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Author for correspondence:

Zaklina Burghard

e-mail:

zaklina.burghard@imw.uni-stuttgart.de

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Bioinspired synthesis of SnO crosses as backbone in artificial sponges

Timotheus Jahnke¹, Stefan Kilper¹, Andrea Knöller¹, Franz Brümmer², Marc Widenmeyer¹, Dirk Rothenstein¹, Zaklina Burghard¹ and Joachim Bill¹

¹Institute for Materials Science, University of Stuttgart, Heisenbergstraße 3, 70569 Stuttgart, Germany

²Institute of Biomaterials and Biomolecular Systems, University of Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart, Germany

ZB, 0000-0003-3906-8582

The distinct electronic properties, including p-type semiconducting and a wide optical band gap, renders SnO suitable for applications such as microelectronic devices, gas sensors and electrodes. However, the synthesis of SnO is rather challenging due to the instability of the oxide, which is usually obtained as a by-product of SnO₂ fabrication. In this work, we developed a bioinspired synthesis, based on a hydrothermal approach, for the direct production of SnO nanoparticles. The amount of mineralizer, inducing the precipitation, was identified, which supports a template-free formation of the nanosized SnO particles at low temperature and mild chemical conditions. Moreover, the SnO nanoparticles exhibit a shape of unique three-dimensional crosses similar to the calcite crosses present in the calcareous sponges. We demonstrated that SnO crosses are evenly distributed and embedded in an organic scaffold by an ice-templating approach, in this way closely mimicking the structure of calcareous sponges. Such scaffolds, reinforced by an active material, here SnO, could be used as filters, sensors or electrodes, where a high surface area and good accessibility are essential.

This article is part of the theme issue 'Bioinspired materials and surfaces for green science and technology (part 2)'.

1. Introduction

Binary metal oxides, such as tin oxide (SnO), are widely used as semiconductors and gas sensors, due to their distinct electronic properties [1–4]. For example, it can be used as a leakage sensor for inflammable gases [5,6]. Furthermore, SnO is suitable for applications as p-type semiconductor, such as microelectronic devices [1,7].

Recently, researchers have shown an increased interest in SnO as anode material for novel metal ion batteries [8,9] due to its large gravimetric capacity [8,10]. For all these applications, a high surface area plays a crucial role [11–13], which can be achieved by fabricating nanosized SnO of various shapes, such as flowers [14], plates [15] and thin films. However, a major drawback of using such small structures with a high surface area is that they often tend to form uncontrollable agglomerates via strong van der Waals interactions. To cope with this issue, one plausible approach would be three-dimensional nanostructuring of the oxide particles, which is a rather challenging task. The use of highly porous scaffolds as matrix, where such particles are separated and evenly distributed would be one option, which is, however, also quite challenging.

Some biological organisms already mastered such challenging tasks by controlling the formation, structure and morphology of the inorganic materials of which they are composed of [16]. For example, calcium carbonate (CaCO_3) exists in the shape of aragonite fibres in cuttlebone [17] or platelets in nacre [18] as well as in calcite or aragonite cross-like spicules in calcareous sponges [19]. Such variety is the result of using different structuring agents [19,20], which selectively guide the mineralization of the CaCO_3 into the desired shapes. In particular, the calcareous sponge (figure 1a,b) consists of a calcite network structure (figure 1c), in which cross-like spicules are uniformly distributed as displayed in the high magnification scanning electron microscope (SEM) micrograph (figure 1d). The species shown, *Clathrina clathrus* (Clathrinidae, Calcarea, Porifera) is a common species in the Mediterranean and Adriatic Seas and is found attached to rocky substrates. Colour *in vivo* is yellow, a ‘beautiful sulfur yellow colour’ [21]. The clathroid corpus is composed of irregularly and loosely anastomosed tubes and large superficial water-collecting tubes were observed (figure 1b). The mineral skeleton is composed entirely of CaCO_3 and composed of equiradiate and equiangular, cylindrical triactines only (figure 1c,d) [21,22]. These spicules serve as the mechanical backbone of the channel-like superstructures, which are important for the sponge to filter microplankton from the seawater [23]. Therefore, the sponge holds an optimized balance between mechanical stability and accessibility, which is likewise desired in the abovementioned SnO-based applications.

While nature optimized the mineralization of CaCO_3 over millions of years, transferring the calcareous sponges’ structural features to technologically relevant materials requires the development of a novel synthesis protocol, which involves an adequate substitute for the structuring agent, thus mineralizer. One promising bioinspired approach is based on a hydrothermal method, which has a high yield, rendering it suitable for large-scale applications. However, the reaction rate and the product are highly sensitive to a large number of parameters, including humidity, temperature and local concentration differences. Synthesizing a defined nanostructured material thus requires exact parameter control. To date, mostly metal oxides, such as TiO_2 [24], ZnO [25] and ZrO_2 [26] have been intensively investigated, but far too little attention has been paid to the investigation of the formation of SnO. This is because it is only considered as an undesired by-product in the synthesis of SnO_2 . In this respect, Wang *et al.* investigated the fabrication of SnO_2 nanosheets, using tin chloride (SnCl_2) salts as a precursor [27]. They found that in this process divalent SnCl_2 is oxidized via several intermediate oxide states to the four valent Sn in SnO_2 and they established a corresponding mechanism, which is based on the oriented attachment of nanoparticles into nanosheets. In addition, they found that the intricate formation of SnO_2 nanosheets is a function of the oxygen content in the autoclave during the oxidation. Accordingly, a lack of oxygen leads to the formation of the unwanted SnO by-product.

Our study turns the initially unwanted by-product into the desired, well-defined and functional nanostructures by controlling the crucial parameters responsible for phase and morphology during the hydrothermal synthesis. We identified the parameters that are responsible

Figure 1. (a) Digital image (width corresponds to 6 cm) of the sponge *Clathrina clathrus* as a living organism with (b) a magnification of its structure. (c) Dark-field microscope image of a calcareous sponge presenting the spicules, which are randomly distributed in the organic network and (d) a highly magnified SEM micrograph reveals the cross-like structure of the single spicules.

for the formation of the SnO in the form of three-dimensional nanostructured crosses. The resulting SnO crosses can be further combined with polymers, such as polyvinylpyrrolidone (PVP) in an ice-templating approach, yielding microstructures similar to the ones found in calcareous sponges. The structure of these crosses was inspired by the calcareous foam *C. clathrus* where stiff three-dimensional cross-like spicules mechanically reinforce an elastic corpus. Such bioinspiration enables the fabrication of functional hybrid materials, which are promising for application as sensors, filters and supercapacitors.

2. Controlling the hydrothermal synthesis

SnO_{2-x} is synthesized by dissolving $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in a ratio of 1 : 1 water to ethanol. This mixture is supplemented by the addition of a defined amount of aqueous ammonia as a mineralizer [27] at room temperature, which is subsequently transferred to a teflon-lined autoclave and treated at 120°C. According to Wang *et al.*, a partial oxidation of the tin (II) cations occurs, subsequently leading to the formation of SnO_2 via the hydroxylated intermediate phase $\text{Sn}_6(\text{OH})_4\text{O}_4$, as schematically depicted in figure 2 (high $\text{Sn(II)}/\text{NH}_3$ ratio) [27]. As initially indicated, the oxygen content is crucial for the formation of SnO_2 . When enough oxygen is accessible, the tin salt precursor ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) is fully oxidized, forming stoichiometric SnO_2 . However, when the amount of oxygen in the autoclave is reduced, non-stoichiometric SnO_{2-x} is obtained [28]. Therefore, in order to favour the formation of SnO, the oxygen concentration in the chemical autoclave has been reduced.

To analyse the formation of the SnO_x nanostructures in detail, an extended systematic study of the hydrothermal process was carried out. In the first attempt, we varied the reaction time,

Figure 2. Schematic illustration of the preparation process of SnO_x nanostructures based on a hydrothermal approach with high and low $\text{Sn(II)}/\text{NH}_3$ ratios. (Online version in colour.)

which allowed a deeper insight into the crystallization mechanism of oxygen-deficient SnO_{2-x} . It should be noted that the influence of atmospheric oxygen was excluded by leaving no residual atmosphere in the autoclave (see the electronic supplementary material, figure S1). However, although the influence of atmospheric oxygen was eliminated, SnO_2 was formed via the hydroxylated state $\text{Sn}_6(\text{OH})_4\text{O}_4$ as indicated in the powder X-ray diffraction (PXRD) pattern in figure 3a. At a reaction time of 30 min to 1 h, under hydrothermal conditions, crystalline $\text{Sn}_6(\text{OH})_4\text{O}_4$ was present. Furthermore, after a reaction time of 2 h, new broader reflections arose, which fit well to the simulated pattern of SnO_2 (ICSD Card Nr. 9163), while the reflections observed before for $\text{Sn}_6(\text{OH})_4\text{O}_4$ disappeared. Taking into account the full width at half maximum (FWHM) of the reflections, the SnO_2 seems to consist of smaller crystallites than the intermediate phase, whereas the majority of the phase is amorphous. Nonetheless, with proceeding reaction time, the reflections become sharper, indicating the crystal growth of the SnO_2 .

Besides the change in phase indicated from PXRD data, corresponding SEM micrographs (figure 3b) provide information about the evolution of the material's morphology. By comparison of the micrographs, it can be concluded that initially, crystals of $\text{Sn}_6(\text{OH})_4\text{O}_4$, according to the corresponding PXRD pattern, are present, which then convert into predominantly amorphous particles after 2 to 4 h. A reaction time of 6 h finally shows enhanced crystallinity, which becomes even more pronounced after 24 h. In addition, it can be seen that all these nanoparticles form secondary particles in the micrometer range. This agglomeration most likely occurs during washing and drying of the product due to strong surface interactions. To find out the structure and crystallinity of the primary particles, a closer inspection of such a secondary particle was carried out by transmission electron microscopy (TEM). Figure 3c shows that needle-like shapes are present, which indicates that anisotropic growth takes place after 6 h of the reaction time. Their crystalline structure is visible on a higher magnification TEM image, as marked by white circles in figure 3d. The inset of the diffraction pattern in figure 3c is in agreement with the diffraction pattern obtained using PXRD in figure 3a. Additionally, it indicates the presence of an amorphous phase, due to the strong diffuse scattering of the primary beam observed on the sides of the

Figure 3. The samples obtained at different reaction times are characterized and in (a) PXRD patterns of the obtained SnO_x product and in (b) its corresponding morphology in an SEM micrograph is displayed. The respective reaction time shown in the top right corner corresponds to the point when the reaction was interrupted by removing the autoclave from the furnace. A corresponding TEM micrograph for a time of 6 h is displayed in (c) as an overview with its corresponding selected area diffraction pattern displayed in the inset, and in (d) a high magnification micrograph is presented. The white circles indicate crystalline needle-shaped particles.

beam stopper. A corresponding Raman investigation is available in the electronic supplementary material, figure S2.

Since the sample after a reaction time of 6 h is partially amorphous, phase purity was verified by chemical analysis. Inductive coupled plasma-optical emission spectroscopy (ICP-OES) and combustion analysis were used to determine the amount of tin, oxygen and hydrogen. We found a chemical composition of $74.9 \pm 0.8 \text{ wt\%}$ tin, $24.1 \pm 0.3 \text{ wt\%}$ oxygen and $0.53 \pm 0.01 \text{ wt\%}$ hydrogen. This composition does not suit stoichiometric SnO_2 , therefore it is assumed that a phase mixture of SnO_2 and $\text{Sn}_6(\text{OH})_4\text{O}_4$ is coexisting, analogous to the observations of Wang *et al.* [27]. This is further supported by the diffraction patterns obtained for reaction times longer than 6 h (figure 3a). A slight shift of the reflections $2\theta = 33^\circ$ and $2\theta = 37^\circ$ is observed indicating the presence of the crystallized precursor phase $\text{Sn}_6(\text{OH})_4\text{O}_4$. Wang *et al.* [27] reported that 13% of the Sn(II) cations were not oxidized to Sn(IV) cations because of the lack of oxygen present in the autoclave, yielding SnO_{2-x} nanosheets. By contrast, in our case, it appeared that by eliminating oxygen, we were able to increase the amount of Sn(II) in a way that the precursor phase is still present after reaction in the final product, guiding the path towards SnO .

Figure 4. (a) PXRD patterns of the obtained SnO_x of the final product obtained from different Sn(II)/NH₃ ratios. (b) Corresponding SEM micrographs showing the morphology of the different products. It is visible that crosses are formed for ratios below 0.37 Sn(II)/NH₃.

Recently, it was found that single atomic layers of SnO can be synthesized on top of a carbon cloth by a hydrothermal method, whereas the presence of ammonia (or urea) appeared to hinder the oxidation of Sn(II) to Sn(IV) [8]. We hypothesized that by adjusting the Sn(II)/NH₃ ratio, a further stabilization of Sn(II) can be achieved, yielding stable SnO. Therefore, in the second attempt at parameter study, the focus was set on the amount of ammonia, which serves as a mineralizer, while keeping the reaction time constant at 6 h. The reaction time of 6 h was chosen because no changes in the PXRD patterns were observed after a reaction time of 6 h (figure 3a). In general, the reaction sequence from SnCl₂ to SnO via the intermediate formation of Sn₆(OH)₄O₄ can be expressed by equations (2.1) and (2.2), involving ammonia as a weak reducing agent.

In order to confirm the hypothesis, different tin chloride and ammonia ratios, thus Sn(II)/NH₃ ratios, were investigated, as listed in the electronic supplementary material, table S1. The crystal structure of the products fabricated under different Sn(II)/NH₃ ratios was investigated using PXRD. The recorded patterns of the ratios 2.2 to 0.5 mainly showed the presence of nanocrystalline SnO₂ (figure 4a). However, after further decreasing the ratio of Sn(II)/NH₃, i.e. adding more ammonia, a significant change in the PXRD pattern was obtained. In contrast to our expectations, the new arising sharp reflections indicate a crystalline material, which can be entirely matched with the simulated pattern of SnO (ICSD CARD Nr. 15516).

Analogous to the previous attempt, the product microstructure was investigated by SEM, as displayed in figure 4b. It can be seen, that for high Sn(II)/NH₃ ratios (ratio 1.11), nanoparticles assemble into agglomerates. Decreasing the ratio (from 1.11 to 0.55) leads to the formation of nanosheets, similar to the nanosheets observed in figure 3b. Importantly, it can be seen that a further decrease in the Sn(II)/NH₃ ratio to 0.37 finally supported the formation of SnO crosses.

The first reported SnO crosses were produced by thermal decomposition at 310°C of tetraphenyltin [29], which required significantly more energy than our synthesis approach (120°C versus 310°C) [8,29], highlighting the advantage of ammonia as a structuring agent for the fabrication of such crosses. Furthermore, Xu *et al.* [29] investigated in detail the crystal formation and found that an initial core is formed upon decomposition with an intersection on the (112)

Figure 5. (a) PXRD patterns during SnO cross formation as a function of time for an $\text{Sn(II)}/\text{NH}_3$ ratio of 0.27. (b) Corresponding SEM micrographs. The scale bar in (b) applies to all micrographs.

plane. According to the results from the PXRD study of our products (figure 4a), the intensity ratio of the reflections at $2\theta = 19.3^\circ$ and $2\theta = 37.1^\circ$ of samples obtained from ratio 0.37 deviated from the simulated pattern. This indicates the presence of a preferred growth along the (1–10) and (112) planes, in accordance with Xu *et al.* [29]. Upon further decreasing the $\text{Sn(II)}/\text{NH}_3$ ratio, the intensity ratio approaches the one of the simulated patterns of SnO (ICSD 15516), letting the texturing vanish, indicating further isotropic growth of the SnO structures, resulting in thicker crosses (figure 4b). Additionally, we have included a Raman investigation in the electronic supplementary material (figure S3) to support the growth mechanism of SnO crosses.

The above-mentioned SnO nanosheets, fabricated on carbon cloth as a template, are synthesized under similar reaction conditions as ours (200°C) [8]. However, our approach uses a lower reaction temperature and the formation of the SnO structures is template-free. This reveals that the absence of a template led to homogeneous nucleation of crosses (figure 4b), which are formed by an initial core and then grow anisotropically along (110) planes according to Xu *et al.* [29].

An alternative description for the formation of such SnO crosses was proposed by Wang *et al.* [27] by applying different cooling rates. They assumed that shock cooling of the autoclave would yield only SnO_2 sheets, but this was not proven. However, they found that slow cooling at room temperature, instead of water cooling, led to an increase in yield of the SnO by-product. We hypothesized that this was probably caused by residual gaseous ammonia (NH_3) re-dissolving at lower temperatures. Based on all these findings, the data collected in our study are in agreement with the chemical reaction pathway of Zhang *et al.* [8] using ammonia as a stabilizing agent, supported by low temperature as shown by Wang *et al.* [27]. As given by equation (2.2), adding more ammonia results in a lower $\text{Sn(II)}/\text{NH}_3$ ratio, which helps to stabilize divalent Sn(II) and leads to the formation of SnO crosses in accordance with the published mechanism [29].

The formation mechanism of SnO crosses was investigated by a time-resolved reaction study with the adjusted $\text{Sn(II)}/\text{NH}_3$ ratio of 0.27, analogous to the study for the ratio 0.55 displayed in figure 1. The PXRD patterns indicate the formation of crystalline SnO_2 after 30 min (figure 5a). The sharp reflections fitting to the simulated pattern of SnO (ICSD 15516) observed for a reaction time of 1 h reveal the favourable formation of a crystalline SnO as a dominant phase, since reflections for SnO_2 are barely visible.

The corresponding SEM investigation reveals that the SnO initially exists in a rather cubic shape, which is covered with some amorphous or nanocrystalline secondary phase (figure 5b).

After 4 h, micrometer-sized plates could be detected, from which basal planes branching occurs upon further increasing the reaction time. After a reaction time of 6 h, the crosses were fully formed and nearly no secondary phase was present. For a reaction time of 24 h, strong precipitation on the surface of the crosses is visible. A Raman investigation corresponding to our time study at a ratio of 0.27 is presented in the electronic supplementary material, figure S4.

A different form of crosses was reported by Cui *et al.*, using KOH as a mineralizer resulting in cross-shaped structures [30]. However, these structures were strongly damaged by the corrosive character of KOH, resulting in very rough edges and partially formed crosses. By contrast, our adjusted chemically softer synthesis parameters in comparison with Cui *et al.* [30] (NH_3 instead of KOH) allowed for the formation of well-defined SnO crosses, because the corrosive decomposition is heavily suppressed and nearly perfect crosses are obtained.

3. Ice-templating artificial sponges

In a final step, the obtained SnO crosses were mixed with an aqueous PVP solution at a ratio of 2 : 1. The dispersion was instantly frozen in liquid nitrogen, with the aim to design an open-porous structure, which resembled that of a calcareous sponge. The formed ice was removed by freeze-drying, resulting in a lamellar microstructure as shown in figure 6a. Hereby, the grown ice crystals have transported the PVP/SnO material to the ice interface/surfaces, leaving upon sublimation voids behind, whereas the PVP/SnO forms wall-like structures. PVP is used as an exemplary linear polymer, which is non-corrosive towards SnO and serves as a mechanical support in the artificial sponge. Hereby, the PVP might be substituted by other linear binders, such as Polytetrafluorethylene or Polyvinylidene fluoride, depending on the requirements of the application (such as high temperature or different solvents).

It can be seen that the microstructure of this artificial sponge is composed of regularly aligned lamellas with different orientations. The lamellas distance and orientation depend on the freezing rate and solution concentration. Upon closer inspection, the crosses are evenly distributed in the artificial sponge and embedded into lamellas as displayed in figure 6b,c. Therefore, they embody a similar backbone in the PVP matrix as the cross-like spicule in the calcareous sponges (figure 1). Moreover, the crosses embedded in the lamella walls might impede mechanical collapse when immersing the artificial sponge in a liquid medium. Such a feature is important for the artificial sponges' mechanical integrity.

4. Conclusion

In this work, we were able to replicate the structural principle of calcareous sponges in a two-step fabrication process. Analogous to the sponges' ability to control the growth of cross-like spicules made of CaCO_3 , we take advantage of ammonia as mineralizer to obtain SnO crosses via a hydrothermal process. Using intricate control over mineralizer concentration and reaction time, we were able to fine-tune the SnO crosses. This procedure yields artificial sponges, in which the SnO crosses are evenly distributed in the walls of the highly porous PVP-based artificial sponge. Thus, the SnO particles embody a similar backbone structure as obtained in the natural calcareous sponges. In particular, for applications based on liquid flow, the crosses are envisioned to defeat a collapse of the soft organic scaffold, which could happen when immersing the sponge in a liquid. Moreover, these porous structures can likewise find applications in filtering, as damping materials, as well as a mechanically stable matrix for other functional materials than SnO.

Experimental set-up

Tin oxide was synthesized by a hydrothermal method, starting with 6 mmol SnCl_2 (Sigma Aldrich) $\cdot 2 \text{H}_2\text{O}$ in an ethanol/water (1 : 1) mixture as an initial reagent. After 10 min of vigorously stirring at RT to dissolve the tin(II) chloride (a clear solution is formed), ammonia was added as mineralizer (6–60 ml 0.45 M $\text{NH}_3(\text{aq})$ (Sigma Aldrich, 32%, p.a.)), which turned the solution

Figure 6. SEM micrographs of the artificial sponge reinforced by SnO crosses. (a) Microstructure composed of lamellas with different orientation and uniform distribution of the SnO crosses. (b,c) Closer inspection of the microstructure reveals that crosses are embedded in the lamellas.

opaque. The dispersion was then transferred to a Teflon-lined autoclave (see the electronic supplementary material, figure S1) ($V = 25$ ml) and treated at 120°C for 0.5–24 h. It was washed three times with ethanol and three times with MilliQ water and centrifuged at $3000 \times g$ RPM after each step, respectively. After washing, the precipitate was dried and poured into a glass beaker. For further measurements, the material was prepared accordingly.

For SEM investigation, the material was drop-casted onto a Si wafer from an aqueous dispersion, and SEM investigations were conducted on a Zeiss Ultra 55 with a FEM cathode. Raman investigations were performed after the powder was pressed with a boron silicate glass plate onto a silicon wafer. The Raman spectra were measured using an argon laser with a wavelength of 488 nm under ambient conditions, with a power of 10 mW. The microscope image was taken on a high-resolution light microscope, whereas the calcareous sponge *C. clathrus* was stored in ethanol and prepared between two glass plates (Carl Roth GmbH).

For PXRD investigations, the sample was placed in the aluminum sample holder and the surface flattened with a boron silicate glass plate, and the measurements were carried out in $\theta/2\theta$ Bragg–Brentano geometry on a Smart-Lab X-Ray Diffractometer from Rigaku Corporation with $\text{Cu-K}_{\alpha 1,2}$ radiation. Cu-K_{β} radiation was filtered by a thin Ni foil (approx. 90% efficiency).

The chemical analysis was performed using ICP-OES in order to investigate the tin content while combustion analysis was performed to determine the oxygen and hydrogen amount (with nitrogen and helium as carrier gases, respectively).

In order to fabricate the artificial sponge, the ice-templating approach was used. The aqueous SnO crosses solution was made of 0.54 g SnO powder (0.27 ratio, 6 h) mixed with 0.254 g Polyvinylpyrrolidone (Sigma Aldrich, $M_w = 55\,000\text{ g mol}^{-1}$) and then dispersed in 0.5 ml deionized H_2O . The obtained solution was then poured into a precooled (77 K) cylindrical elastomer mould with a diameter of 8 mm and a height of 10 mm, and immersed for 5 min in liquid nitrogen. Subsequently, the mould was transferred to a climate chamber at 248 K (Vötsch VC 7018) and stored for 7 min, in order to remove the sample from the mould. The obtained free-standing frozen sample was transferred to a freeze drier (P4 K Peter Piatkowski) and freeze-dried over 22 h. The foam was removed after drying and sputtered (SCD 40) with gold to ensure sufficient conductivity to perform SEM investigations.

Data accessibility. This article has no additional data.

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