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Template-free inorganic synthesis of silica-based nanotubes and their self-assembly to mesocrystals†

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A novel synthesis approach for silica-based nanotubes (NTs) was discovered in the purely inorganic system containing the molecular compounds $OP(NH_2)_3$, $SP(NH_2)_3$ and $SiCl_4$ in evacuated and sealed silica glass ampoules. Without any solvent or structure directing template the amorphous NTs self-organise to form orthogonally ordered, 3D hyperbranched mesocrystals, exhibiting an interesting material for nanofluidic device applications.

Silica, the most abundant solid compound on earth, occurs in a multitude of crystalline and amorphous forms and has been used for a diverse range of applications (*e.g.* as ceramics, quartz oscillators) for a long time.[1,2] The discovery of one-dimensional silica nanotubes (NTs)[3] has generated considerable attention towards the search for further functionalities, *e.g.* in gas storage, drug/gene-delivery, sensing, catalysis or nanofluidic systems.[4] Triggered by this high potential, research concerning new synthesis methods for silica-based hollow NTs is a topic of great interest. While two-dimensional, layered compounds exhibit an intrinsic rolling up tendency,[5,6] the preparation of purposeful NTs of three-dimensional, isotropic materials like silica, however, usually requires structure-directing templates.[7,8] Therefore, physical templates such as porous alumina membranes or previously fabricated nanowires in combination with atomic layer deposition (ALD), organic surfactants in self-assembled gels or biological templates were drawn into consideration.[3,9–14] In principle, these methods allow a precisely controlled growth of silica NTs. In some cases, however, the template-assisted synthesis exhibits laborious multiple-step reactions with partially toxic organic substances involved. Apart from that the process of removal of the template could be a severe problem causing collapse of a newly prepared tubular silica nanostructure.[4]

Silica (SiO_2) is isoelectronic to phosphorus oxonitride (PON) and phosphorus oxonitride imide (PN(NH)) while a structural analogy is consequent. The related compound classes of nitridophosphates and oxonitridophosphates exhibit structural chemistry with many variants including *e.g.* highly condensed layered as well as open-

framework structures.[15–20] In the course of our systematic investigation of these silicate-analogous compound classes, we discovered a novel approach for a template- and solvent-free synthesis of silica-based NTs. In a purely inorganic reaction, actually trying to synthesise a silicon oxonitridophosphate, we simply performed a reaction of a mixture of phosphoryl triamide $OP(NH_2)_3$ (ref. 21) and thiophosphoryl triamide $SP(NH_2)_3$ (ref. 7 and 22) with silicon tetra-chloride $SiCl_4$ in a closed system of a sealed silica glass ampoule (see ESI†). For systematically exploring the system, we performed the synthesis at different temperatures from 300 to 700 °C (in steps of 100 °C) while maintaining all other conditions constant. Additionally, some of the syntheses were carried out with an increased amount of $SiCl_4$ in the ampoule. A structure-directing agent was not added at any step of the synthesis. The synthesis products were mainly recovered as homogeneous, dry, grey solids.

A scanning electron microscopy (SEM) image of a representative as-synthesised sample is shown in Fig. 1. Overall, the reaction products consist of three different morphologies. There are vitreous, shapeless flakes as the main product, amorphous clusters of hollow particles, and finally, although no structure-directing agent was added, amorphous silica-based NTs that usually form nettings. The length of the NTs goes up to several micrometers, while the hollow particles as the shortest version of the NTs are the lower endpoint with a size less than 150 nm. Our systematic series of experiments
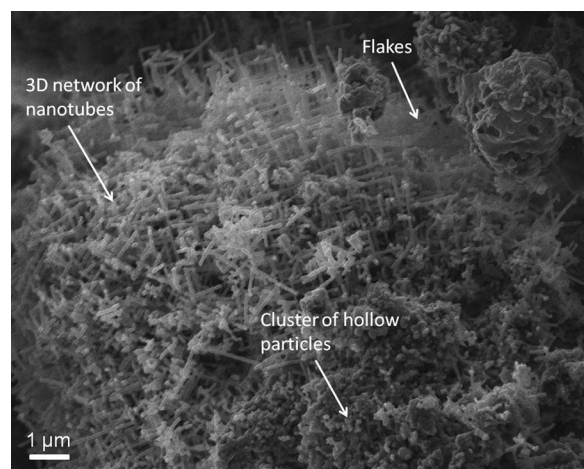
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Fig. 1 SEM image of the as-synthesised sample showing nanotubes tending to form 3D networks, shapeless flakes and cluster of particles.

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performed at different synthesis temperatures from 300 to 700 °C shows, besides the reproducibility, a temperature dependency concerning the relative amount of NTs and hollow particles and the cross-sectional dimensions of the NTs. Although all morphologies emerge at each synthesis temperature, the NT structures are rather more frequent at higher temperatures than at lower ones and *vice versa* for the hollow particles.

Transmission electron microscopy (TEM) studies reveal a bamboo-like growth of the NTs (see Fig. 2b) which is also observed for CN_x NTs.[23] From TEM images the mean cross-sectional diameters and wall thicknesses of the NTs have been determined for each synthesis temperature. The wall thicknesses decrease from 24(3) nm for a synthesis temperature of 300 °C to 15(2) nm for 700 °C. The diameters are narrower when the synthesis is performed at higher temperatures. They range from 126(24) nm for a synthesis temperature of 300 °C down to 72(17) nm for 700 °C. The large deviation is due to the bamboo-like structure. Accordingly, with our new template-free approach a control concerning the diameter of silica-based NTs is feasible. The observed cross-sectional dimensions are within the typical range reported for silica nanotubes.[4] For a deeper insight into the system and more detailed analysis of the different morphologies, we performed a series of further TEM investigations. Bright-field images of a typical vitreous flake and an array of NTs synthesised at 700 °C are shown in Fig. 2a and b. The flake appears porous with differently sized holes indicating intensive gas formation. The NTs have a partially lopsided growth and are orthogonally branched in all three directions in space as already illustrated in Fig. 1. Furthermore, the hollow nature of the NTs is clearly observable in Fig. 2b, where identification of walls by a different mass–thickness contrast is possible. This is even more evident in Fig. 2c, where an exemplary, high-magnification TEM image of a single tube, synthesised at 700 °C, is presented. As is obvious in Fig. 2d, where different shaped hollow particles as the shortest

version of NTs are shown, all NTs are originally closed. Open ends are only generated by breakage during sample preparation (Fig. 2c). Electron diffraction (ED) experiments (insertion in Fig. 2a and b) for all morphologies showed no Bragg intensities. Consequently, as already suggested by powder diffraction measurements of samples, the flakes as well as the tube structure are characterised as amorphous. This amorphous character is definitely present from the beginning (as-synthesised material) and was confirmed by independent measurements using acceleration voltages of 80 and 300 kV. No difference in shape was observed, when working under these different conditions. In addition the NTs were found to be surprisingly stable under electron bombardment.

Investigations concerning the composition were performed employing energy dispersive X-ray spectroscopy (EDX). Using the TEM, we extensively analysed the different morphologies in a sample synthesised at 700 °C (Fig. 1) by recording a number of spectra at different spots. For both, the flakes and the NTs, the elements Si, P, O and N were detected (see ESI Fig. S1†). Semi-quantitative analyses resulted in an approximate atomic ratio of Si : P of 4 : 1 for the NTs which was inverted (1 : 4) for the flake material. While O is predominantly incorporated in the NTs (together with Si), N is mainly contained in the flakes (together with P). Another result from the EDX investigation is that the composition of the hollow particles is similar to that of the NTs. Hence one can conclude that the NTs and the hollow particles exhibit the same material. Consequently, from our template- and solvent-free inorganic synthesis approach two products, namely (Si)/P/(O)/N amorphous flakes and phosphorus- and nitrogen-doped silica or even phosphorus-doped silicon oxonitride NTs are yielded. In addition to these determined compositions, regarding the starting materials ($OP(NH_2)_3$, $SP(NH_2)_3$), one can assume that hydrogen is more or less present in all structures. This is not separately verified for each structure but experiences with other oxonitridophosphates[17,18] and infrared spectra from the material do suggest this. Assuming that the materials are most probably built up from 3D interconnected SiX_4 and PX_4 tetrahedra, respectively, hydrogen is either included in connecting positions X as –NH– or as terminal –OH or –NH₂ groups. As we know from the chemistry of nitridosilicates or nitridophosphates, these functionalities can also exist after high temperature treatment. The mixing of Si/P/O/N/NH in the materials is also fully comprehensible regarding the structural chemistry of crystalline SiO_2, PON and PN(NH). All three compounds exhibit the cristobalite structure type[1,24,25] so that continuous solid solutions $Si_{1-x}P_xO_{2-x-y}N_x(NH)_y$ ($x \leq 1$, $y \leq 2$ and $x + y \leq 2$) seem possible.

An important critical condition for the silica-based NTs is definitely the content of oxygen in the mixture of starting materials. As rather little O is introduced by our synthesis approach, the yield of flakes is much higher than that of the NTs. However, the reaction with the highest possible O content, the transformation of only $OP(NH_2)_3$ with $SiCl_4$, resulted not in the formation of NTs but in a vitreous Si/P/O/N compound. In contrast, the reaction of only $SP(NH_2)_3$ with $SiCl_4$ yielded no NTs as well but a nanocrystalline Si/P/N compound different from the only known phase $SiPN_3$ in this system.[26] This indicates that interplay between the different reactants is responsible for the NT growth.

As a first hypothesis we visualize the growth of the silica-based NTs as follows: starting from weakly condensed inorganic polymer agglomerations Si/(P)/O/(N) nuclei are built and form small cells (hollow particles) filled with gas. The polymer agglomeration in
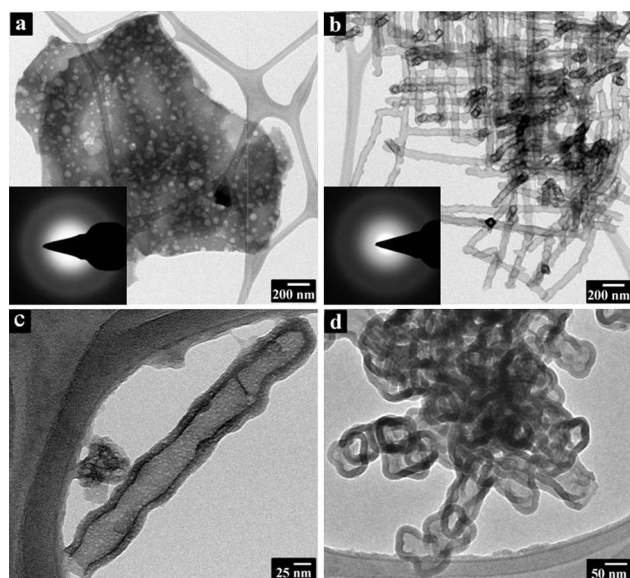

Fig. 2 TEM images of as-synthesised samples of (a) an amorphous flake with different sized pores, (b) an array of orthogonally branched silica-based NTs (both with the ED pattern as insertion), (c) single silica-based NT synthesised at 700 °C and (d) a cluster of hollow particles synthesised at 400 °C.

Fig. S2 (see ESI†) is a sign of such a starting point. While elevating the temperature in the following, more gas (NH$_3$, HCl, H$_2$S) is generated within the condensation process and the cells become more and more elongated and combine to more or less long and hyperbranched NTs. Thereby it seems that the growth is accompanied by a respective self-separating process towards Si/O and P/N resulting in a dropout of the flake material. This is comprehensible regarding the higher oxophilia of Si and NTs found growing nearby or on top of the flake material. The elongation and combination of the shapeable hollow particles are probably driven by the reduced pressure in the system (here, an ampoule), which also assists length growth in other assemblies.[27] Branching has mostly been observed orthogonally. This is probably effected by a maximal repulsion of the branches. Although of course further investigations are necessary, this model seems probable as NT structures are more frequently found at higher temperatures, while hollow particles are more frequently found at lower temperatures (see above).

As indicated, the described synthesis depends on the amount of SiCl$_4$. If the amount of SiCl$_4$ is increased to excess (67.6 μl, 0.589 mmol) keeping all other parameters like pressure, heating rate and dwell time constant, at a synthesis temperature of 700 °C impressive 3D assemblies of hyperbranched silica-based NTs are obtained. As presented in the SEM images in Fig. 3, mesocrystals with octahedral habitus are formed. These well-regulated nanopipe systems that can be isolated from the surface of the flake materials, afford interesting opportunities for constructing novel 3D nanofluidic devices. While other fabrication methods for inorganic nanofluidic devices usually require multiple production steps associated with templates,[9,28–30] our method exhibits a simple one-pot synthesis comprising only one single step. Another benefit in this context is that the silica-based NTs involve N, so harder and more thermally and chemically stable pipes could be provided for e.g. bioseparation[31] or fast mass transport[32] in nanofluidic devices. Strong N-doped silica is also interesting as glasses with variable refractive indices in optical applications (e.g. fiber Bragg gratings).[33]

In conclusion, a novel inorganic solvent-free synthesis approach for silica-based NTs is presented. This exceedingly interesting and promising system has to be further investigated with respect to the yield increase and growth mechanism. A detailed analysis is also desirable as this pure inorganic system creates fascinating mesostructures that are similarly found in nature.[34]
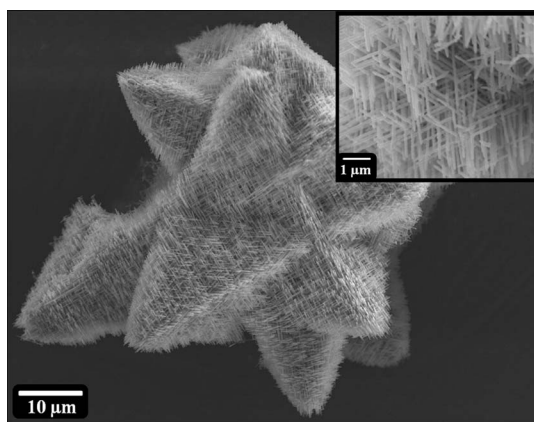

Fig. 3 SEM images of an as-synthesised sample showing an isolated intergrown mesocrystal and a zoomed-in view into the mesocrystal.

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