Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supporting Information

Understanding the formation of aligned, linear arrays of Ag nanoparticles

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Gelatin film preparation: 10 w/w% gelatin solutions were prepared for each aqueous ammonia concentration (0.1, 0.3, 0.7, 1.0, 1.5 or 3.0 w/w%). The mixtures were vigorously shaken for 1 minute and heated at 65 °C in a pressure stable tube (BD Falcon) for 4 h. The hot solutions were spin-coated (SAWATEC SM-180-BT) onto a glass slide (3 x 3 x 0.1 cm) (Menzel) with 300 and 500 rpm coating speeds and were dried overnight at ambient temperature. Eight kinds of gelatins (*I* - *VIII*) were used. Their manufacturing methods were: Type A: acidic fusion, Type B: alkaline fusion of the raw material. *Gelatin I*: gelatin for analytics granular (Acros-Organics), *II*: from porcine skin, Type A, *III*: from cold water fish skin, *IV*: from porcine skin, Type A, *V*: from bovine, Type B, *VI*: from bovine + porcine bones, for ballistic analysis Type A, *VII*: from porcine skin, Type A, (*gelatins II - VII* were purchased from Sigma-Aldrich), *VIII*: kitchen gelatin, from porcine, (RUF). The source and manufacturing process of the gelatin have a significant influence on its mechanical and chemical properties. Only alkaline gelatin films showed band formation, except *Gelatin IV*, in which band formation was also observed under neutral conditions. This may be the result of the alkaline manufacturing process of the gelatin. In the rest of the neutral and acidic gelatin films precipitates formed without a specific pattern (i.e. no band formation was observed).

A set of gelatin solutions containing aqueous HCl (0.01 M, 0.1 M and 1.0 M) (VWR) and aqueous citric acid (0.01 M, 0.1 M and 1.0 M) (ACROS) instead of ammonia (VWR) were also used.

Other hydrogels: agarose (OmniPur Agarose, EMD chemicals/Merck), agar-agar (Agar (microagar), Apollo), polyethylene-glycol (PEG (MW4000), VWR) and polyvinyl-alcohol (PVA) (Acros-Organics).

Stamp preparation: 6 w % agarose solution prepared with degassed milliQ water, was heated in a microwave oven (700 W) and poured on a pre-shaped polydimethylsiloxane (PDMS) mould containing 500 μm diameter holes. The degassed and cooled agarose film was peeled off from the mould, cut into 0.4 cm x 0.4 cm pieces and soaked in aqueous AgNO3 solution (0.3 M) (Acros-Organics) for 48 h.

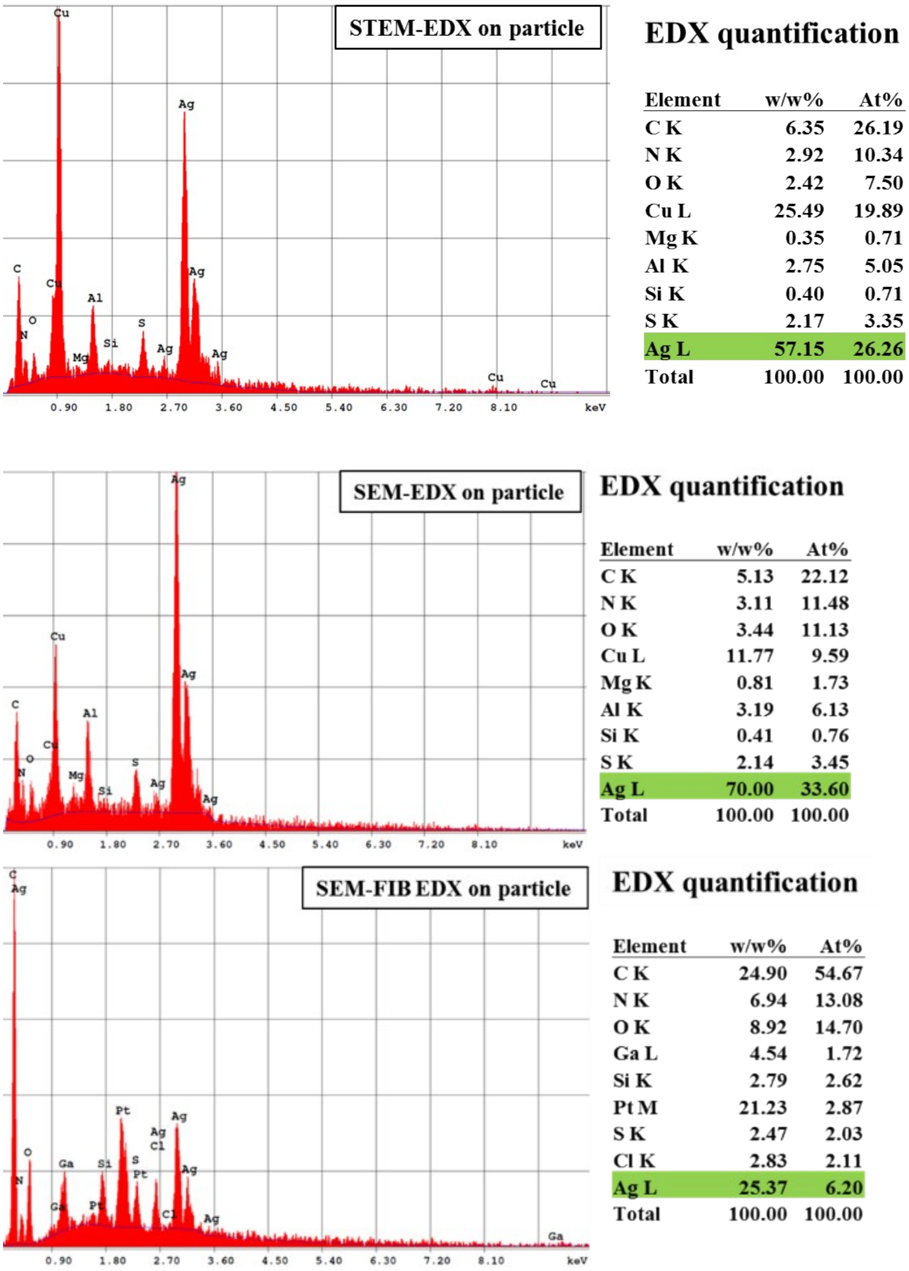
Stamping: The soaked stamps were dried on a filter paper for 2-6 minutes and placed on the gelatin films for 30, 60, 90, 120 and 180 minutes.

Characterization: Images of the formed bands were acquired using optical microscopy (Leica DMLP) and 3D Laser Scanning Microscope (Keyence VK-X200), which uses a violet laser with 408 nm at 0.95 mW. The resolution for the profile (height) measurements is 0.5

nm. All samples were irradiated for 30 minutes with UV-A/UV-C hand lamp (256 and 365 nm, 6 W) before optical measurements. Atomic Force Microscope (AFM) (Bruker Dimension 3100) images were obtained in contact mode. Scanning electron microscopy (SEM) (FEI Nova Nano SEM 230), Scanning electron microscopy – focused ion beam (SEM-FIB) and Scanning transmission electron microscopy (STEM) (both on FEI Helios Nano Lab 650) were used to acquire high resolution images of the bands. Energy dispersive X-ray spectroscopy (EDX) (Genesis Apex Energy Dispersive Spectroscopy System) was used to obtain information about the composition of the materials forming the bands. X-ray photoelectron spectroscopy (XPS) (Thermo Scientific VG ESCALAB 210) was used for qualitative analysis of Liesegang band forming material.

Electron microscopy study:

To determine the material composition of the particles forming the periodic bands, electron microscopy images and energy dispersive X-ray (EDX) spectra were obtained (10 and 20 KeV). Individual particles in ~ 90-150 nm thin microtome cuts (cross sections) of a band were analyzed by scanning transmission electron microscopy (STEM). Ag, C, N, O, S, Cu, Al, and very small amounts of Mg and Si were detected in the EDX spectrum (Figure 2b). The Al and Cu peaks originate from the TEM-grid and the sample holder in the vacuum chamber. The amounts of C, N, O and S are comparable to those found in the gelatin reference. The high intensities of the Ag peaks indicate that the material forming the particles contains silver. The same elements were found using scanning electron microscopy (SEM-EDX, 5 and 10 KeV)) (Figure 2c,d) and SEM_FIB (Figure 2e,f). To confirm that the shear forces applied while preparing the microtome cut using a diamond blade had not changed the silver-containing nanoparticles, measurements were also conducted on focus ion beam cuts (FIB) (Figure 2e). The same elements were found in Ga ion FIB cuts as in the microtome cuts (Figure 2f). In addition, the SEM-FIB cross section images (Figure 2e) clearly show how the nanoparticles form well developed and distinguishable bands inside the gelatin layer and on top of it.



EDX quantification

Element	w/w%	At%
C K	6.35	26.19
N K	2.92	10.34
O K	2.42	7.50
Cu L	25.49	19.89
Mg K	0.35	0.71
Al K	2.75	5.05
Si K	0.40	0.71
S K	2.17	3.35
Ag L	57.15	26.26
Total	100.00	100.00

EDX quantification

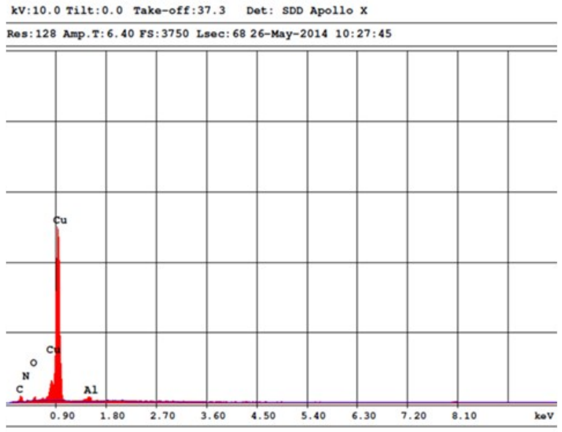
Element	w/w%	At%
C K	5.13	22.12
N K	3.11	11.48
O K	3.44	11.13
Cu L	11.77	9.59
Mg K	0.81	1.73
Al K	3.19	6.13
Si K	0.41	0.76
S K	2.14	3.45
Ag L	70.00	33.60
Total	100.00	100.00

EDX quantification

Element	w/w%	At%
C K	24.90	54.67
N K	6.94	13.08
O K	8.92	14.70
Ga L	4.54	1.72
Si K	2.79	2.62
Pt M	21.23	2.87
S K	2.47	2.03
Cl K	2.83	2.11
Ag L	25.37	6.20
Total	100.00	100.00

Figure 1S EDX spectra of the particles forming the bands; further details for Figure 1 in the main paper.

Background (Cu-TEM grid + Thermowax)



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EDAX ZAF Quantification (Standardless)
Element Normalized
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Element    Wt %    At %   K-Ratio     Z        A        F
  C K      5.15   20.13   0.0153   1.2480   0.2381   1.0002
  N K      1.30    4.36   0.0058   1.2325   0.3639   1.0008
  O K      1.75    5.13   0.0116   1.2181   0.5430   1.0021
  CuL     89.23   65.92   0.8497   0.9710   0.9807   1.0001
  AlK      2.57    4.47   0.0174   1.1321   0.5972   1.0000
 Total   100.00  100.00
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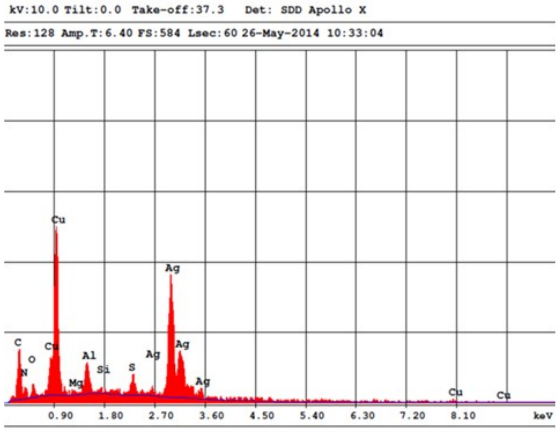
STEM-EDX on particles forming the finestructured bands



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Element Normalized
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Element    Wt %    At %   K-Ratio     Z        A        F
  C K      6.35   26.19   0.0329   1.2862   0.4037   1.0001
  N K      2.92   10.34   0.0184   1.2699   0.4952   1.0002
  O K      2.42    7.50   0.0088   1.2548   0.2893   1.0003
  CuL     25.49   19.89   0.1566   0.9995   0.6145   1.0005
  MgK      0.35    0.71   0.0025   1.2253   0.5941   1.0014
  AlK      2.75    5.05   0.0228   1.1734   0.7056   1.0024
  SiK      0.40    0.71   0.0038   1.1946   0.7854   1.0046
  S K      2.17    3.35   0.0233   1.1758   0.8984   1.0150
  AgL     57.15   26.26   0.5118   0.9008   0.9942   1.0000
 Total   100.00  100.00
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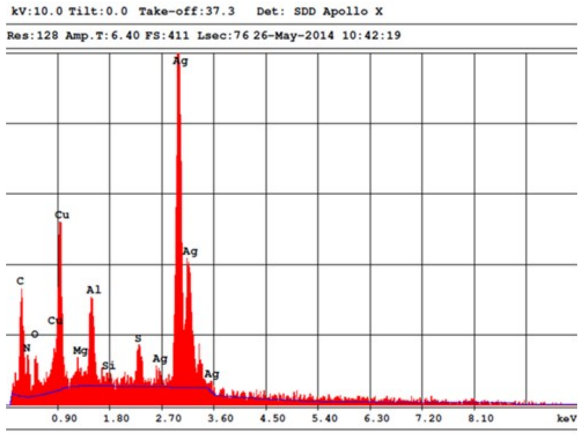
STEM-EDX on particles which changed its structure during observations



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Element Normalized
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Element    Wt %    At %   K-Ratio     Z        A        F
  C K      4.62   22.23   0.0280   1.3183   0.4600   1.0001
  N K      3.24   13.37   0.0232   1.3015   0.5507   1.0001
  CuL     12.34   11.23   0.0704   1.0236   0.5569   1.0006
  MgK      0.85    2.03   0.0067   1.2609   0.6178   1.0018
  AlK      3.35    7.17   0.0292   1.2055   0.7226   1.0031
  SiK      0.43    0.89   0.0042   1.2257   0.7960   1.0059
  S K      2.23    4.02   0.0248   1.2060   0.9038   1.0197
  AgL     72.93   39.07   0.6724   0.9252   0.9966   1.0000
 Total   100.00  100.00
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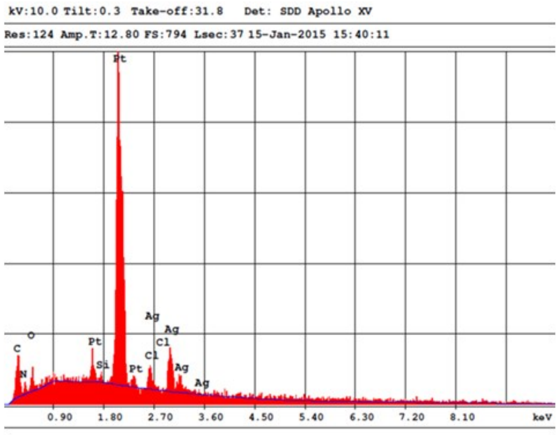
SEM-EDX measurement on a particle forming the bands in the silver Liesegang system



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EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : User  C:\Savecalib18072012\SEC Genesis\BCNOF_19072012.sec

Element    Wt %    At %   K-Ratio     Z        A        F
  C K      4.59   29.74   0.0179   1.4540   0.2687   1.0000
  N K      2.62   14.58   0.0106   1.4344   0.2805   1.0000
  O K      2.12   10.33   0.0082   1.4159   0.2725   1.0000
  SiK      0.30    0.82   0.0033   1.3604   0.8243   1.0009
  PtM     72.72   29.02   0.6620   0.8954   1.0167   1.0001
  ClK      1.88    4.13   0.0189   1.2829   0.7831   1.0033
  AgL     15.77   11.38   0.1390   1.0360   0.8505   1.0000
 Total   100.00  100.00
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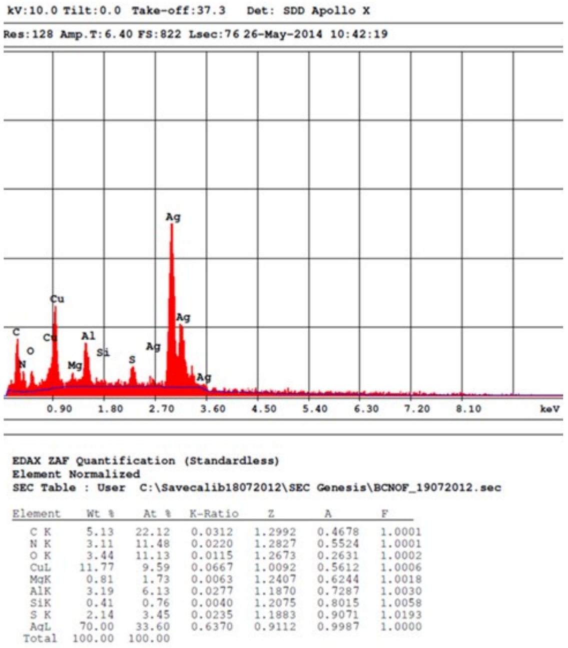
Table 1S STEM-EDX spectra and quantitative material analysis.

SEM-EDX measurement on a particle found on the Cu-TEM grid used for STEM-EDX analysis



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EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : User  C:\Savecalib18072012\SEC Genesis\BCNOF_19072012.sec

Element    Wt %     At %   K-Ratio     Z         A         F
  C K      5.13    22.12   0.0312   1.2992    0.4678    1.0001
  N K      3.11    11.48   0.0220   1.2827    0.5524    1.0001
  O K      3.44    11.13   0.0115   1.2673    0.2631    1.0002
  CuL     11.77     9.59   0.0667   1.0092    0.5612    1.0006
  MqK      0.81     1.73   0.0063   1.2407    0.6244    1.0018
  AlK      3.19     6.13   0.0277   1.1870    0.7287    1.0030
  SiK      0.41     0.76   0.0040   1.2075    0.8015    1.0058
  S K      2.14     3.45   0.0235   1.1883    0.9071    1.0193
  AqL     70.00    33.60   0.6370   0.9112    0.9987    1.0000
 Total   100.00   100.00
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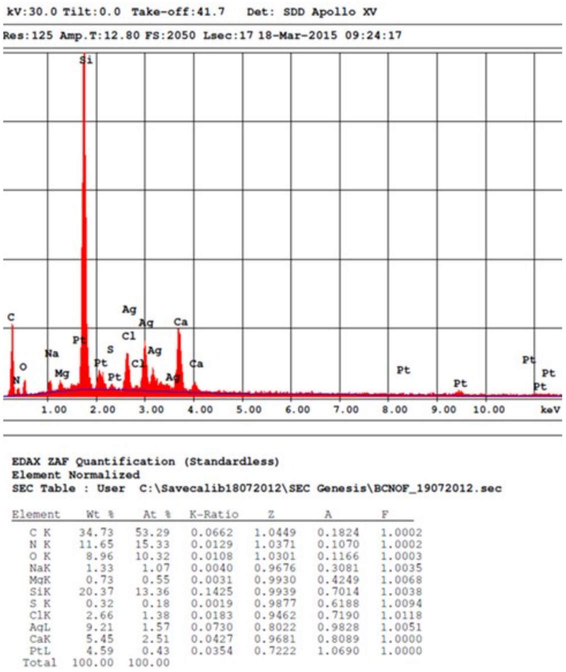
SEM-EDX measurement on a particle forming the bands in the silver Liesegang system



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EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : User  C:\Savecalib18072012\SEC Genesis\BCNOF_19072012.sec

Element    Wt %     At %   K-Ratio     Z         A         F
  C K     34.73    53.29   0.0662   1.0449    0.1824    1.0002
  N K     11.65    15.33   0.0129   1.0371    0.1070    1.0002
  O K      8.96    10.32   0.0108   1.0301    0.1166    1.0003
  NaK      1.33     1.07   0.0040   0.9676    0.3081    1.0035
  MqK      0.73     0.55   0.0031   0.9930    0.4249    1.0068
  SiK     20.37    13.36   0.1425   0.9939    0.7014    1.0038
  S K      0.32     0.18   0.0019   0.9877    0.6188    1.0094
  ClK      2.66     1.38   0.0183   0.9462    0.7190    1.0118
  AqL      9.21     1.57   0.0730   0.8022    0.9828    1.0051
  CaK      5.45     2.51   0.0427   0.9681    0.8089    1.0000
  PtL      4.59     0.43   0.0354   0.7222    1.0690    1.0000
 Total   100.00   100.00
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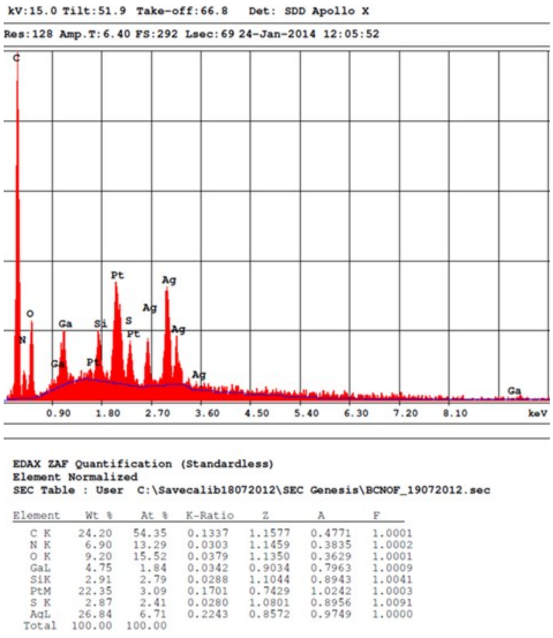
SEM-FIB-EDX measurement on a particle forming the bands in the silver Liesegang system



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EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : User  C:\Savecalib18072012\SEC Genesis\BCNOF_19072012.sec

Element    Wt %     At %   K-Ratio     Z         A         F
  C K     24.20    54.35   0.1337   1.1577    0.4771    1.0001
  N K      6.90    13.29   0.0303   1.1459    0.3835    1.0002
  O K      9.20    15.52   0.0379   1.1350    0.3629    1.0001
  GaL      4.75     1.84   0.0342   0.9034    0.7963    1.0009
  SiK      2.91     2.79   0.0288   1.1044    0.8943    1.0041
  PtM     22.35     3.09   0.1701   0.7429    1.0242    1.0003
  S K      2.87     2.41   0.0280   1.0801    0.8956    1.0091
  AqL     26.84     6.71   0.2243   0.8572    0.9749    1.0000
 Total   100.00   100.00
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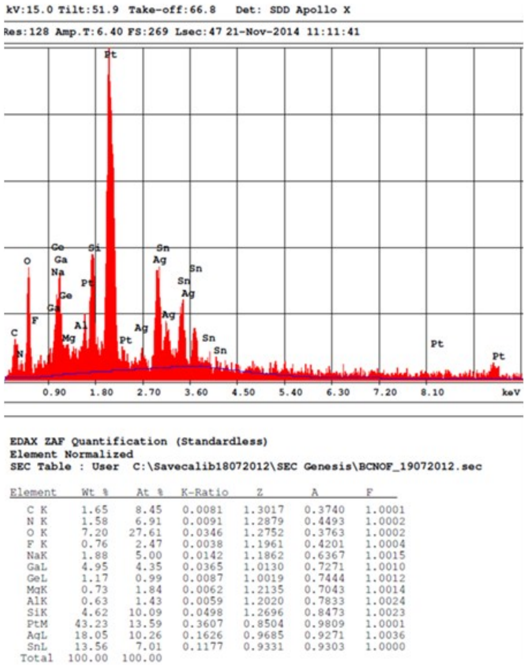
SEM-FIB-EDX measurement on a particle forming the bands in the silver Liesegang system on FTO-glass



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EDAX ZAF Quantification (Standardless)
Element Normalized
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Element    Wt %     At %   K-Ratio     Z         A         F
  C K      1.65     8.45   0.0081   1.3017    0.3740    1.0001
  N K      1.58     6.91   0.0091   1.2879    0.4493    1.0002
  O K      7.20    27.61   0.0346   1.2752    0.3763    1.0002
  F K      0.76     2.47   0.0038   1.1961    0.4201    1.0004
  NaK      1.88     5.00   0.0142   1.1862    0.6367    1.0015
  GaL      4.95     4.35   0.0365   1.0130    0.7271    1.0010
  GeL      1.17     0.99   0.0087   1.0019    0.7444    1.0012
  MqK      0.73     1.84   0.0062   1.2135    0.7043    1.0014
  AlK      0.63     1.43   0.0059   1.2020    0.7833    1.0024
  SiK      4.62    10.09   0.0498   1.2696    0.8473    1.0023
  PtM     43.23    13.59   0.3607   0.8504    0.9809    1.0001
  AqL     18.05    10.26   0.1626   0.9685    0.9271    1.0036
  SnL     13.56     7.01   0.1177   0.9331    0.9303    1.0000
 Total   100.00   100.00
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Table 2S SEM-EDX spectra and quantitative material analysis of the silver Liesegang system.

The EDX measurement was monitored to show how the energy of the incident electron beam can change the structure of the particles. A video of this this can be found online:

Video S1 see attached

XPS study

XPS measurements were performed using a VG ESCALAB 210 system equipped with a monochromatized Al Kα (hν=1486.6 eV) radiation source with the pass energy of 20 eV used for all narrow scan measurements (Figure S3) and 100 eV pass energy for survey scans (Figure 3d). Normal electron escape angle and a step size of 0.05 eV and were used. The Gaussian broadening of the spectrometer (convolution of the spectral resolution (which itself is a convolution of the analyzer resolution and the source resolution) and thermal broadening) was calibrated as 0.55 eV for the 20eV analyzer pass energy. The energy positions of the spectra were calibrated with reference to the $4f_{7/2}$ level of a clean gold sample at 84.0 eV binding energy.

An attempt of charge correction of the spectra by shifting of all energy values in a way that the component of the C1s signal appears at the literature value of 284.8 eV for amorphous carbon(0), present in all films was not successful. A flood gun for different voltages was also used but no physical meaning was found for C, S, O and Ag charge corrected peaks. The XPS data are presented in the paper without true binding energies and were shifted arbitrarily for ease of comparison.

Deconvolution of the Ag3d peak revealed a shift between doublets ranging from 1.4 to 3.3eV (Figure S3) and spectra were fitted with two or three doublets. In comparison to literature data, a maximum shift of 1eV is typically measured[1] between Ag and AgO, while Ag_2S binding energy is close to metallic silver[2]. Our measurements are influenced by a shift to higher binding energy due the size of the Ag nanoparticles (Figure 3b and S4) as measured by Lopez-Salido et al.[3] for Ag or Pd[4], and also by a peak broadening depending on the particle size[3].

Fitting of the core level lines was performed using Doniach-Sunjic (asymmetrical Lorentzian) functions,[5] with a background substraction,[6] using UNIFIT for Windows (Version 2015) software.[7] A convolution of an asymmetry function, Lorentzian and Gaussian line shapes was used to fit the individual peaks. After this, the intensities were estimated by calculating the integral of each peak; the atomic concentrations were then derived using Scofield sensitivity factors.[8]

(1) M. F. J. Al-Kuhaili, *Phys. D: Appl. Phys.* 2007, **40**, 2847–2853.

(2) A. N. Buckle, R. Woods, *Colloids Surfaces A: Physicochem. Eng. Aspects* 1995, **104**, 295-305.

(3) I. Lopez-Salido, D. C. Lim, Y. D. Kim, *Surface Science*, 2005, **588**, 6–18.

(4) I. Aruna, B. R. Mehta, L. K. Malhotra, S. M. Shivaprasad*,* *J. Appl. Phys.* 2008, **104**, 064308.

(5) Doniach, S.; Sunjic, M. *J. Phys. C: Solid State Phys.* 1970, **3**, 285–291.

(6) Shirley, D. *Physical Review B* 1972, **5**, 4709–4714.

(7) Hesse, R.; Chassé, T.; Szargan, R. *Fresenius Journal of Analytical Chemistry* 1999, **365**, 48–54.
(8) Scofield, J. H. *Journal of Electron Spectroscopy and Related Phenomena* 1976, **8**, 129–137.

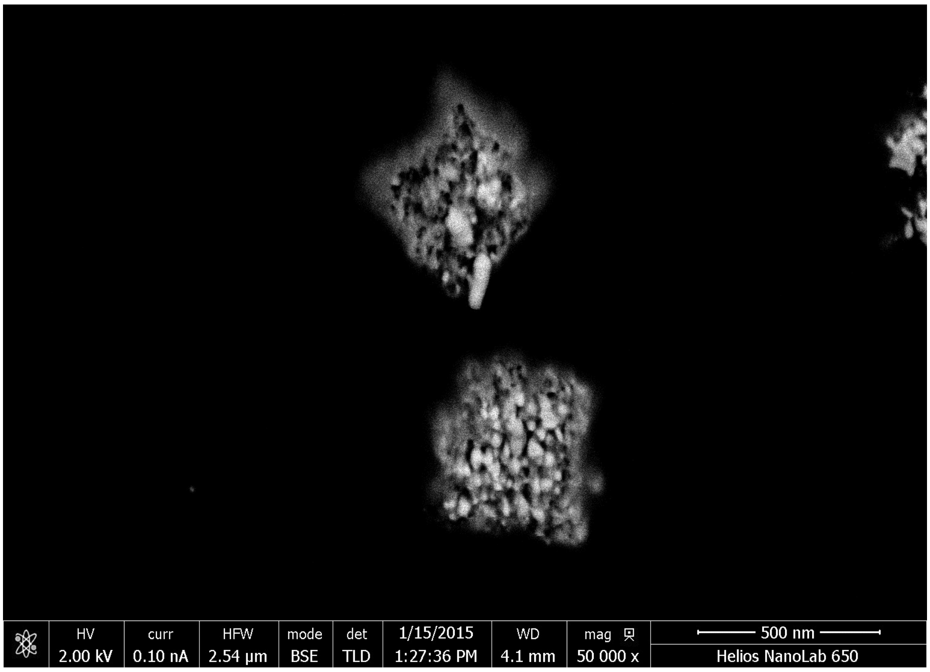

Figure 2S Backscattered electron SEM-FIB image showing the size of the nanoparticles forming bigger sized nanoparticle clusters which form the periodic precipitation bands.

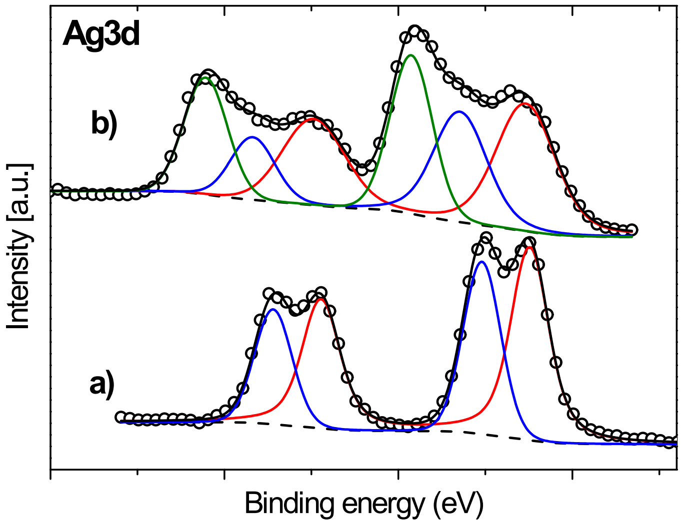

Figure 3S Ag3d core level spectra measured by XPS of gelatin film containing bands in two different positions (a) and (b). The spectra have been normalized for comparison. Open circles are measured data and full lines are mathematical fit. The red and blue and olive lines correspond to several oxidation state of Ag, the black one to the fit sum and dashed lines is the background of inelastically scattered electrons. The XPS data are presented without charge correction and binding energy was shifted arbitrarily to ease comparison.

Annealing process

Silver(I) oxide starts to decompose at 160°C and gelatin at around 220°C, determined by thermogravimetric analysis. Complete gelatin removal was observed at and above 360°C. A sintering time of 12 h (overnight) was necessary for full gelatin removal at 360°C. At higher temperatures (≥380°C) complete removal of gelatin without destruction of the fine structures was observed after 3 h.