

Shaping tin nanocomposites through transient local conversion reactions

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Supporting Information

Growth of BaCO₃/SiO₂ nanocomposites

A substrate (e.g. 2x2 cm slide of aluminum, stainless steel or silicon) was vertically positioned in a 100 mL beaker containing BaCl₂ dihydrate (74 mg, 0,3 mmol) and Na₂SiO₃ (16 mg, 0,13 mmol) dissolved in 15 mL of water. The reaction vessel was loosely covered with a Petri dish to allow CO₂ from the air to diffuse slowly into the reaction mixture. Typical growth times ranged between 1.5-2.0 hours after which the substrate was removed from the solution and washed with deionized water. The structures were kept in this water for 5 minutes before converting them to Sn₃(OH)₂O₂ nanocomposites. The composition of the structures was determined using SEM, EDS and XRD (See Figure 1). The used reference for the XRD-diffractogram can be found in the Crystallography Open Database (COD 1000033).

Conversion of BaCO₃/SiO₂ to Sn₃(OH)₂O₂/SiO₂ nanocomposites

Anhydrous SnCl₂ (948 mg, 100 mM) was dissolved in 50 mL degassed water. Subsequently a substrate with BaCO₃/SiO₂ nanocomposites was placed in the solution for 30 seconds. The resulting nanocomposites were washed in two demineralized water baths followed by an acetone bath. After drying to the air, the converted nanocomposites were analyzed using SEM, XRD and EDS (See Figure 1). The used reference for the XRD-diffractogram can be found in the Crystallography Open Database (COD 9011384).

Conversion to Sn₃(OH)₂O₂/SiO₂ to SnO₂/SiO₂ nanocomposites

A substrate containing Sn₃(OH)₂O₂/SiO₂ nanocomposites was placed in the middle of a single zone horizontal tube furnace. The oven was heated to 200° C for 3 hours and subsequently heated to 600° C for 3 hours to convert the nanocomposites to SnO₂/SiO₂. SEM, EDS and XRD analysis was performed (Figure 3), where XRD confirmed formation of SnO₂ (Reference used is COD 1534785).

Conversion to Sn₃(OH)₂O₂/SiO₂ to CH₃NH₃SnX₃/SiO₂ nanocomposites

A substrate containing Sn₃(OH)₂O₂/SiO₂ nanocomposites was placed in the middle of a single zone horizontal tube furnace. Subsequently an alumina boat containing methyl ammonium halide (bromine or iodine) was placed next to the substrate. The pressure inside the tube was lowered to below 0.1 mbar using a vacuum pump. The tube was then flushed with nitrogen until atmospheric pressure was reached. This process was repeated twice to purge the system of oxygen. Afterwards the temperature of the furnace was set to 120° C and a 30 sccm

flow of nitrogen was applied to increase the pressure to 70 mbar. After 30 minutes the reaction was stopped and the oven was passively cooled to room temperature. XRD, EDS and PL measurements (Figure 4) confirmed the formation of a tin halide perovskite (references used for the XRD measurements are COD 2104791 and 4335632 for the bromide and iodide perovskite respectively).

Scanning Electron Microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDS) characterization

Samples were loaded into the SEM without applying a conductive metal coating. SEM images were obtained using a FEI Verios 460 equipped with an Everhart-Thornley detector (ETD) and a circular backscatter detector (CBS). The images were recorded at 5 kV and 10 kV respectively using a 100 pA current in both instances. EDS was measured with the same electron microscope using an Oxford X-Maxⁿ energy dispersive X-ray spectrometer with an accelerating voltage of 20 kV using a 100 pA current.

X-ray diffraction (XRD) characterization

X-ray diffraction measurements were performed using a Bruker D2 Phaser (Bragg-Brentano geometry) using a K-alpha Cu X-ray source with an emission energy of 8.0415 keV. The samples were mounted inside a chamber filled with ambient air at room temperature. All measurements were performed using a 1.0 mm beam knife to reduce unwanted scattering and optimize the low angle part of the diffractogram. A nickel filter was used to reduce the 20-30% contribution from the k-beta Cu X-ray source. A divergence slit of 0.1 or 1 mm was used to control the illuminated area of the sample, based on the spread of the material on the substrate. Diffracted X-rays were detected using a Lynxeye detector and were collected for at least 12 hours with a scan interval ($\Delta 2\theta$) of 0.01°.

Grain size determination from XRD patterns

The average grain size was determined using the Debye Scherrer Equation:

$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

where τ is the mean size of the crystalline domains, K is the shape factor and is estimated to be 0.9, λ is the wavelength of the x-ray source (1.54060 Å), β is the line broadening at half height (fwhm) and θ is the Bragg angle. A complete list of all the crystal sizes can be found in Table S1.

Crystal	Average Grain Size (nm)
BaCO ₃	21
Sn ₃ (OH) ₂ O ₂	33
SnO ₂	10
CH ₃ NH ₃ SnBr ₃	81
CH ₃ NH ₃ SnI ₃	90

Table S1. Average grain sizes for all synthesized and converted crystals.

Infrared Spectrometry (IR) Characterization

IR spectra were recorded using a Bruker Vertex 80v FT-IR spectrometer equipped with an ATR module (Platinum ATR Diamond) by first measuring a background after 30 minutes to flush water vapor and CO₂ out and then measuring the nanocomposites after a similar 30 minutes wait time.

Photoluminescence and fluorescence microscopy characterization

The photoluminescence measurements were performed on a WITec alpha 3000 SR. A 532 nm laser and a 405 nm laser (Thorlabs fiber coupled laser source S1FC405) were used to excite the iodide and bromide perovskite

respectively. The signal was collected with a WITec UHTS 300 spectrometer and the corresponding detector (DV401A-BV-352).

Mechanism of Conversion

Letting bulk conditions reach the nanocomposites

To demonstrate the importance of the temporal local reaction zone, a substrate with nanocomposites was kept in a conversion solution for 2 minutes. At this time, the BaCO_3 has completely dissolved and the local reaction zone has disappeared. Without the locally increased pH, the $\text{Sn}_3(\text{OH})_2\text{O}_2$ inside the nanocomposites dissolves, leaving behind an empty SiO_2 shell (Figure S1).

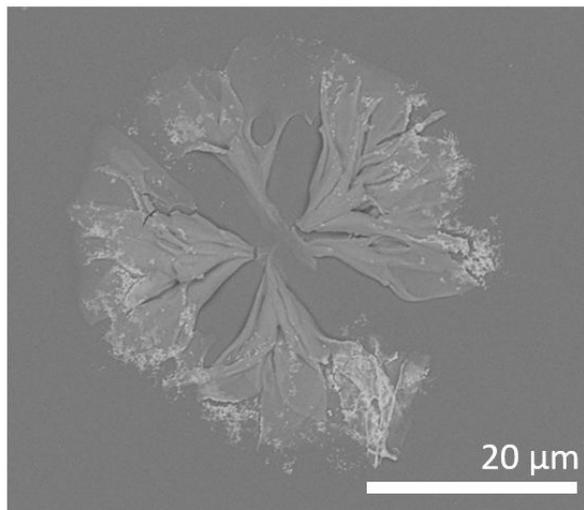


Figure S1. Nanocomposite kept in a SnCl_2 conversion solution for 2 minutes. As the local reaction zone disappears around the nanocomposites after 30 seconds, this nanocomposite is depleted of its tin content.

Increasing pH throughout the entire solution

To discover the mechanism behind the conversion, we investigated the reaction of tin with water in the absence of the nanocomposites. Specifically, tin was dissolved in water and kept under nitrogen atmosphere, which resulted in a white precipitate forming after 30 minutes. This white precipitate was collected *via* vacuum filtration and analyzed using XRD. Comparing the obtained XRD diffractogram (figure S2, top) with AMCSD 0015835 confirmed the formation of Abhurite ($\text{Sn}_{21}\text{O}_6(\text{OH})_{14}\text{Cl}_{16}$). Abhurite also formed under atmospheric conditions (figure S2, middle) at an accelerated rate (within 5 minutes), where an amorphous bump was observed in the XRD pattern. In contrast, we observed that during the conversion of nanocomposites hydroromarchite was formed rather than abhurite. Moreover, whereas in the bulk solution abhurite forms after more than 30 minutes, the nanocrystals within the composites convert into hydroromarchite within 30 seconds.

We hypothesize that this difference in precipitation behavior is caused by an increase in the local pH during the ion-exchange: Abhurite is stable at pH 2-5.5, while hydroromarchite only precipitates above a pH of 3.5 (Edwards, R., Gillard, R. D. & Williams, P. A. *Mineral. Mag.* **56**, 221–226 (1992)), far above the solution's pH of 2.0. Direct observation of the local pH is however difficult. Therefore, to test this hypothesis, we deliberately increased the pH in the solution to induce the formation of hydroromarchite. To this aim we added 1M NaOH (10 mL added to a 50 mL solution) at the start of the experiment. Precipitation formed almost instantly, comparable to the 30 second conversion we observe previously for hydroromarchite in the presence of the nanocomposites. Moreover, analyzing this precipitate with XRD (Figure S2, bottom) confirmed the formation of hydroromarchite (compared with COD 9011384) whereas no abhurite peaks were observed. Hence, increase of the pH indeed favors the formation of hydroromarchite over abhurite. In the case where nanocomposites are used, we find that the precipitate only forms locally in the nanocomposites. Thus, we concluded that the local basic conditions, induced by the dissolving of BaCO_3 , enables the hydroromarchite to form inside the nanocomposites.

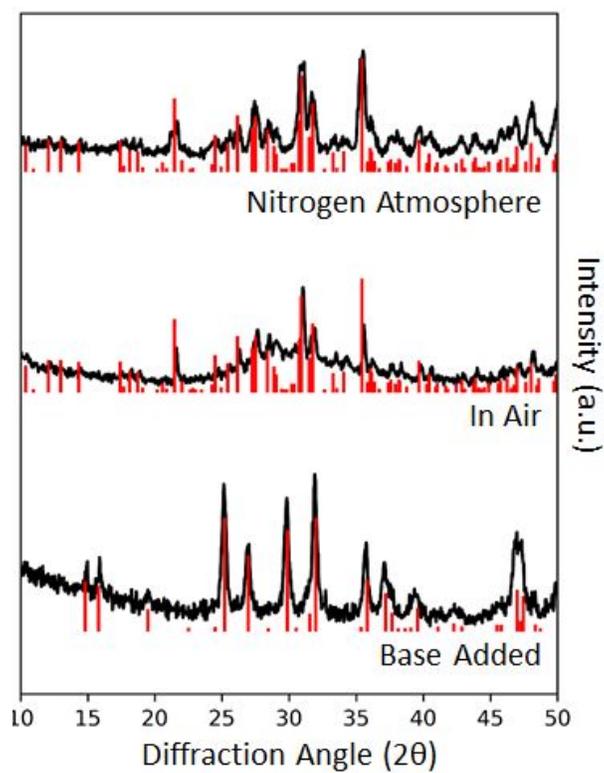


Figure S2. XRD of precipitate formed in water when dissolving SnCl_2 under nitrogen (top), in air (middle) and after adding 1M NaOH (bottom). Reference spectra (red lines) are AMCS D 0015835 for abhurite, and COD 9011384 for hydroromarchite.