Electronic Supporting Information

Probing the mystery of Liesegang band formation: revealing the origin of self-organized dual-frequency micro and nanoparticle arrays

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EDX quantification

EDX measurements were carried out at different sample locations to obtain information about the core structure and the surrounding material. The EDX measurements were performed on the core structures in the small and large bands as well as on the material surrounding the core. For references a gelatin film, the Si_3N_4 substrate and the material between the particles were also analyzed. It is evident that the amount of silver in the core is much higher than the amount of silver found in the surrounding material. The observed values for silver and chromium can be found in the EDX material analysis below the EDX spectra (Figure S1).

The values for carbon, nitrogen, oxygen and sulfur can be neglected as these are the main elements of the gelatin matrix, as it's evident from the EDX spectrum of gelatin. As the sulfur peak overlaps with parts of the platinum peak, it was sometimes a problem to detect sulfur in the specimen. The gallium peak arises from the gallium-ion beam which contaminates the sample weakly during the milling process. The silicon signal and parts of the nitrogen signal are due to the Si_3N_4 membranes which were used as carrier substrates. The platinum peak originates from both the platinum sputter coating layer and the deposition layer. For these reasons only the silver and chromium peaks were relevant to determine the material composition of the nanoparticles in the bands.

Background measurement (only gelatin)

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kV:25.0 Tilt:0.2  Take-off:39.8   Det: SDD Apollo XV
Res:125 Amp.T:12.80 FS:2113 Lsec:38 18-Mar-2015 09:36:10
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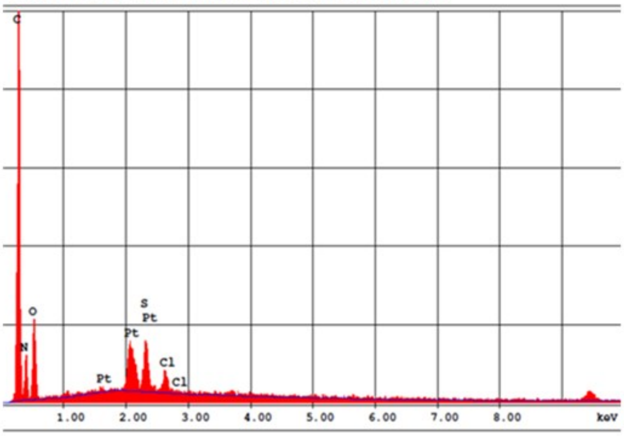

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EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : User  C:\Savecalib18072012\SEC Genesis\BCNOF_19072012.sec

Element   Wt %    At %   K-Ratio     Z       A       F
   C K   40.65   48.59   0.1665   1.0171  0.4025  1.0005
   N K   27.79   28.49   0.0401   1.0090  0.1429  1.0004
   O K   23.83   21.39   0.0320   1.0017  0.1341  1.0000
   PtM    5.03    0.37   0.0529   0.7475  1.4070  1.0003
   S K    1.79    0.80   0.0150   0.9577  0.8756  1.0011
   ClK    0.90    0.37   0.0075   0.9072  0.9173  1.0000
  Total 100.00  100.00
```

Material in the core structures in small bands

```
kV:10.0 Tilt:51.9  Take-off:66.8   Det: SDD Apollo X
Res:128 Amp.T:6.40 FS:221 Lsec:25 27-Jan-2015 13:53:05
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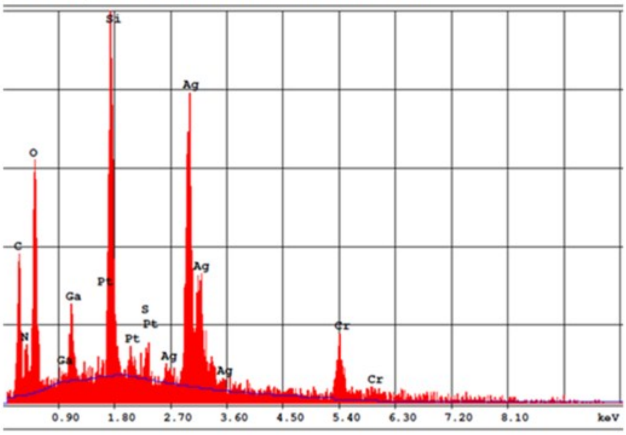

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EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : User  C:\Savecalib18072012\SEC Genesis\BCNOF_19072012.sec

Element   Wt %    At %   K-Ratio     Z       A       F
   C K    2.37    8.98   0.0184   1.2562  0.6191  1.0002
   N K    2.60    8.46   0.0241   1.2405  0.7481  1.0004
   O K    7.99   22.76   0.0548   1.2258  0.5599  1.0006
   GaL    2.57    1.68   0.0201   0.9457  0.8258  1.0015
   SiK   10.69   17.36   0.1162   1.1659  0.9272  1.0056
   PtM    2.23    0.52   0.0170   0.7704  0.9916  1.0004
   S K    1.11    1.59   0.0124   1.1479  0.9564  1.0173
   AgL   50.94   21.54   0.4477   0.8788  0.9978  1.0023
   CrK   19.51   17.11   0.1982   1.0278  0.9887  1.0000
  Total 100.00  100.00
```

Material surrounding the core structures in small bands

```
kV:10.0 Tilt:51.9  Take-off:66.8   Det Type:SDD Apollo X  Res:128  Amp.T:6.40
FS : 449  Lsec : 27                                     27-Jan-2015 13:44:27
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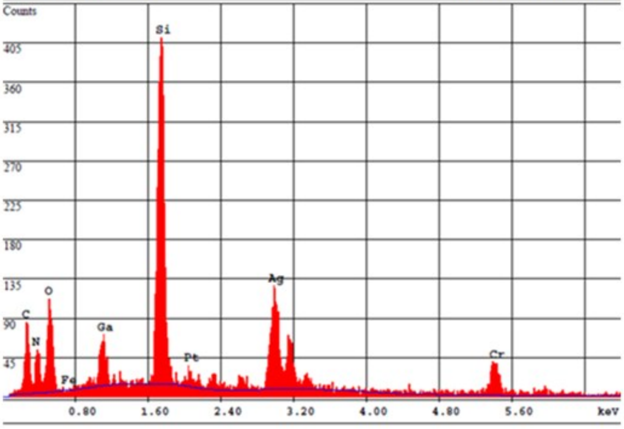

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EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : User  D:\EDAX_Savecalib_21062012_install\SEC Genesis\BCNOF_210620:

Element   Wt %    At %   K-Ratio     Z       A       F
   C K    3.27   11.03   0.0212   1.2214  0.5300  1.0002
   N K    3.93   11.35   0.0325   1.2063  0.6849  1.0004
   O K    4.65   11.75   0.0329   1.1922  0.5943  1.0008
   FeL    0.00    0.00   0.0000   0.9808  0.6242  1.0005
   GaL    4.04    2.34   0.0315   0.9160  0.8490  1.0020
   SiK   21.59   31.11   0.2294   1.1321  0.9346  1.0038
   PtM    3.07    0.64   0.0226   0.7484  0.9823  1.0002
   AgL   35.89   13.46   0.3052   0.8524  0.9946  1.0029
   CrK   23.55   18.32   0.2318   0.9929  0.9913  1.0000
  Total 100.00  100.00
```

Material filling the space between particles (small bands)

```
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Res:128 Amp.T:6.40 FS:2369 Lsec:54 27-Jan-2015 10:04:48
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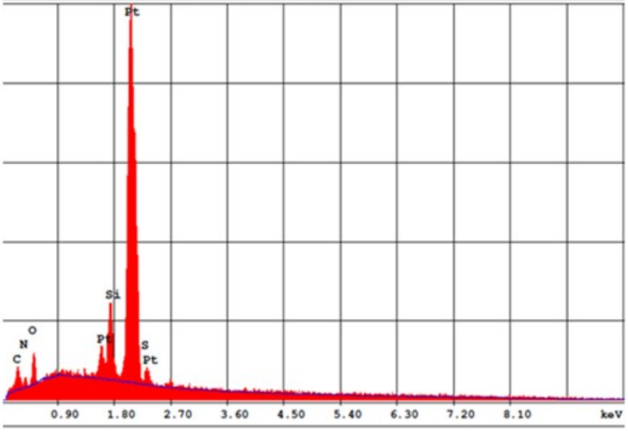

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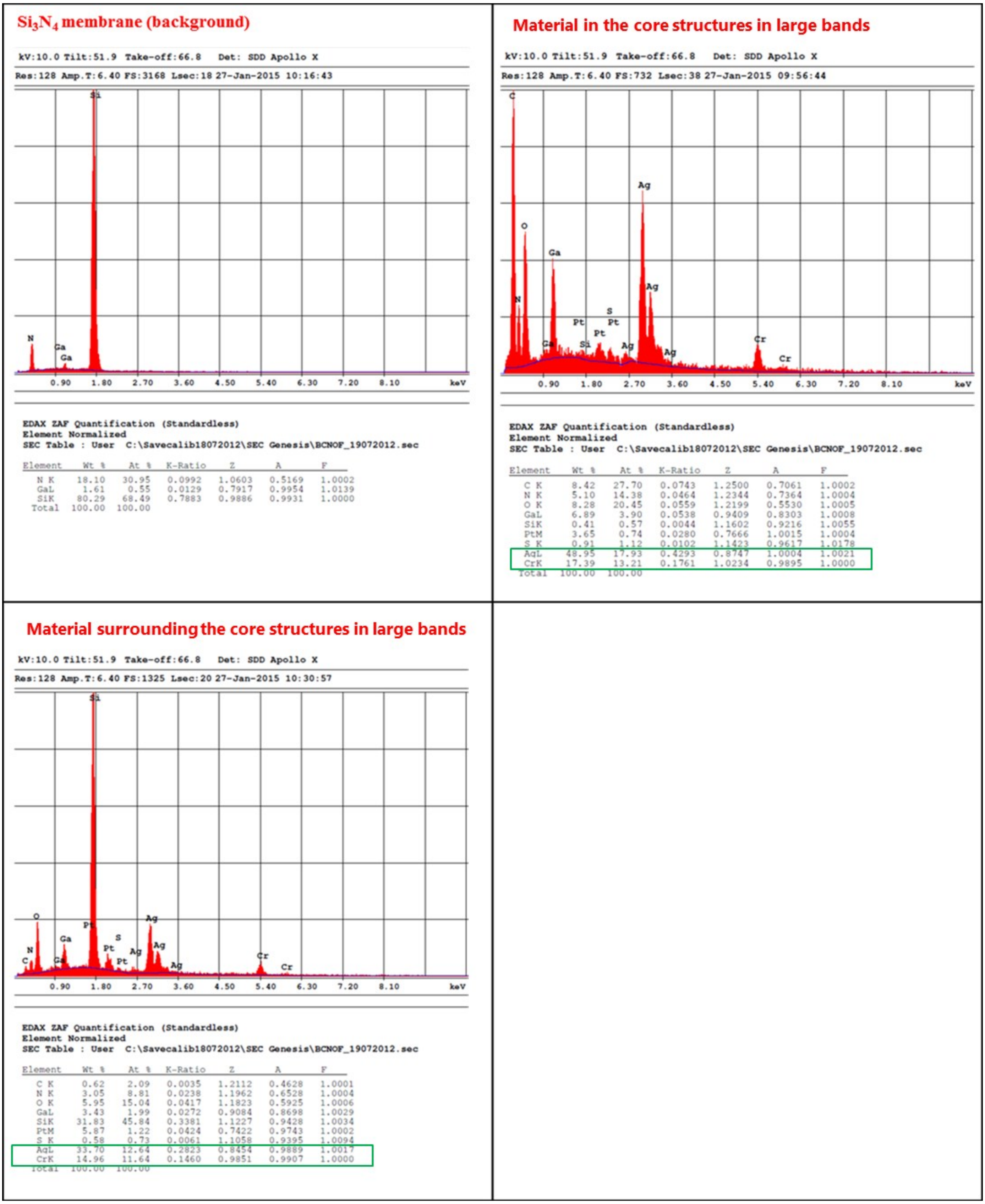
EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : User  C:\Savecalib18072012\SEC Genesis\BCNOF_19072012.sec

Element   Wt %    At %   K-Ratio     Z       A       F
   C K    2.40   16.72   0.0087   1.4714  0.2452  1.0000
   N K    2.32   13.82   0.0091   1.4514  0.2710  1.0001
   O K    3.27   17.08   0.0150   1.4325  0.3212  1.0000
   SiK    4.67   13.90   0.0544   1.3780  0.8458  1.0001
   PtM   86.88   37.24   0.7919   0.9065  1.0056  1.0000
   S K    0.47    1.24   0.0044   1.3527  0.6845  1.0000
  Total 100.00  100.00
```



Si_3N_4 membrane (background)

```
kV:10.0 Tilt:51.9  Take-off:66.8   Det: SDD Apollo X
Res:128 Amp.T:6.40 FS:3168 Lsec:18 27-Jan-2015 10:16:43
```

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

Element    Wt %     At %   K-Ratio     Z        A        F
   N K     18.10    30.95   0.0992   1.0603   0.5169   1.0002
   GaL      1.61     0.55   0.0129   0.7917   0.9954   1.0139
   SiK     80.29    68.49   0.7883   0.9886   0.9931   1.0000
  Total   100.00   100.00
```

Material in the core structures in large bands

```
kV:10.0 Tilt:51.9  Take-off:66.8   Det: SDD Apollo X
Res:128 Amp.T:6.40 FS:732 Lsec:38 27-Jan-2015 09:56:44
```

```
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      8.42    27.70   0.0743   1.2500   0.7061   1.0002
   N K      5.10    14.38   0.0464   1.2344   0.7364   1.0004
   O K      8.28    20.45   0.0559   1.2199   0.5530   1.0005
   GaL      6.89     3.90   0.0538   0.9409   0.8303   1.0008
   SiK      0.41     0.57   0.0044   1.1602   0.9216   1.0055
   PtM      3.65     0.74   0.0280   0.7666   1.0015   1.0004
   S K      0.91     1.12   0.0102   1.1423   0.9617   1.0178
   AgL     48.95    17.93   0.4293   0.8747   1.0004   1.0021
   CrK     17.39    13.21   0.1761   1.0234   0.9895   1.0000
  Total   100.00   100.00
```

Material surrounding the core structures in large bands

```
kV:10.0 Tilt:51.9  Take-off:66.8   Det: SDD Apollo X
Res:128 Amp.T:6.40 FS:1325 Lsec:20 27-Jan-2015 10:30:57
```

```
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      0.62     2.09   0.0035   1.2112   0.4628   1.0001
   N K      3.05     8.81   0.0238   1.1962   0.6528   1.0004
   O K      5.95    15.04   0.0417   1.1823   0.5925   1.0006
   GaL      3.43     1.99   0.0272   0.9084   0.8698   1.0029
   SiK     31.83    45.84   0.3381   1.1227   0.9428   1.0034
   PtM      5.87     1.22   0.0424   0.7422   0.9743   1.0002
   S K      0.58     0.73   0.0061   1.1058   0.9395   1.0094
   AgL     33.70    12.64   0.2823   0.8454   0.9889   1.0017
   CrK     14.96    11.64   0.1460   0.9851   0.9907   1.0000
  Total   100.00   100.00
```

Figure S1. EDX spectra of the particles forming the bands; specifically: spectra of the core structure of the particles in the small and large bands, the surrounding material of the core structure, the material between the particles, a gelatin film and the Si_3N_4 substrate. Material analysis/quantification of the EDX measurements can be seen under the corresponding spectrum.

Dichromate/chromate equilibrium

The concentration of chromate and dichromate ions as a function of pH can be seen in the Figure S5.

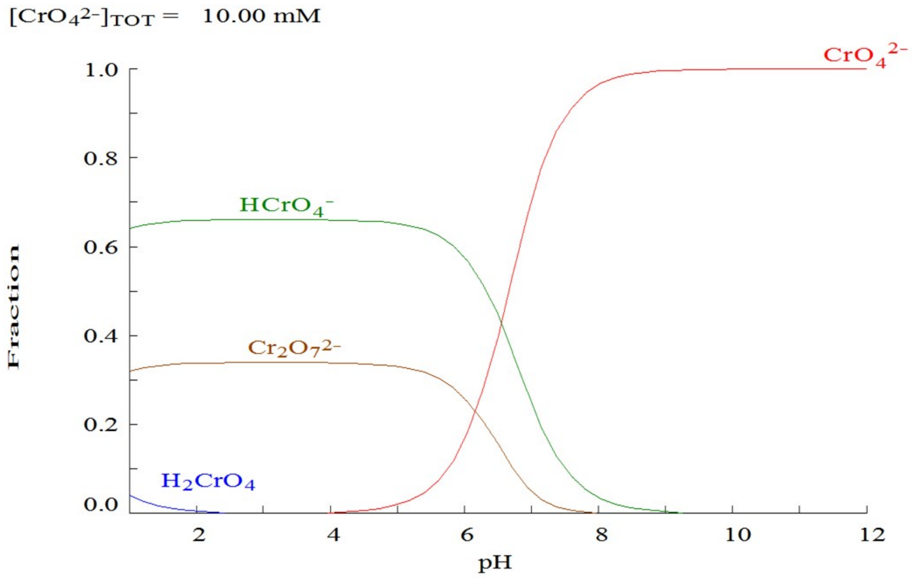


Figure S2 Chemical equilibrium of the chromate and dichromate ions as a function of pH. The diagram was created by Medusa-Hydra chemical equilibrium software.

Sample preparation and monitoring setup

0.5 mL of a hot gelatin solution (10 w/w%, *type 0*, 60°C, 0.03 w/w% NH_4OH) containing potassium dichromate (0.01 M) as inner electrolyte was doctor-bladed onto a microscope cover slip (60 x 24 x 0.16 mm). After drying for 24 h, the cover slip was mounted onto an adapter (Figure S2), with the gelatin layer pointing downward. The agarose stamp containing 0.3 M $AgNO_3$ as inner electrolyte was prepared according to standard procedures. After drying on a dust free paper for 10 minutes, the stamp was placed on a clean microscope slide with the pins bound upwards. The monitoring and precipitation process was started, while the cover slip was placed on the stamp, with the gelatin layer pointing towards the stamp pins (Figure S2). The cover slip adapter was necessary to stabilize the thin slip during the observation process.

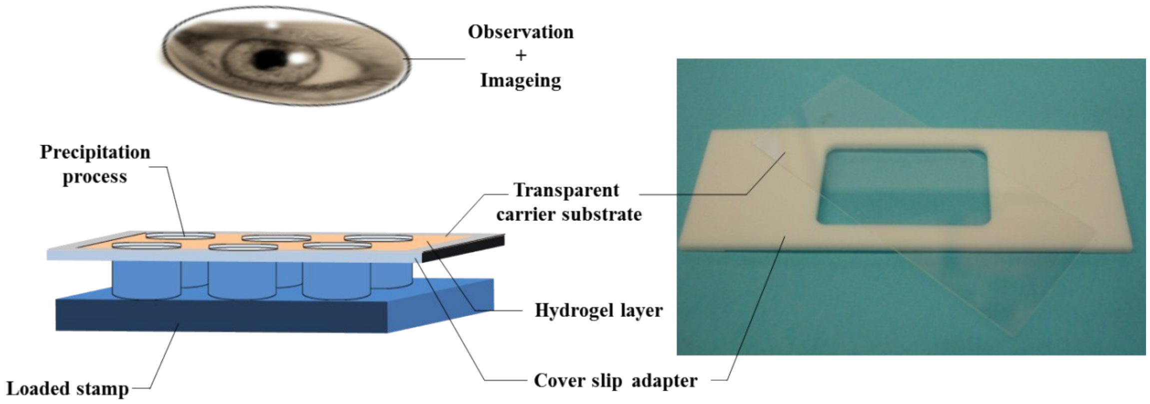


Figure S3. Sample setup for real time observation of the precipitation process under a stereo microscope. Schematic representation of the setup (left) and a photograph of the cover slip adapter (right).

Video processing

After two hours, the precipitation process was finished and the monitoring process was stopped. The recorded video was then edited (*Microsoft Movie Maker*) to prepare a time lapse movie of the precipitation process where 1 s equals 1 min in real time. In this video it is easy to see that the location of the bands is fixed once they are formed. It is also possible to observe that a white precipitate is formed first before the first bands appear. VideoS1 can be find attached.

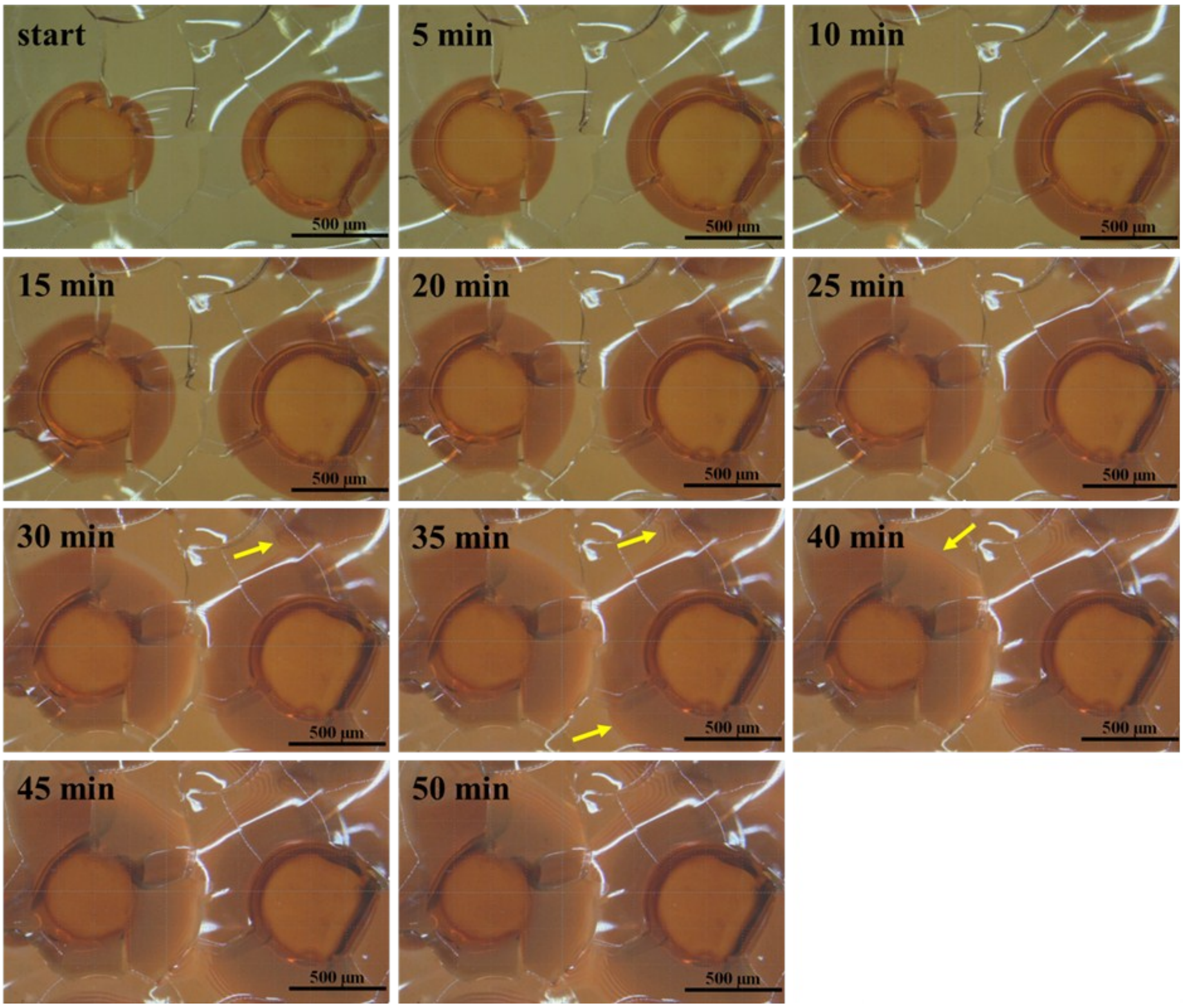


Figure S4. Time lapse photographs taken from the monitored precipitation process occurring in the classical Liesegang system. Yellow arrows indicate the formation of the precipitation bands.

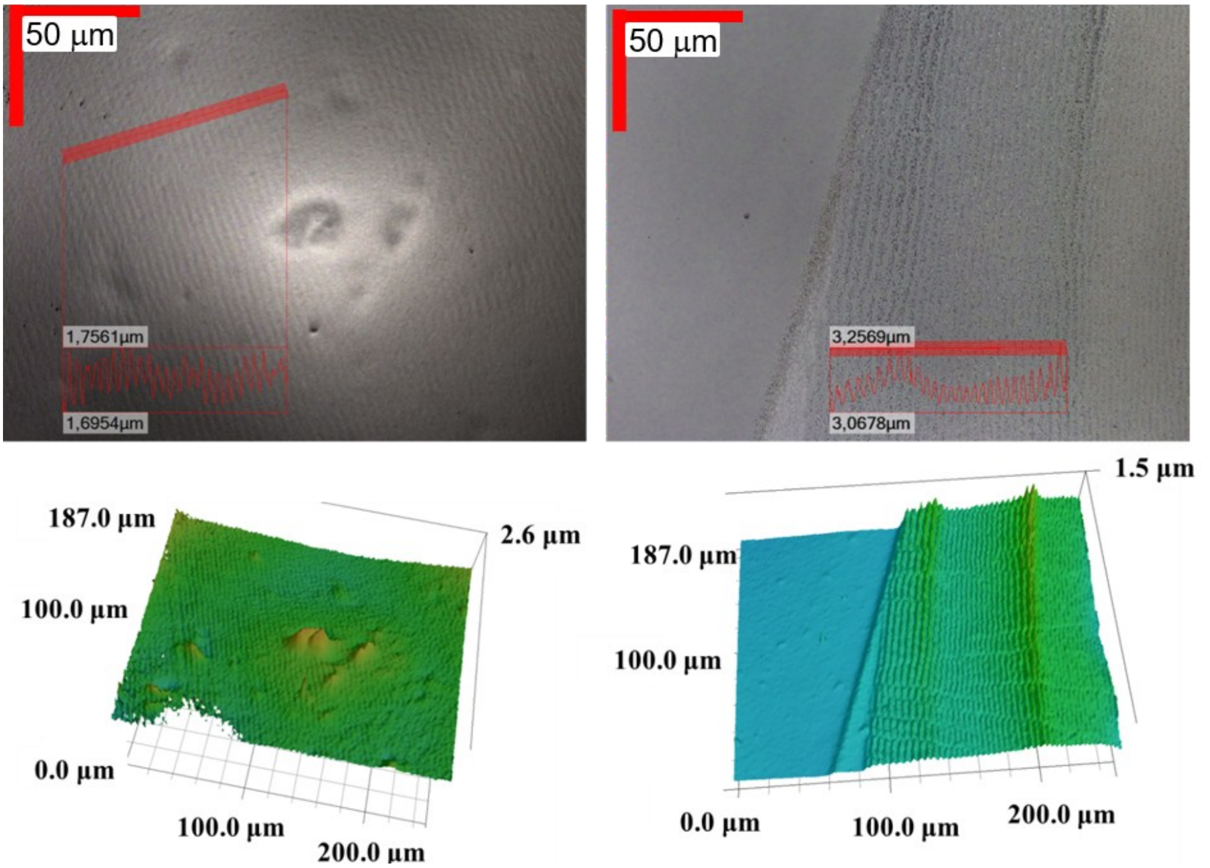


Figure S5 Comparison of the silver nitrate/ammonium hydroxide/gelatin system (left) and the classical silver nitrate/ammonium hydroxide/dichromate/gelatin Liesegang system (right). The 10 w/w% gelatin films containing 0.3 w/w% aqueous ammonia were stamped for 45 minutes with stamps that were loaded for 48 h in a 0.3 M $AgNO_3$ solution in both experiments. The gelatin film contained an additional 0.01 M $K_2Cr_2O_7$ in the classical system. Top images: optical images with measured surface profiles (average of 10 lines). The different height values originate from different starting values (Z-axis). Only the difference between the upper and lower values are of interest. Bottom images: 3D laser profiles showing the fine-structures observed in both systems.