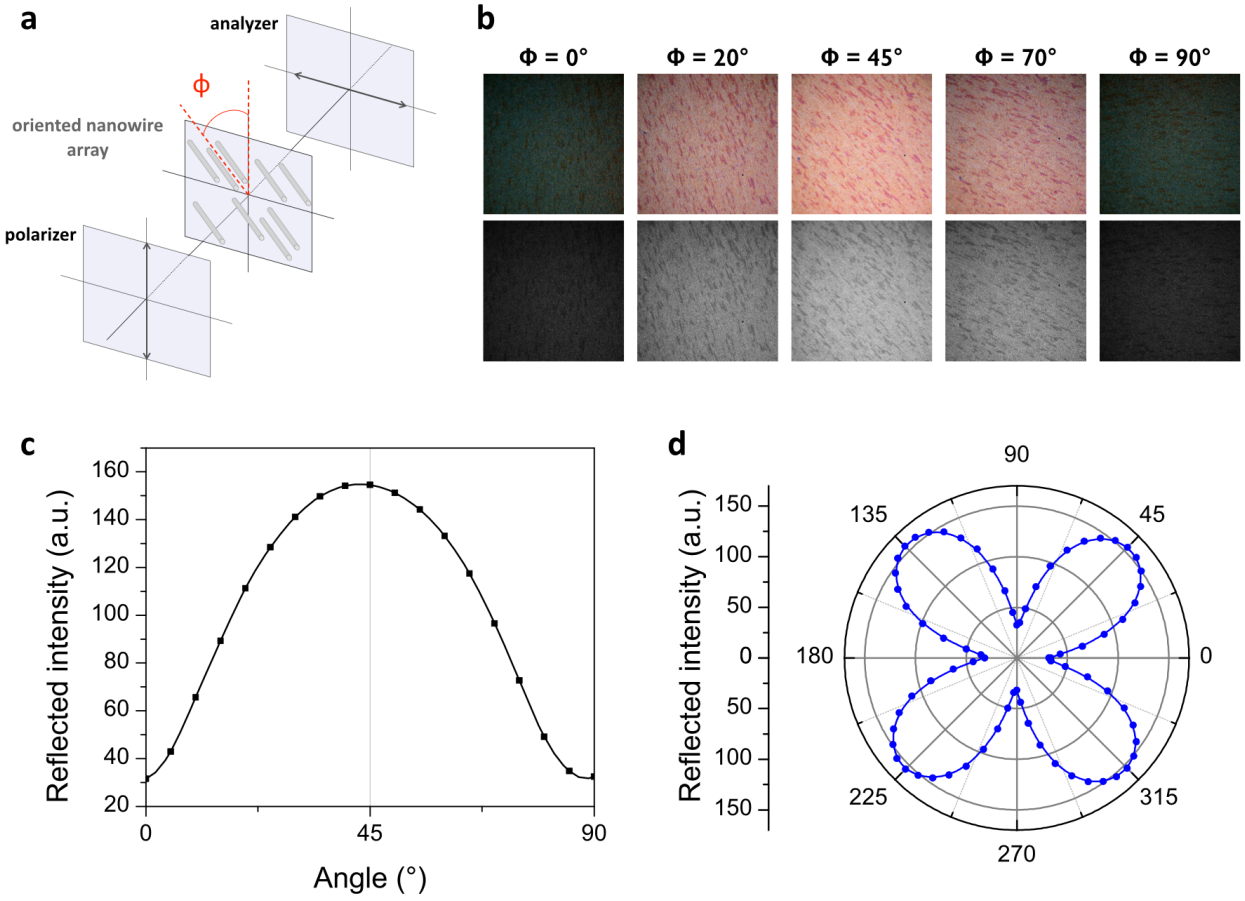

Figure S4. a) Optical scheme of the crossed polarizer configuration. For sake of simplicity, the scheme is presented in transmission mode, however, the measurements have been made with an optical microcope in the reflection mode. b) Reflection optical micrographs for different angles ϕ between the nanowire orientation direction and the incident light polarization plane. The upper row shows the original color micrographs, and the lower row the corresponding gray-scale micrographs used to quantify the reflected intensity. The size of the optical micrographs is approximately 2 x 2 mm^2. c) Reflected intensity as function of the angle ϕ. The reflected intensity is calculated as the average gray value on the optical micrographs. d) polar plot of the reflected intensity as function of ϕ.

The reflected intensity under polarized white light has been measured with an optical microscope in the crossed-polarizer configuration (Figure S4a). The sample is placed between the two polarizer oriented at 90° from each other, and the angle Φ between the nanowire orientation direction and the incident light polarization plane has been varied. For each angle, a micrograph has been taken (Figure S4b, upper row), and transformed to a 8-bit gray-scale picture

(Figure S4b, lower row). The average gray-value is measured for each picture and plotted as function of Φ (Figure S4c and d). The intensity is minimum when the nanowires are oriented along the same direction as either the polarizer or the analyzer (Φ = 0°, 90°, 180°, 270°), and the reflected intensity is maximum when the nanowires are oriented exactly between the polarizer and analyzer axes (Φ = 45°, 135°, 225°, 315°).

S-VI/ AgNW thin film with different orientations in each layer

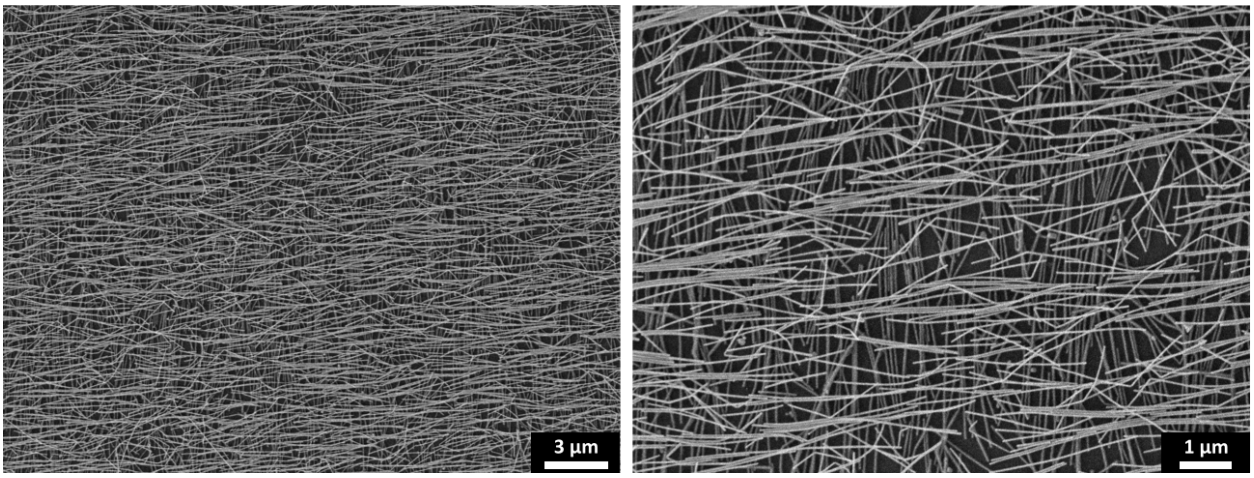

Figure S5. SEM pictures at two different magnifications of a 2-layer thin film in which the second layer is aligned perpendicularly to the first one.

In order to illustrate the fact that the orientation can be different in each layer, Figure S5 shows SEM pictures of a 2-layer sample in which the top layer is deposited with its orientation direction perpendicular to the bottom layer. The thin film architecture is the same as the other films presented in this paper, i.e. the architecture can be denoted as: $PEI/AgNW_{oriented\ at\ 0°}/PEI(PSS/PAH)_5PSS/PEI/AgNW_{oriented\ at\ 90°}$. The second silver nanowire layer has been deposited using the same conditions as the first nanowire layer, apart from the fact that the sample has been rotated 90° around the substrate normal.

References

1. Yang, C.; Gu, H.; Lin, W.; Yuen, M. M.; Wong, C. P.; Xiong, M.; Gao, B. Silver Nanowires: From Scalable Synthesis to Recyclable Foldable Electronics. *Adv. Mater.* **2011**, *23*, 3052-3056.
2. Liu, J.-W.; Wang, J.-L.; Huang, W.-R.; Yu, L.; Ren, X.-F.; Wen, W.-C.; Yu, S.-H. Ordering Ag nanowire arrays by a glass capillary: A portable, reusable and durable SERS substrate. *Sci. Rep.* **2012**, *2*, 987.
3. Rezakhaniha, R.; Agianniotis, A.; Schrauwen, J. T. C.; Griffa, A.; Sage, D.; Bouten, C. V. C.; Vosse, F. N.; Unser, M.; Stergiopulos, N. Experimental investigation of collagen waviness and orientation in the arterial adventitia using confocal laser scanning microscopy. *Biomech. Model. Mechanobiol.* **2012**, *11*, 461-473.