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Insight in the 3D morphology of silica-based nanotubes using electron microscopy

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ABSTRACT

Amorphous silica-based nanotubes (SBNTs) were synthesized from phosphoryl triamide, $OP(NH_2)_3$, thiophosphoryl triamide, $SP(NH_2)_3$, and silicon tetrachloride, $SiCl_4$, at different temperatures and with varying amount of the starting material $SiCl_4$ using a recently developed template-free synthesis approach. Diameter and length of the SBNTs are tunable by varying the synthesis parameters. The 3D mesocrystals of the SBNTs were analyzed with focused ion beam sectioning and electron tomography in the transmission electron microscope showing the hollow tubular structure of the SBNTs. The reconstruction of a small SBNT assembly was achieved from a high-angle annular-dark field scanning transmission electron microscopy tilt series containing only thirteen images allowing analyzing beam sensitive material without altering the structure. The reconstruction revealed that the individual nanotubes are forming an interconnected array with an open channel structure.

1. Introduction

One-dimensional (1D) inorganic nanomaterials like nanowires (NWs), nanotubes (NTs) or −rods exhibit fascinating properties such as efficient transport of electrons and optical excitations and are therefore promising for a variety of applications. Different approaches do exist to synthesize and grow those nanostructures which can further be directed into two-dimensional (2D) or even three-dimensional (3D) structures. This is essential for nowadays science and technology (Agrawal et al., 2015; Betzler et al., 2014; García-Calzón and Díaz-García, 2012; Joshi and Schneider, 2012; Yang et al., 2011). 1D nanostructures, for instance, are used as building blocks for applications like sensors, electronics, and photonics or as nanofillers in composites (Fan et al., 2015; Joshi and Schneider, 2012; Ni et al., 2015). Their properties are based on several specific parameters. They possess a very high surface-to-volume ratio due to their length and diameter dimensions (Bréchignac et al., 2007). Nanomaterials offer a range of new applications. Various growth methods allow tailoring diverse 1D nanostructures (e.g carbon NTs (CNTs), metal oxide NWs and NTs, III–V or II–VI based heteronanostructures and metallic NWs) (Bréchignac et al., 2007; Joshi and Schneider, 2012) and their 2D or 3D architectures for respective applications. The most frequently applied synthesis methods for NTs employ structure-directing templates (Bréchignac et al., 2007; García-Calzón and Díaz-García, 2012; Rao and Govindaraj, 2009; Yang et al., 2011). This includes inorganic templates like porous alumina membranes or inorganic nanomaterials (nanowires, −rods, or −tubes), organic self-assembled gels or biological and biomolecular templates like proteins and peptides (Fan et al., 2015; García-Calzón and Díaz-García, 2012; Rao and Govindaraj, 2009; Yang et al., 2011). A benefit of template-based approaches is the control of diameter and length of the NTs and the great variety of synthesis routes, e. g. sol-gel, hydrothermal or microemulsion synthesis methods. After growth, the template must be removed by dissolution or calcination, which often cannot be achieved completely. The challenge is to liberate the NTs without damage or even full collapse. Furthermore, by removal of the template, the orientation or ordered arrangement of the NTs may be lost; the nanostructures may even collapse entirely. The importance of developing template-free approaches is revealed by a new method reported

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by Ren et al. (Ren et al., 2014). Silica fibers are synthesized using the centrifugal jet spinning technique. After spinning and annealing SNT fibers are obtained.

To design 2D or 3D structures control over dimensions of the nanomaterials is indispensable and investigation of prepared nano-structures require analyzing methods with high resolution. Transmission electron microscopy (TEM) and its analytical techniques allow an in-depth characterization at the nanoscale. Nevertheless, conventional TEM depicts a 2D projection of a 3D object. To overcome this problem of loss by 2D projections, series of TEM or scanning TEM (STEM) images at various tilt angles can be acquired and 3D reconstruction of an object can be achieved. A range of techniques is currently applied where weighted back-projection (WBP) and the iterative techniques like simultaneous iterative reconstruction technique (SIRT) are the most prominent ones (Biermans et al., 2010; Midgley and Dunin-Borkowski, 2009). STEM imaging is often used for electron tomography experiments as diffraction artifacts and phase contrast effects in TEM mode can hinder or mislead the interpretation of the data (Hyun et al., 2008). Electron tomography is a powerful tool to obtain insight in the full 3D morphology of micro- and nano-sized objects (Britt et al., 2013; Biermans et al., 2010; Midgley and Dunin-Borkowski, 2009). Not only the external morphology can be determined but also the inner structure of e.g. NTs can be made visible in 3D (Hungría et al., 2009; Suh et al., 2013).

In this paper, we report about controlling the diameter and length of template-free synthesized amorphous silica-based nanotubes (SBNTs) that build 3D mesocrystals by varying the synthesis conditions such as temperature and ratio of the starting materials. In the recently reported novel template-free approach for SBNTs phosphoryl triamide, $OP(NH_2)_3$, (Klement and Koch, 1954) thiophosphoryl triamide, $SP(NH_2)_3$, (Schnick, 1989) and silicon tetrachloride, $SiCl_4$, were mixed under inert gas atmosphere, sealed in silica glass ampoules and heated to different temperatures ranging from 200 to 700 °C (Sedlmaier et al., 2012). We obtained the reaction products, flakes and NTs as well as hollow particles as side product, consisting all of Si, P, O, and N which were amorphous in X-ray and electron diffraction (Dennenwaldt et al., 2014; Sedlmaier et al., 2012). The SBNTs exhibit a bamboo-like structure. With electron energy loss spectroscopy (EELS) in the TEM on the nanoscale we found that the bonding behavior of the elements and the electronic structure of the SBNTs is a mixture of silicon dioxide (SiO_2) and silicon nitride (Si_3N_4) (Dennenwaldt et al., 2014). Furthermore, the SBNTs show a much higher stability against bases (Dennenwaldt et al., 2014) compared to SNTs reported in the literature (Hu et al., 2010). In the present work, the 3D arrangement, the internal morphology, diameter and length of these SBNTs is elucidated with focused ion beam (FIB) microscopy, TEM and STEM-HAADF tomography and correlated to the synthesis conditions. In comparison to our earlier studies we synthesized SBNTs using a higher $SiCl_4$ precursor concentration and contrast the results to the SBNTs synthesized with a lower $SiCl_4$ precursor concentration.

2. Materials and methods

2.1. Scanning electron microscopy

A JSM-6500F SEM (JEOL Ltd., Tokyo, Japan) with a field emission source operated at 4.0–12.0 kV equipped with an EDX detector model 7418 (Oxford Instruments, Oxfordshire, UK) was used to acquire SE images. For SEM sample preparation powder was placed on a cylindrical brass sample holder fixed with self-adhesive carbon plates (Plano, Wetzlar, Germany) and sputtered with carbon (sputter device: BAL-TEC MED 020, BAL-TEC AG, Balzers, Netherlands).

2.2. Transmission electron microscopy

For TEM sample preparation powder was suspended in ethanol and the solution was dropped on a lacey C-coated Cu grid (Lacey S166-2, PLANO). TEM studies were performed on a Titan 80–300 keV S/TEM equipped with an EDX detector and an energy filter for EELS measurements and on a 200 kV FEI monochromated F20 UT Tecnai (STEM/TEM) located at the NCEM in Berkeley. The tilt series used for the reconstruction has been acquired at 80 keV in STEM-HAADF mode using a tilt range of ±70° with steps of 10°. The inner diameter of the HAADF detector was 37 mrad, the outer diameter 200 mrad and the convergence angle 16.7 mrad using a condenser aperture of 50 μm.

2.3. Focused ion beam microscopy

A 3D assembly of the SBNTs was investigated by FIB sectioning on a Zeiss NVision40 FIB microscope. SE images were acquired with a low acceleration voltage of 2.5 kV. A carbon protection layer was deposited on the SBNT mesocrystal with successive ion beam induced deposition with a beam current of 300 pA at 30 kV. Cutting and thinning were performed at 30 keV, the polishing 30 keV with a beam current of 30 pA followed by 10 pA.

2.4. Synthesis of the SBNTs

According to our recently published work (Sedlmaier et al., 2012) the triamides $OP(NH_2)_3$ (Klement and Koch, 1954) (18.6 mg, 0.196 mmol) and $SP(NH_2)_3$ (Schnick, 1989) (70.0 mg, 0.630 mmol) were 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). After exchanging the inert gas to dry nitrogen at the Schlenk-line, $SiCl_4$ (Sigma-Aldrich, 99.998%) was then dropped onto the mixture. For the low concentration 33.8 μL (0.294 mmol) were added and for the high concentration 67.6 μL (0.589 mmol). During the synthesis nitrogen was used as inert gas. After having frozen the reaction mixtures in the ampoule with liquid nitrogen, the ampoules were sealed (to a length of approximately 11 cm) under reduced pressure and subsequently heated in a conventional tube furnace in horizontal position to 200 °C and different target temperatures (300–700 °C in steps of 100 °C, dwell times of 12 and 48 h, heating and cooling rate 1 K min^{-1}). The reaction products were obtained as a dry, gray solid.

2.5. Algorithm and reconstruction

After STEM-HAADF image acquisition the alignment was performed via ImageJ, (Rasband, 19972011) using the TomoJ add-on (Messaoudi et al., 2007) which includes a landmark-based alignment script (Sorzano et al., 2009). A masked SIRT was used to obtain an adequate segmentation and a good starting model to achieve the actual morphological reconstruction. This step was accomplished by a discrete algebraic reconstruction technique step (Zürner et al., 2012). Thirteen images have been used for reconstruction of the SBNTs fragment.

3. Results and discussion

First experiments concerning the influence of the $SiCl_4$ precursor concentration were made at 700 °C (Sedlmaier et al., 2012). Here, the amount of the Si source was increased while all other parameters (ratio of other starting materials, heating rate, temperature and dwell time) were kept constant. In the current work we performed a systematic study where we varied the temperature and the $SiCl_4$ concentration, with the main goal to elucidate the