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Supporting Information

Template-free Inorganic Synthesis of Silica-Based Nanotubes and their Self-Assembly to Mesocrystals

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1. Experimental

Synthesis: In a typical procedure, $OP(NH_2)_3$ (18.6 mg, 0.196 mmol) and $SP(NH_2)_3$ (70.0 mg, 0.630 mmol) were thoroughly mixed and ground in an argon-filled glove box and transferred into a flame-dried silica glass ampoule (wall thickness 2 mm, inner diameter 11 mm). While using dry nitrogen[1] as inert gas, $SiCl_4$ (33.8 µl, 0.294 mmol; Sigma-Aldrich, 99.998%) was added and dropped onto the mixture of the triamides. After freezing with liquid N_2, the ampoule was sealed (to a length of approx. 11 cm) under reduced pressure and subsequently heated in a conventional tube furnace in horizontal position to 200 °C and different target temperatures ranging from 300–700 °C (in steps of 100 °C) with dwell times of 12 and 48 h (heating and cooling rate: 1 $Kmin^{-1}$), respectively. Emerging condensation products such as NH_3, H_2S and HCl are (partially) deposited as $(NH_4)_2S$ and NH_4Cl at the places in the ampoule that cool first. After breaking the ampoules, the samples were recovered as dry, gray solids.

Electron Microscopy: First morphological investigations of the reaction products were made on a JSM-6500F scanning electron microscope (SEM) (JEOL Ltd., Tokyo, Japan) with a field emission source operated at 4.0 to 12.0 kV. All images shown are secondary electron images. The average chemical composition was studied with an energy-dispersive X-ray spectrometry (EDS) detector model 7418 (Oxford instruments, Oxfordshire, UK). Powders were placed on a brass sample carrier fixed with self-adhesive carbon plates (Plano, Wetzlar, Germany). The samples were sputtered with carbon (sputter device: BAL-TEC MED 020, BAL-TEC AG, Balzers, Netherlands) before loading them into the SEM chamber, since the reaction products were not electrically conducting.

To obtain more detailed information about the NTs and flakes, a FEI Titan 80–300 S/TEM transmission electron microscope (TEM) with a field emission gun, a Gatan Tridiem image filter and an EDAX EDS detector for analytical measurements was employed. Diffraction patterns were recorded with a Gatan UltraScan 1000 (2k × 2k) CCD camera. For sample preparation, the grayish solids were suspended in ethanol (99.9 %), ultrasonicated for 10 min and few drops of the suspension were placed on a copper grid coated with an amorphous, holey carbon layer (Lacey S166-2, PLANO). After plasmacleaning for 10-30 s, the TEM measurements were performed at 300 and 80 kV, respectively. For this, the grids were mounted on a double tilt holder with a maximum tilt angle of 30°.

2. EDX measurements of the two reaction products

The chemical composition of the reaction products were investigated with EDX on the FEI Titan 80–300 S/TEM. Fig. S1a shows the EDX spectrum of SiO_2-based NTs. The elements Si, O, P and N were detected. Cu results from the Cu grid and Cl from the starting material. The EDX measurement of a flake (Fig S1b) reveals the presence of the elements Si, O, P and N. The Cu stems again from the grid and S from the starting material. The amount of Si is much higher than the amount of P in the NTs and vice versa for the flakes.

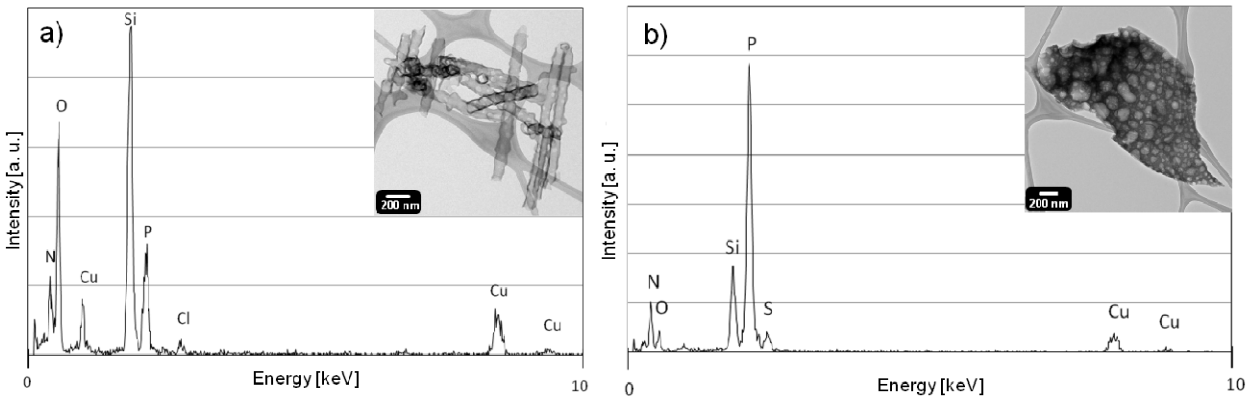

Figure S1. EDX measurements of a) SiO_2-based NTs and b) a flake.

3. Image showing a polymeric Si/P/O/N/H agglomeration

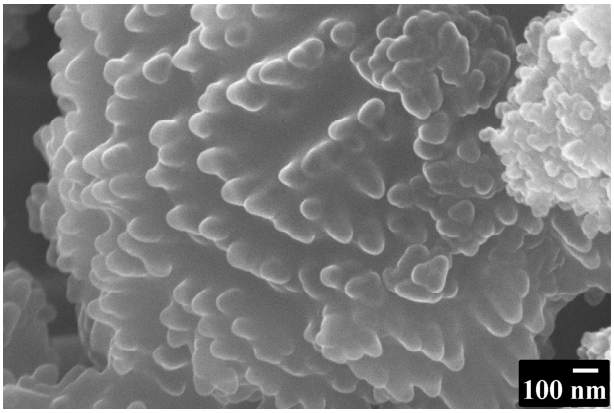

Figure S2. SEM image of a polymeric agglomeration indicating the starting point for NT growth.