Bioinspired Scaffolding by Supramolecular Amines Allows the Formation of One- and Two-Dimensional Silica Superstructures

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EXPERIMENTAL MATERIALS.

Pinacyanol chloride, Sodium phosphate monobasic, sodium phosphate dibasic, (NH₄)₂MoO₄, Tartaric acid, and ascorbic acid were supplied by Sigma-Aldrich and used as received. Milli-q water or analytical grade ethanol was used for all experiments.

SAMPLE PREPARATION.

Pinacyanol acetate (PIC) was prepared from its chloride variant by counterion exchange with silver acetate in ethanol. The soluble fraction was dried under a nitrogen atmosphere and vacuum. Samples containing 1mM to 5 mM PIC were dissolved in weak phosphate buffer (from 1 mM to 5 mM) at a pH=7.4.

100µL of TEOS and 500 µL of the corresponding PIC solution in PIC were mixed at 1400 RPMs in a thermomixer for 24 h at 20 °C. The samples were centrifuged at 10000 rpm followed by careful removal of the unreacted TEOS with a pipette. The samples were further redisposed in ethanol and washed for at least 3 times before electron microscopy observations.

MOLYBDATE BLUE ASSAY

The amount of silica produced at different ethanol volume fraction was quantified by the molybdate blue assay. For this purpose, the silica obtained from the PIC reactions with TEOS incubated during 24 h was washed with ethanol, 1 M HCl and water, and further and dried in vacuum at 80 °C for 24 h. The solid was dissolved with 400 mL of 1 M NaOH, followed by acidification with 60 µL of a 25 wt% H₂SO₄ solution. Addition of 135 µL of (NH₄)₂MoO₄ (5 wt%), 135 µL of Tartaric acid (10%), and 135 µL of ascorbic acid (1 wt%) afforded the silico-molybdenum complex. The total amount of silica was computed by measuring the optical density at 820 nm in a plate reader.

SCANNING ELECTRON MICROSCOPY

SEM observations were performed in an FEI Nova600i NanoLab using a beam power of 10 kV and a spot size of 4.5Å. Washed samples were deposited and dried in a silicon wafer before the gold sputtering following by observations.

TRANSMISSION ELECTRON MICROSCOPY

Images were acquired using an FEI Tecnai 20, type Sphera TEM instrument operating at 200 kV (LaB6 filament) with a bottom-mounted 1024 × 1024 Gatan msc 794™ CCD camera.

Before measuring, the samples were deposit on a carbon-coated 200 – mesh grids (CF200-Cu, Aurion) by drying a drop of the particle dispersion in ethanol.

TIRF MICROSCOPY

Images were acquired on a commercial Nikon N-STORM microscope setup. In brief, the Nikon Eclipse Ti-E is equipped with a 100x Apo TIRF oil emersion objective (NA1.49). Excitation was
achieved with a laser combiner (Agilent Technologies, MLC4008) containing a laser diode. The setup was equipped with an automated adjustable mirror to allow tuning of the incident angle. For the detection of fibers at the interface, total internal reflection or highly inclined laser illumination were used. Excitation and emission light was filtered a Nikon N-STORM quad-band polychroic filter, and detection was performed using an EMCCD camera (Andor Ixon3) with pixel sizes of 160 nanometers. Time-lapse acquisitions of fibers at the interface were detected with continuous imaging at 60ms exposure times under low laser powers to avoid bleaching.

**UV-VIS SPECTROSCOPY**

Samples were measured in 2 mM quartz cuvettes in a Shimadzu UV-3102 PC UV-vis NIR scanning spectrophotometer. The absorbance, $A$, was converted into the molar absorption coefficient, $\varepsilon$, using the Beer-Lamber law:

$$A = \varepsilon c l$$

Where $c$ and $l$ are the dye concentration and cuvette path length, respectively.

**SMALL ANGLE X-RAY SCATTERING AND MODELLING**

All experiments were performed on a SAXSLAB GANESHA 300 XL system equipped with a GeniX-Cu ultra-low divergence microfocus sealed-tube source producing X-ray photons with a wavelength $\lambda = 1.54$ Å at a flux of $1 \times 10^8$ Ph s$^{-1}$. The 2D scattering data was recorded on a Pilatus 300 K silicon pixel detector with 487 x 619 pixels of 172 µm x 172 µm in size. The scattering intensity was measured as a function of the scattering vector, $q$:

$$q = \frac{4\pi \sin (\theta)}{\lambda}$$

SAXS profiles were obtained for samples containing 10 mM of PIC and different amounts of PB (from 0 mM to 5 mM). The samples were measured in 2.0 mm quartz capillaries (Hilgenberg), mounted with custom-built capillary holders. A known sample-to-detector distance of 713 mm (calibrated using AgBe standard) rendered the q-range of $0.015 < q < 0.445$ Å$^{-1}$. The scattering patterns were approximated to a core-shell model using SASview package (available for download [http://www.sasview.org](http://www.sasview.org)):

$$P(q) = \frac{\text{scale}}{V_s} F^2(q, \alpha) \sin (\alpha) + \text{background}$$

$$F(q, \alpha) = (\rho_c - \rho_s)V_c \sin \left( q \frac{1}{2} L \cos (\alpha) \right) 2J_1(q(R + T) \sin (\alpha)) \frac{1}{2}LRq^2 \cos (\alpha) \sin (\alpha)$$

$$+ (\rho_s - \rho_{\text{solvent}})V_s \sin \left( q \left( q \frac{1}{2} L + T \right) \cos (\alpha) \right) 2J_1 \left( q(R + T) \sin (\alpha) \right) \frac{q(R + T) \sin (\alpha)}{q \left( q \frac{1}{2} L + T \right) \cos (\alpha)}$$

Where the $c$, $s$, solvent subindexes refer to the core, shell, and solvent, respectively. $\alpha$, $V$, $L$, $R$, $T$, and $\rho$ refers to the angle between the axis of the cylinder and $q$, volume fraction, length, the radius of the core, shell thickness, and electron density, respectively. $J_1$ is the first-order Bessel function.

For fitting our patterns, we fixed the electron density of the solvent and the core to the same value as pure water (0.33 e/Å$^3$), the scale to the PIC concentration (c.a. 0.5 g/cm$^3$) and the shell thickness to theoretical thickness of a quinoline moiety in PIC molecule. We also assumed that the length was outside of the resolution limit of our equipment (infinity long fibers). During the fitting, we let the
electron density of the shell and the radius to float. Figure S1 shows one example of the model. Notice that this model does not fit at low q, possibly due to structural factor features that are not considered in the model. All of the samples yielded similar fitting values for the radius (c.a. 4 nm) and electron density of the shell (c.a. 0.55 e/Å³).

Figure S1. Representative fit of a core-shell cylinder in a sample containing 10 mM PIC and 4 mM PB.
Figure S2. Scanning electron microscopy micrograph of silica nanostructures obtained at room temperature in 1 mM PIC using pre-hydrolyzed TMOS as a precursor.

Figure S3. From left to right: representative examples of nummulites, fibers, and spherulites formed by PIC solutions with TEOS.
Figure S4. Representative example of the coexistence of silica fibers with nummulites.