

Supporting information

Self-Assembly of Colloidal Single-Layer Carbon Nitride

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Materials and Methods

1. Preparation of bulk GCN and colloidal SLCN species.

To produce bulk GCN melamine (Sigma-Aldrich, no additional purification) was placed into an open quartz vessel and annealed in air in an oven at a selected temperature T_{pc} varied from 400 °C to 700 °C for a certain period of time t_{pc} . This period was kept constant at 1 h for all temperatures and varied from 0.5 to 2 h for $T_{pc} = 700$ °C. The oven temperature was elevated from 25 °C to 650 °C with a rate of $\sim 10^\circ$ per min. The mass yield of the product was 15–16%. The g-CN was cooled to room temperature, grinded in a mortar, and stored under ambient

conditions in the dark.

Colloidal SLCN was produced by the exfoliation of bulk GCN samples in an aqueous solution of NEt_4OH (Sigma-Aldrich, no additional purification, 1.36 M, 20 w.%) kept at the boiling point, 98-100 °C. In a typical procedure, 1.0 g GCN was mixed with 20 mL aqueous NEt_4OH solution and kept for 6-8 h at the boiling temperature with magnetic stirring and using a reflux condenser to avoid solvent evaporation. The bulk GCN was completely dissolved yielding a mass concentration of 50 g/L and a molar concentration of C_3N_4 units of 0.54 M. The solutions were optically transparent and retained stability toward aggregation and formation of a sediment for many months.

Purification of freshly exfoliated SLCN colloids was performed by adding a non-solvent – 2-propanol, collecting the precipitate, and redispersing it in deionized (DI) water. In a typical procedure, 1 mL of non-purified SLCN colloid was mixed with 14 mL 2-propanol, the mixture kept stirred for 15 min, and then subjected to centrifugation at 5000 rpm for 5 min. The precipitate was separated from the supernatant and redispersed (this process is spontaneous) in 1 mL DI water.

2. Spectral characterization of bulk GCN and colloidal SLCN.

PL spectra of the bulk GCN samples were registered using a BlackComet spectrometer (StellarNet Inc.) in the range of 190-1000 nm using a UV LED (360-370 nm, Thorlabs) as an excitation source. Absorption and PL spectra of colloidal SLCN solutions were registered in standard 10.0 mm quartz optical cuvettes using a Black Comet CXR-SR UV/vis/NIR spectrometer (StellarNet Inc., USA) equipped with miniature deuterium/halogen lamps (absorption spectra) or a 390 nm diode (PL spectra) as an excitation source and 100 μm slits in the range of 220-1100 nm. Colloidal solutions were diluted prior to the measurements (0.001 mL per 2.5 mL DI water). Absorption spectra were acquired for an accumulation time of 100 ms with five consecutively taken spectra averaged and the absorbance of a cuvette with pure DI water subtracted from the final spectrum. PL spectra were registered with an acquisition time of 500 ms and normalized to the absorbance of the colloids at 390 nm.

Raman spectra were excited using a 532 nm solid state laser and registered with a spectral resolution of about 2 cm^{-1} using a LabRam HR800 or Xplora micro-Raman system equipped with CCD detectors. The incident laser power under the microscope objective (50x) was 0.1 - 0.01 mW.

FTIR spectra were recorded in the attenuated total reflectance (ATR) mode using a Vertex 70 spectrometer (Bruker) equipped with a Platinum ATR diamond accessory in the range of 400-4000 cm^{-1} and with a spectral resolution of 0.4 cm^{-1} . A drop of a colloidal SLCN sample was

placed on the surface of the ATR diamond and FTIR spectra were taken automatically each 15 s till the complete drying of the colloidal droplet. The spectra of bulk GCN were taken by pressing a GCN pellet to the diamond surface.

XPS measurements were performed with an ESCALAB 250Xi X-ray Photoelectron Spectrometer Microprobe (Thermo Scientific) equipped with a monochromatic Al K_{α} (1486.68 eV) X-ray source. A pass energy of 200 eV was used for survey spectra and 20 eV for high-resolution core-level spectra (providing a spectral resolution of 0.5 eV). Spectra deconvolution and quantification were performed using the Avantage Data System (Thermo Scientific). The linearity of the energy scale was calibrated by the positions of the Fermi edge at 0.00 ± 0.05 eV, Au4f7/2 at 83.95 eV, Ag3d5/2 at 368.20 eV, and Cu2p3/2 at 932.60 eV measured on *in situ* cleaned metal surfaces. To prevent charging, the samples were measured applying a built-in charge compensation system.

The hydrodynamic size of colloidal SLCN particles was determined by the dynamic light scattering (DLS) spectroscopy on a Malvern ZetaSizer Nano S at 22 °C.

Photographs of luminescent GCN samples were registered at ambient conditions under illumination with a UV lamp (350-370 nm).

3. Structural characterization of bulk GCN and SLCN species.

X-ray diffractograms were collected using a Rigaku SmartLab diffractometer in an angle range of $2\theta = 5-100^{\circ}$ with a step rate of 0.05° per min using 9 kV copper K_{α} irradiation. The samples were produced by drop-casting SLCN colloids on a glass plate at room temperature. The drop-cast solutions were dried in vacuum. Equal amounts of the various colloidal samples were deposited on the glass plates to enable comparison of the peak intensities.

In the *in situ* XRD experiments a drop of colloidal SLCN solution was placed on a cleaned glass substrate and the diffraction patterns were taken periodically each 2 min in the range of $2\theta = 10-40^{\circ}$ till the complete drying of the droplet. No specific control of the atmosphere inside the diffractometer chamber was performed during the measurements.

AFM images were acquired with an AFM 5500 from Keysight (Agilent). The AFM tip had a radius of 10 nm and the Si cantilever a resonance frequency of 180 kHz. The samples were prepared by drop-casting of a very diluted (from 5 parts per 1000 to 40-70 parts per 1000 parts of DI water) SLCN colloids on a freshly cleaved mica surface and dried in a nitrogen stream at room temperature. No ultrasound treatment of the colloidal samples was performed before the preparation of the samples. The original concentrated SLCN samples were diluted, drop-casted on mica, and measured by AFM within 5-10 min after the event of dilution to minimize possible contamination of the samples. Freshly-cleaved mica and pure tetraethylammonium hydroxide

solution were used as “blank” experiments to evaluate the roughness of the substrate and height background of the pure colloidal stabilizer (NEt_4OH).

The height distributions of SLCN sheets were plotted based on AFM measurements of the height profiles for several hundred separate sheets. The AFM images were processed using the Gwyddion software (with “plane subtraction” and “aligning rows” filters, and zero leveling) and marked by using the edge-detection grain marking tool of Gwyddion and the distributions of mean height were plotted for each image.

Figures

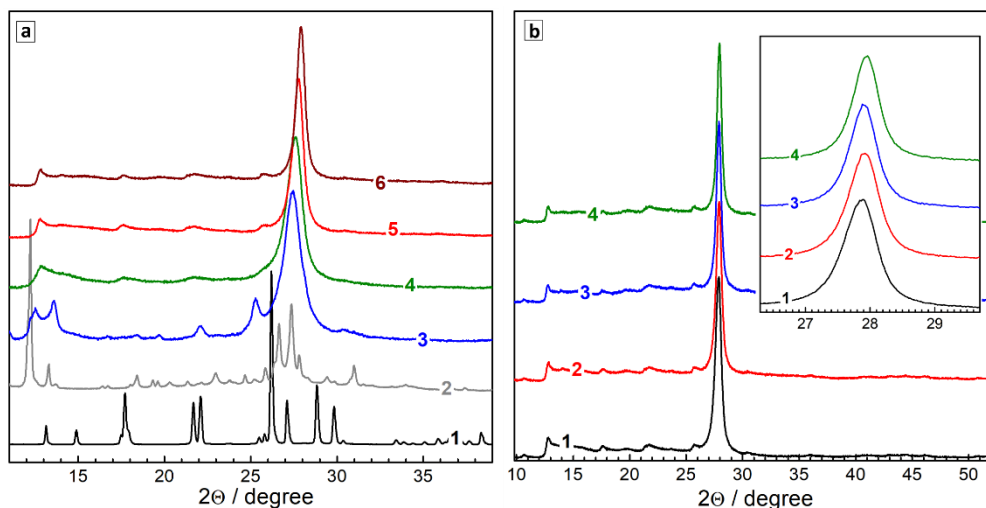


Figure S1. (a) XRD patterns of melamine (curve 1) and GCN samples produced at 400 °C (2), 500 °C (3), 600 °C (4), 650 °C (5), and 700 °C (6) during 60 min polycondensation. (b) XRD patterns of GCN produced at 700 °C for polycondensation durations of 30 min (curve 1), 60 min (2), 90 min (3), and 120 min (4). Insert shows an enlarged fragment with the (002) peaks.

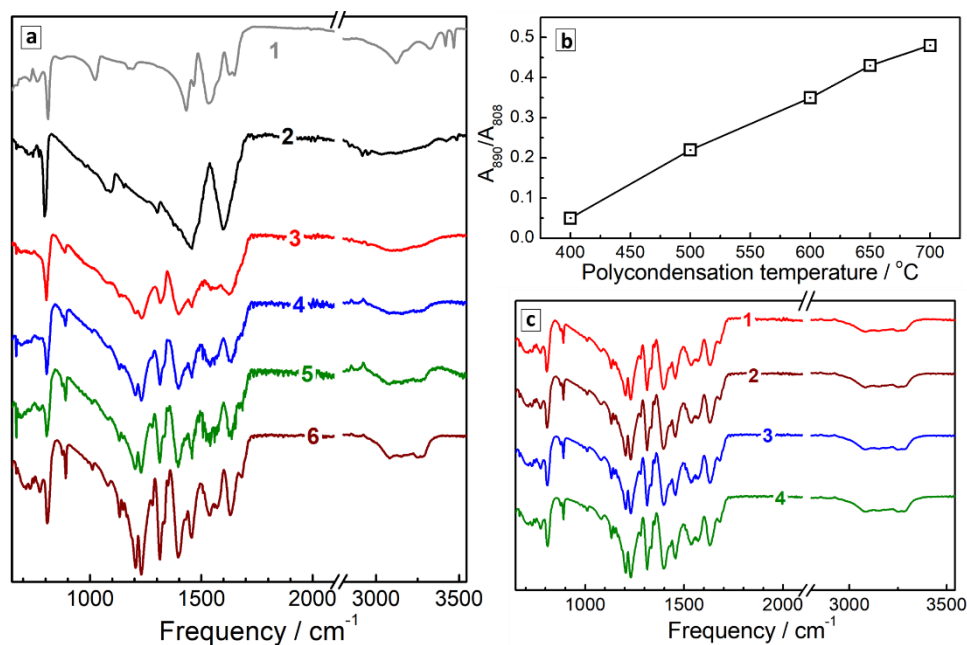


Figure S2. (a) FTIR spectra of melamine (curve 1) and bulk GCN samples produced at 400 °C (2), 500 °C (3), 600 °C (4), 650 °C (5), and 700 °C (6) with 1 h polycondensation. (b) Ratio of band intensities at 808 and 890 cm⁻¹ as a function of polycondensation temperature. (c) FTIR spectra of bulk GCN samples produced at 700 °C for polycondensation durations of 30 min (curve 1), 60 min (2), 90 min (3), and 120 min (4).

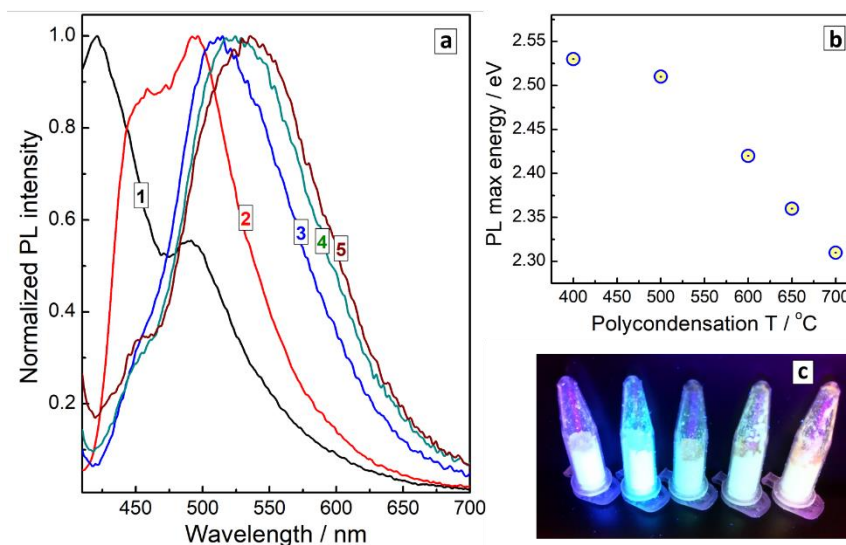


Figure S3. (a) Normalized PL spectra of bulk GCN powders prepared at 400 °C (1), 500 °C (2), 600 °C (3), 650 °C (4), and 700 °C (5) with 1 h polycondensation. (b) The energy of the longer-wavelength PL band maximum as a function of the polycondensation temperature. (c) Photographs of bulk GCN samples produced at 400, 500, 600, 650, and 700 °C (from left to right) taken under UV illumination (350-390 nm).

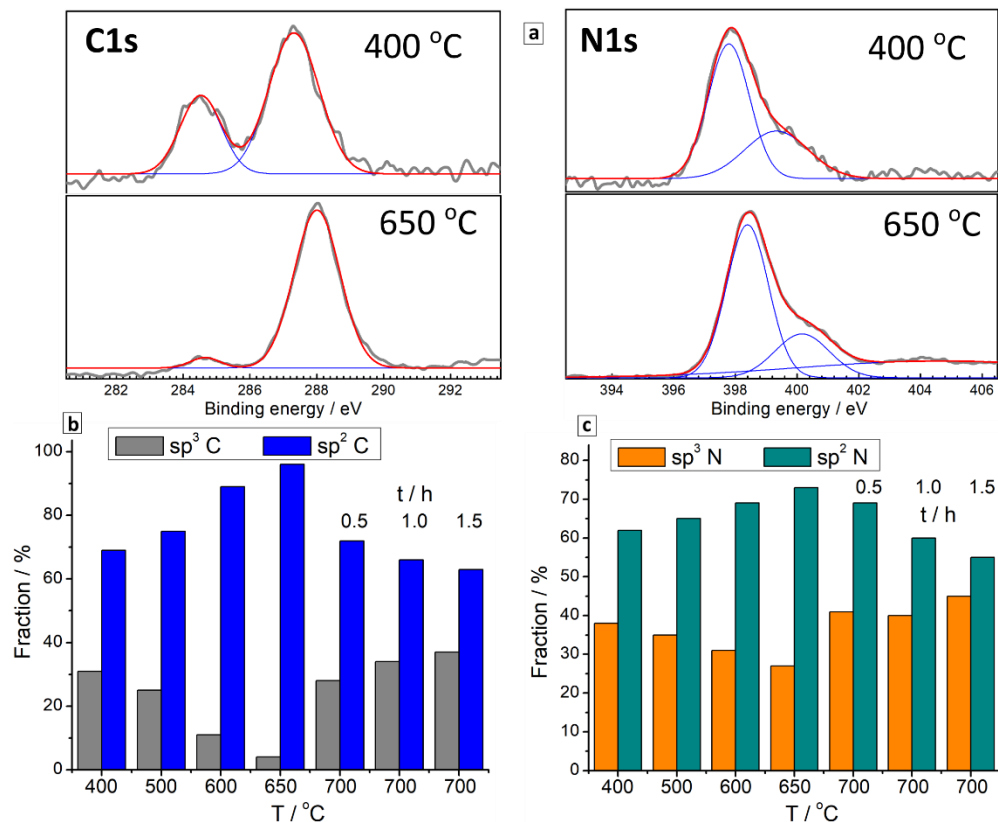


Figure S4. (a) X-ray photoelectron spectra (N1s and C1s electron binding energy ranges) of bulk GCN samples produced at 400 and 650 °C. Gray lines are experimental spectra, blue lines - single Gaussian components, red line - resulting fitting curve. (b,c) Atomic fractions of different forms of carbon and nitrogen in bulk GCN samples produced at different conditions determined by XPS: 400 to 700 °C for 1 h (left part of the graphs) and 0.5 to 1.5 h at 700 °C (right part of the graphs).

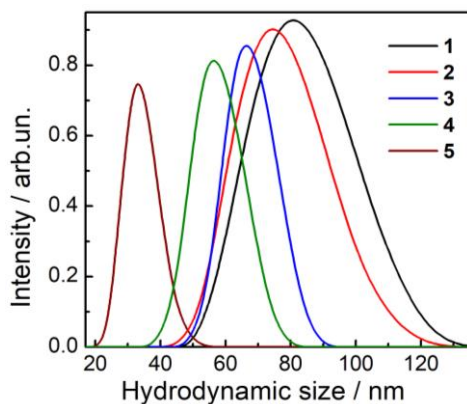


Figure S5. Volume-averaged distributions of the hydrodynamic size of colloidal SLCN sheets produced from GCN samples synthesized at different polycondensation temperature of 400 °C (curve 1), 500 °C (2), 600 °C (3), 650 °C (4), and 700 °C (5). $t_{pc} = 1$ h.

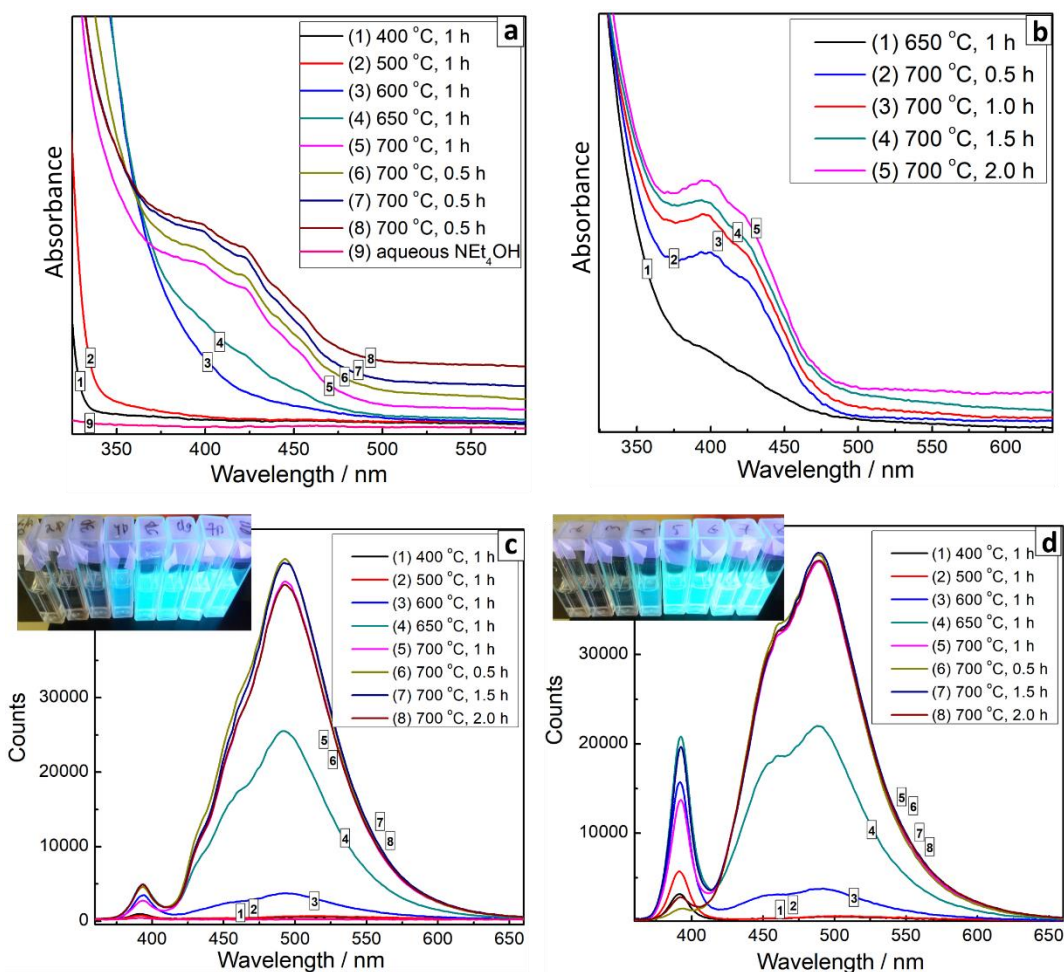


Figure S6. (a,b) Absorption spectra and PL (c,d) of nonpurified (a,c) and purified (b,d) SLCN exfoliated from bulk GCN synthesized at different conditions. Curves 5-8 in (a) and 3-5 in (b) are artificially elevated to avoid overlapping. Inserts in (c,d): photographs of colloidal solutions under illumination with UV light (350-390 nm).

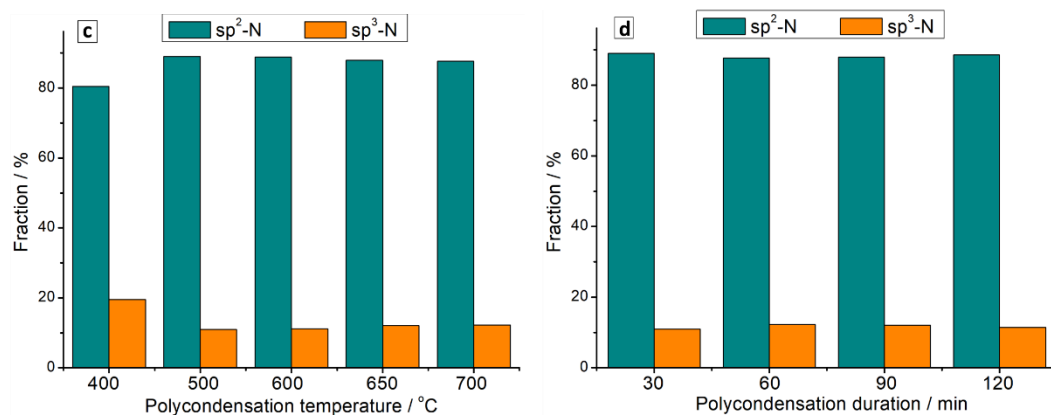


Figure S7. Atomic fractions of different forms of carbon and nitrogen in dried colloidal SLCN samples produced at different conditions determined by XPS.

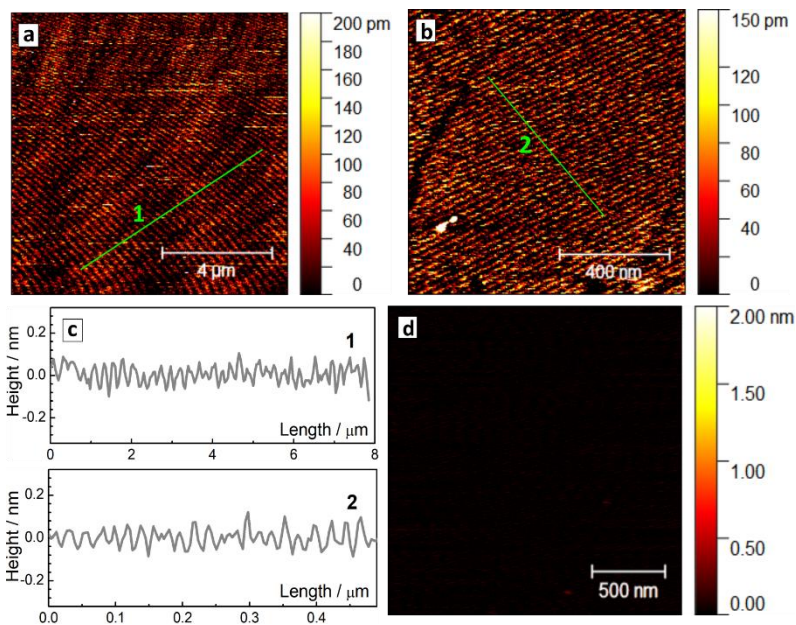


Figure S8.

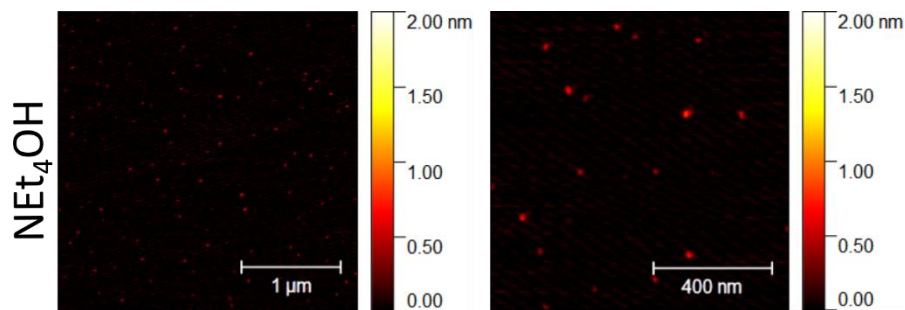


Figure S9. AFM images of dried residuals of NET_4OH sample produced in the same conditions as SLCN samples.

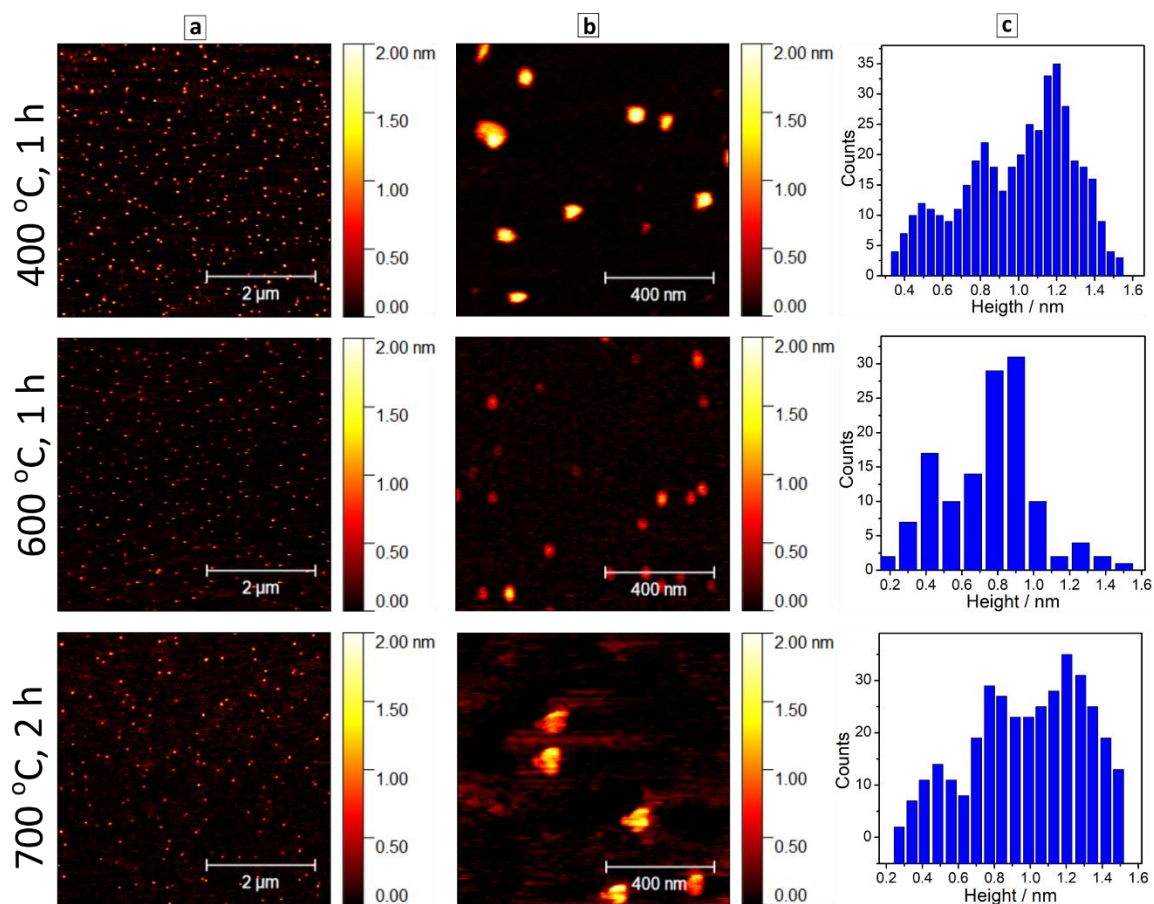


Figure S10. (a,b) AFM images of non-purified SLCN samples exfoliated from bulk GCN produced in different conditions. (c) Height distribution of SLCN particles based on the AFM measurements.

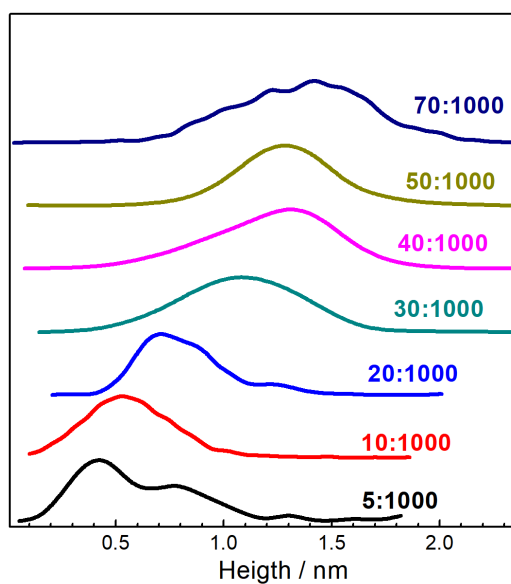


Figure S11. Height distributions calculated from AFM images for purified SLCN-700-p samples on mica produced at different dilution of the original colloidal solution.

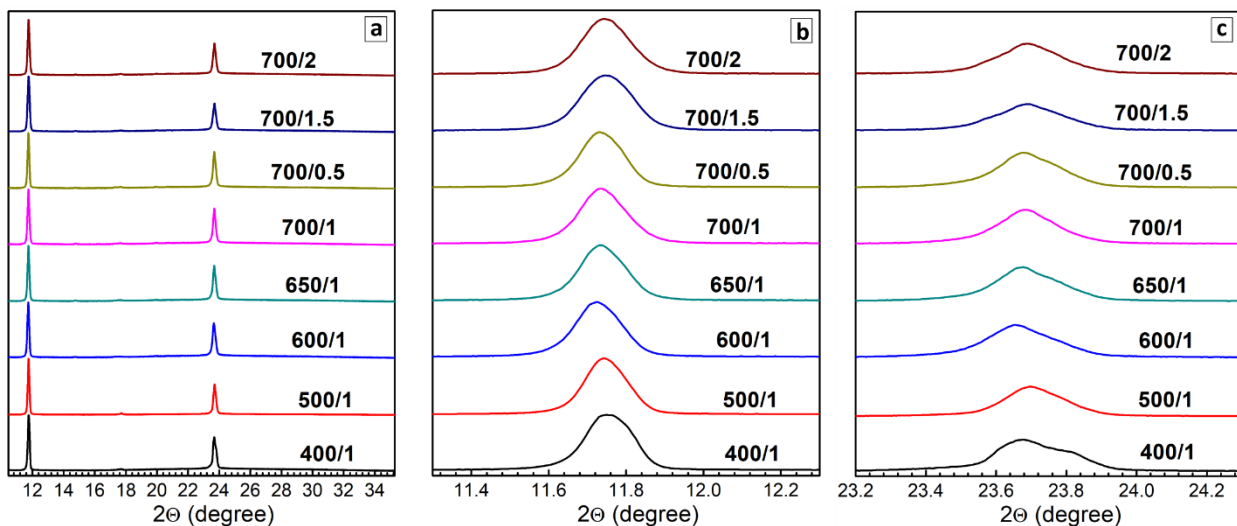


Figure S12. XRD of intercalates produced by drying purified colloidal SLCN samples produced at different combinations of T_{pc}/t_{pc} as provided in the figures. Graphs show the same XRD profiles presented at different angle ranges.

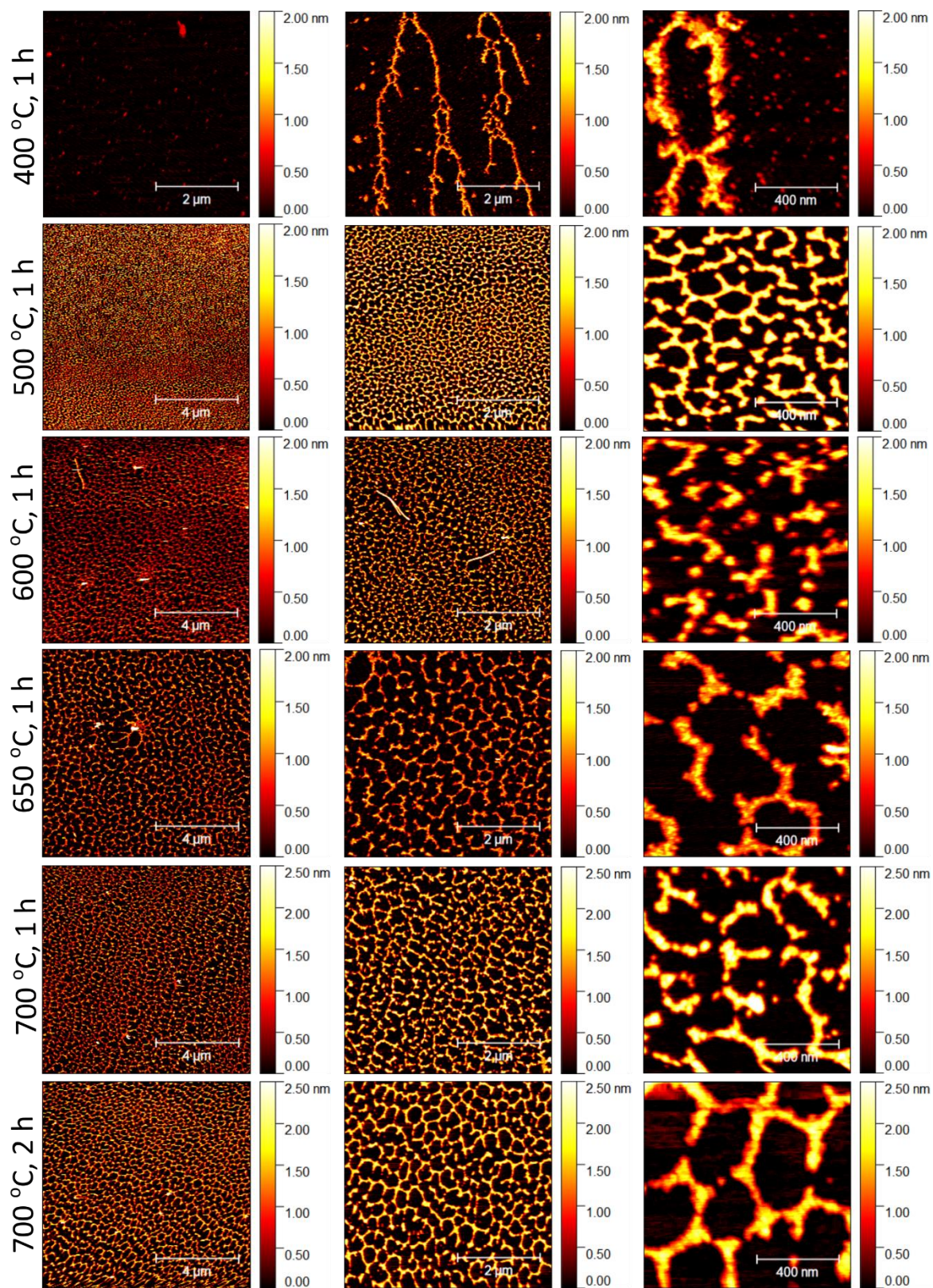


Figure S13. Collection of AFM images of SLCN samples produced in different conditions. Dilution is 40:1000.

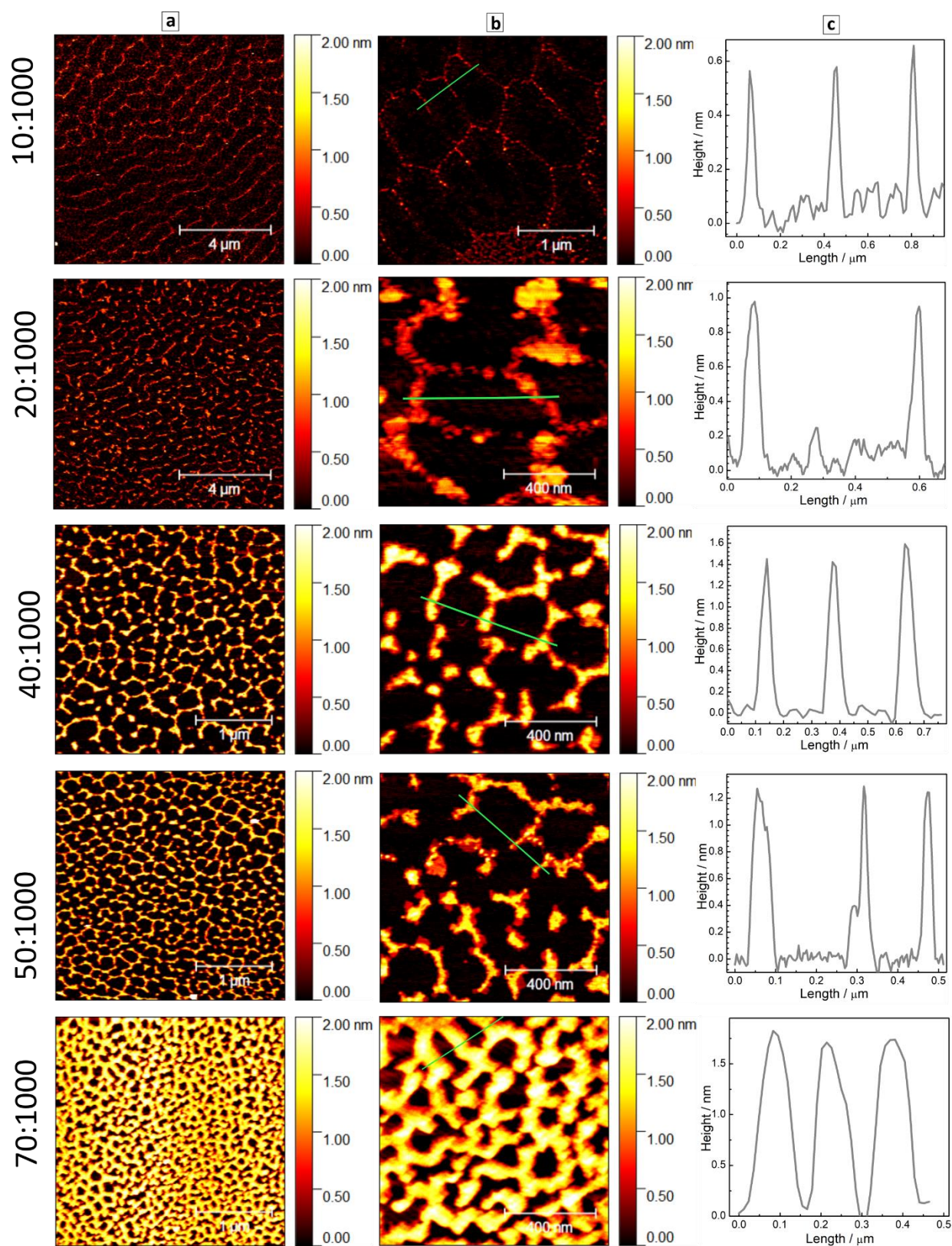


Figure S14. AFM images (a,b) and height profiles measured for SLCN-700-p samples on mica prepared at a different dilution of the original colloidal solution.