Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Dark–induced vertical growth of chemobrionic architectures in silver based precipitating chemical gardens

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A. Experimental Section

Preparation of the Materials

To prepare the silver silicate chemical garden like architectures, accurately weighed analytical grade 330 mg of silver nitrate (purchased from Finar Limited, *utilized this silver nitrate after three months after opening the bottle*) was homogenized via crushing in an agate mortar and the powder was placed at the bottom of a 15 ml Borosil glass tube. 0.5M sodium silicate solutions were prepared using sodium silicate solution (from Finar Limited, 27-35% assay) and Milli-Q water. 10 ml of this 0.5M sodium silicate solution was gradually added down the side of the glass tube, and the glass tube was covered with aluminium foil. Without shaking, this mixture was kept in the dark viz. in a dark cabinet undisturbed. An identical glass tube containing a similar (0.5M sodium silicate + 330 mg silver nitrate powder) mixture was kept under the light (either daylight/natural light or the light (incandescent) from light bulbs in a typical laboratory setting). After almost 2-4 hours, yellow needle-like vertical structures appeared in the glass tubes that were kept in the dark (Supporting information Figure S1a). Such structures were not observed in the glass tube kept in the light. After 22 hours several yellow-colored vertical structures were observed in the reaction mixtures in the glass tubes kept in dark (Supporting information Figure S1f). The structures were collected with utmost care and kept for 7 days to completely air-dry (*air-drying was performed under regular laboratory light and not under dark*). After that, they were utilized for characterization. Because such dark induced reactions led to the production of silver based vertically grown chemical garden like structures in very small quantities (viz. one milligram from one reaction vessel), for characterization purpose, several such (almost several hundreds of reaction vessels) reactions were carried out in the dark to obtain gram scale quantities of the silver silicate chemical gardens.

Characterization of the Materials

PERKIN-ELMER (Spectrum Two) Spectrometer was employed to obtain FTIR (Fourier Transform Infra-Red) data from 4000 cm^{-1} to 400 cm^{-1} wavenumber range with a sweeping rate of 4 cm^{-1}. During the FTIR spectra data collection the temperature was maintained around 25^{o}C. Powder X-ray diffraction (PXRD) patterns were obtained using a Philips X'pert

MPD System from 2θ range 10° to 80° with a scan rate of 1°. Zeiss ULTRA-55 FE-SEM Field Emission Scanning Electron Microscope has been used to obtain the microstructural images for morphological information of the materials. The sample was also characterized by Raman Spectroscopy using Renishaw InVia Raman Microscope with 532nm laser.

B. Supporting Information Figures

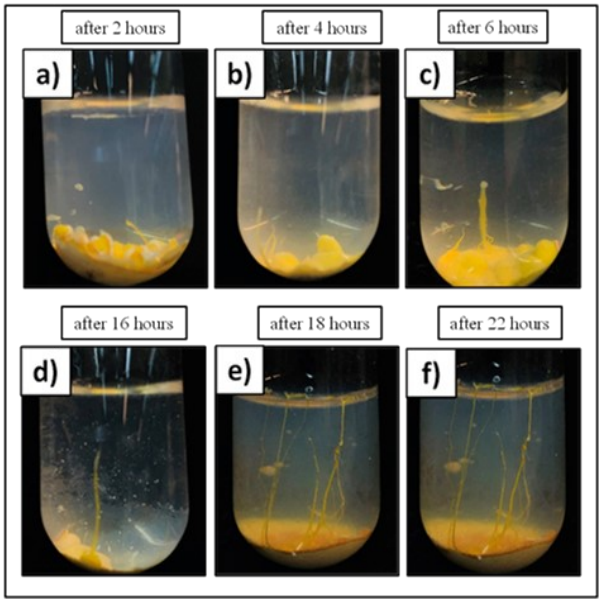

Figure S1. Photographs showing the time lapse images during the growth of the vertical structures. Different glass tubes were employed at different times for obtaining the photographs.

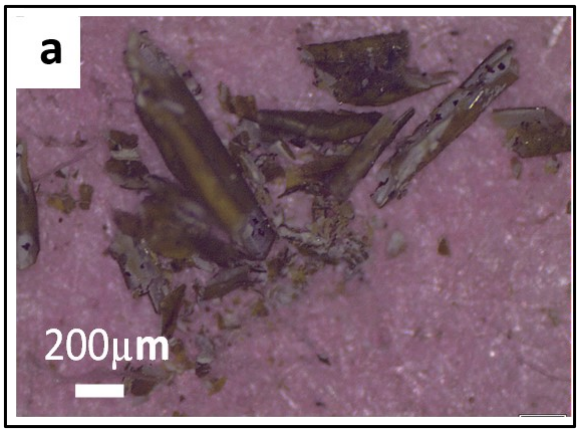

Figure S2. Optical microscopic image of the crushed and air-dried silver based chemical garden.

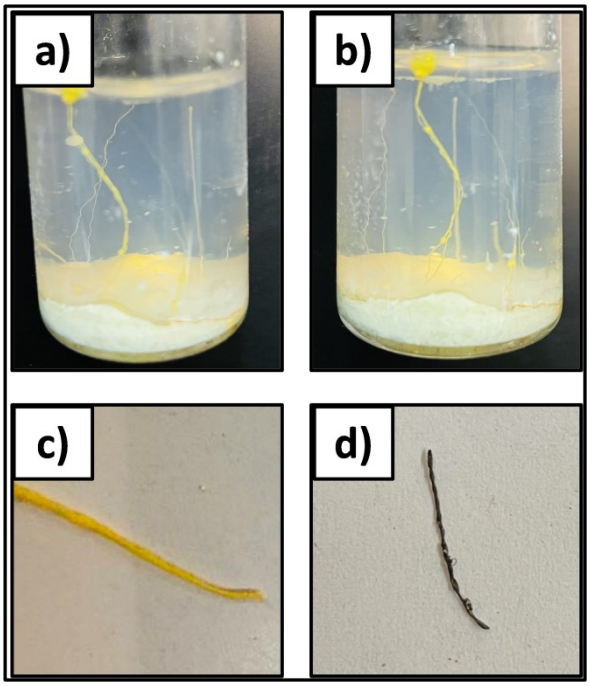

Figure S3. a) Camera images of the vertically grown tubes under dark (immediately after taking out from the dark cabinet). **b)** The same reaction vessel kept in light for 2 days (after removing from the dark cabinet). **c)** Photographic image of the freshly collected vertically grown tube from the reaction vessel **d)** Photographic image of a vertically grown tube after keeping the tube in light for 12-14 hours.

It is evident from the Figure S3c-d above that the fresh yellow tube consisting majorly silver silicate got decomposed to greyish black metallic silver tube over time when removed and kept in light for at least 12 hours duration. It is also observed that when such grown yellow tubes were kept intact in the reaction vessel containing the reaction mixture the decomposition was either absent or occurred at a very low rate (Figure S3a-b).

Figure S4. a) Small prominent free-standing vertical structures were observed in the reaction kept under light in which newly purchased silver nitrate (from Finar Limited) was utilized

Figure S4. b) No prominent free-standing vertical structures were observed when the reaction was carried out under direct sunlight with the newly purchased silver nitrate (from Finar Limited). Growth is seen on the walls of the glass tube and no free-standing structures were present.

Nonetheless, we also tried the dark and light reactions by utilizing aged silver nitrate from a different chemical manufacturer viz. Merck & Co. The results are depicted below in the Figures S4c-d. Figure S4c is the reaction vessel kept under light producing no vertical structures and Figure S4d represents the dark reaction where very prominent free-standing vertical yellow tubes are observed similar to the dark reaction in which Final Limited aged silver nitrate salt was utilized.

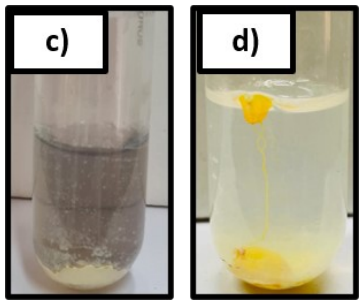

Figure S4. c) Light reaction and **d)** Dark reaction, by utilizing aged silver nitrate from Merck & Co. There were no vertical tubes in the reaction carried out under light and there were vertically grown structures observed in the reaction carried out under dark condition.

Because silver salts are extremely light sensitive, we initially focused on the dark induced growth. Later on, we turned our attention on the growth of the silver based chemical gardens under light, which is less perceptible. Some vertical structures were observed even under light conditions when a newly purchased silver nitrate salt was utilized in the experiment as can be seen from the Figure S5a. This may necessitate further investigation but we observe scrupulously that as the silver nitrate ages, it does not give rise to tubes in light and only produces tubes in dark conditions, whereas freshly purchased silver nitrate does give rise to some vertically grown structures but the same silver nitrate if it ages a similar reaction would produce no such vertical structures. Also, we observe that there are no such structures when the reaction was carried out under direct sunlight even when newly purchased silver nitrate was utilized in such a reaction (Figure S5b). This again supports the fact that silver nitrate would give rise to chemical garden like vertical tubes majorly in dark.

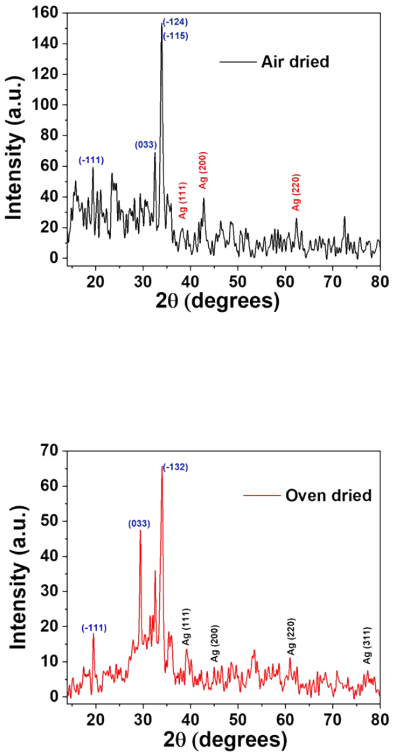

Figure S5. PXRD patterns of the vertically grown silver silicate chemical garden after air-drying for more than seven days and oven-drying at 108 oC for 10 minutes (air-drying and oven-drying carried out in light and not in dark).

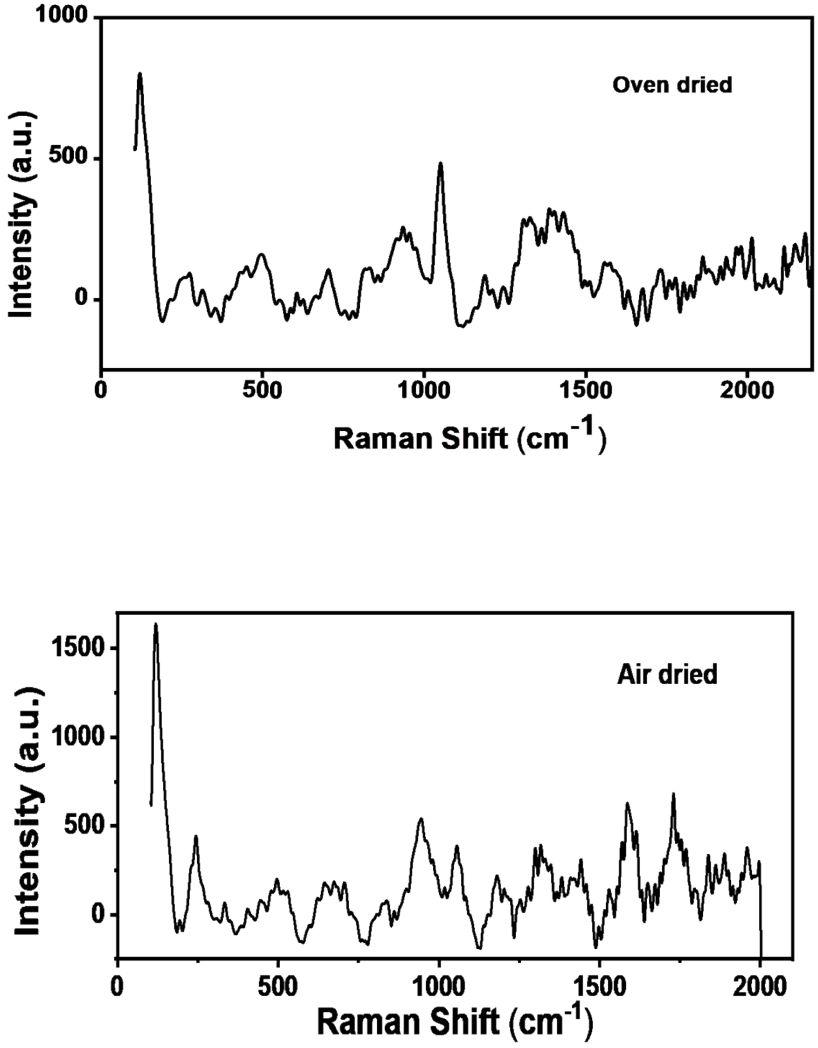

Figure S6. Raman Spectra of the vertically grown oven dried and air-dried silver silicate chemical gardens.

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