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Shaping Tin Nanocomposites through Transient Local Conversion Reactions

Hans C. Hendrikse, Stivell Hémon-Charles, Lukas Helmbrecht, Eliane P. van Dam, Erik C. Garnett, and Willem L. Noorduin*

ABSTRACT: Shape-preserving conversion offers a promising strategy to transform self-assembled structures into advanced functional components with customizable composition and shape. Specifically, the assembly of barium carbonate nanocrystals and amorphous silica nanocomposites (BaCO₃/SiO₂) offers a plethora of programmable three-dimensional (3D) microscopic geometries, and the nanocrystals can subsequently be converted into functional chemical compositions, while preserving the original 3D geometry. Despite this progress, the scope of these conversion reactions has been limited by the requirement to form carbonate salts. Here, we overcome this limitation using a single-step cation/anion exchange that is driven by the temporal pH change at the conversion nanocomposite. We demonstrate the proof of principle by converting BaCO₃/SiO₂ nanocomposites into tin-containing nanocomposites, a metal without a stable carbonate. We find that BaCO₃/SiO₂ nanocomposites convert in a single step into hydroromarchite nanocomposites (Sn₃(OH)₂O₂/SiO₂) with excellent preservation of the 3D geometry and fine features. We explore the versatility and tunability of these Sn₃(OH)₂O₂/SiO₂ nanocomposites as a precursor for functional compositions by developing shape-preserving conversion routes to two desirable compositions: tin perovskites (CH₃NH₃SnX₃, with X = I or Br) with tunable chemical functionalization of the nanocomposites with magnetite mesocrystals, and silane chemistry enables integration of functional chemical compositions into advanced morphologies for next-generation optoelectronic devices.
that the temporary local concentration gradients in the reaction zone may offer new reaction mechanisms for previously impossible conversion reactions.

In this article, we demonstrate that chemical gradients in the local reaction zone enable conversion of barium carbonate nanocomposites (BaCO$_3$/SiO$_2$) into a selection of tin-containing nanocomposites. A straightforward cation exchange is not possible in this conversion, as tin does not form a stable carbonate salt. However, we find that the transient local conversion conditions, along with the poor solubility of tin in water, result in a concurrent cation/anion exchange toward hydroromarchite (Sn$_3$(OH)$_2$O$_2$). Meanwhile, the inert silica maintains the macroscopic shape and fine details of the original nanocomposite, as previously demonstrated.

Furthermore, we explore the versatility and tunability of these Sn$_3$(OH)$_2$O$_2$/SiO$_2$ nanocomposites as precursors for functional compositions by developing shape-preserving conversion routes to two desirable compositions: transparent, conducting cassiterite (SnO$_2$), and semiconducting tin perovskite (CH$_3$NH$_3$SnX$_3$, with X = I or Br). Hence, by demonstrating this conversion mechanism, we open up pathways to new functional materials with controllable shapes.

**RESULTS AND DISCUSSION**

We study the ion exchange to tin from BaCO$_3$/SiO$_2$ coral-shaped nanocomposites. We assemble BaCO$_3$/SiO$_2$ coral shapes following previously reported procedures. Subsequently, these coral shapes are immersed in an aqueous solution of 100 mM SnCl$_2$ under a nitrogen atmosphere (see Supporting Information for details). Within 30 s of immersion, the barium ions in the nanocomposites are completely replaced by tin according to energy-dispersive X-ray spectroscopy (EDS, Figure 1).

**Figure 1.** Conversion from BaCO$_3$/SiO$_2$ to Sn$_3$(OH)$_2$O$_2$/SiO$_2$ nanocomposites. (A) SEM images of (different) nanocomposites before (left) and after (right) conversion, showing that the coral-like shape is retained despite significant changes to the nanocrystal morphology (see respective close-up SEM images). (B) EDS measurements of nanocomposites before (top) and after (bottom) conversion, indicating full replacement of barium with tin. (C) XRD characterization showing the conversion of BaCO$_3$ to Sn$_3$(OH)$_2$O$_2$ (red lines indicate reference peaks). (D) IR spectrum showing the disappearance of the fingerprint peak of a carbonate anion at $\sim$1450 cm$^{-1}$ after conversion to Sn$_3$(OH)$_2$O$_2$.

**Figure 2.** Proposed conversion mechanism of BaCO$_3$ to Sn$_3$(OH)$_2$O$_2$ in nanocomposites. Sn$^{2+}$ hydrolysis decreases the pH of water (I). High pH is indicated by light blue (left) and low pH is indicated by purple (middle, right). Locally, the pH increases again by dissolving BaCO$_3$ (II, middle, indicated by light blue around the nanocomposite), which causes Sn$_3$(OH)$_2$O$_2$ to precipitate (III). Once all BaCO$_3$ is dissolved, the local pH decreases to the bulk pH, thereby initiating dissolution of Sn$_3$(OH)$_2$O$_2$ (right, IV).
Figure 1 B). Furthermore, scanning electron microscopy (SEM) shows excellent shape preservation with sub-micrometer fidelity, despite significant changes to the nanocrystal morphology (Figure 1A).

Remarkably, X-ray diffraction (XRD, Figure 1C) reveals that the nanocrystals inside the nanocomposites are composed of hydroxoromarchite (Sn$_3$(OH)$_2$O$_2$) with an average grain size of 33 nm (see Supporting Information). Thus, besides the barium cations being replaced for tin, the carbonate anions are also substituted with oxyhydroxide. Infrared spectroscopy (IR) confirms that the characteristic carbonate fingerprint peak (∼1450 cm$^{-1}$) of BaCO$_3$ disappears after the conversion (Figure 1D). Hence, both cations and anions are replaced in a single step during this shape-preserving chemical conversion.

We hypothesize that during the concurrent shape-preserving cation/anion exchange, a cascade of reactions occurs (Figure 2). First, in the bulk solution, the following reaction occurs:

\[ \text{Sn}^{2+}(aq) + 2\text{H}_2\text{O}(l) \rightarrow \text{Sn}^{4+}(aq) + 2\text{H}^+(aq) \]  

This acidic solution leads to the dissolution of BaCO$_3$ nanocrystals in the nanocomposite and thereby locally increases the pH in the close vicinity of the nanocomposite.

\[ \text{BaCO}_3(s) + 2\text{H}^+(aq) \rightarrow \text{Ba}^{2+}(aq) + \text{H}_2\text{O} + \text{CO}_2(aq) \]  

This increased local pH, combined with the high tin concentration in the solution, results in the formation of the desired Sn$_3$(OH)$_2$O$_2$ (III):

\[ 3\text{Sn}^{4+}(aq) + \text{H}_2\text{O}(l) \rightarrow \text{Sn}_3(\text{OH})_2\text{O}_2(s) + 3\text{H}^+(aq) \]  

Consistent with this mechanism, deliberately increasing the pH of the bulk solution to 13–14 by adding a base (1.0 M NaOH) results in precipitation of Sn$_3$(OH)$_2$O$_2$ in the entire solution via III (see Supporting Information).

Allowing the conversion to continue after the formation of the desired Sn$_3$(OH)$_2$O$_2$ results in an undesired reaction IV, which causes the dissolution of the nanocrystals:

\[ \text{Sn}_3(\text{OH})_2\text{O}_2(s) + 3\text{H}^+(aq) \rightarrow 2\text{Sn}^{4+}(aq) + \text{H}_2\text{O}(l) \]  

This reaction occurs once all BaCO$_3$ is dissolved and the local pH decreases to the acidic pH of the bulk solution. Due to this, Sn$_3$(OH)$_2$O$_2$ in the nanocomposites dissolves as it is only stable at a pH above 3.5 (bulk pH = 2.0), leaving the empty silica scaffold behind (see Supporting Information). Thus, the suggested mechanism indicates that preservation of the local reaction zone is essential for the conversion.

The importance of this local reaction zone can be demonstrated by simply disturbing the experiment. Already gently stirring the reaction solution or shaking the substrate disturbs the local gradients, resulting in either incomplete conversion or depletion of the nanocomposite. Collectively, these experiments suggest that dissolution of BaCO$_3$ creates a local transient reaction zone that enables the precipitation of Sn$_3$(OH)$_2$O$_2$ in the nanocomposite with preservation of the original 3D shape.

This shape-preservation reaction to Sn$_3$(OH)$_2$O$_2$/SiO$_2$ nanocomposites opens up opportunities for developing further conversion pathways toward shape-controlled 3D morphologies with desirable tin compositions. We explore this potential for the conversion of Sn$_3$(OH)$_2$O$_2$ to tin dioxide (cassiterite, SnO$_2$). SnO$_2$-based materials are widely used for optoelectronic and battery applications, where shape-controlled 3D morphologies could offer new and improved functionalities. Previous studies have already shown that Sn$_3$(OH)$_2$O$_2$ crystals can be converted into SnO$_2$ via dehydration and subsequent oxidation as follows:

\[ \text{Sn}_3(\text{OH})_2\text{O}_2(s) \rightarrow 3\text{SnO}(s) + \text{H}_2\text{O}(g) \]  

\[ 2\text{SnO}(s) + \text{O}_2(g) \rightarrow 2\text{SnO}_2(s) \]  

So far, these reactions have only been performed on bulk crystals where the initial shape preservation was lost during conversion, as the mechanical stress during the dehydration...
and oxidation processes destroys the morphology of the original crystal. In contrast, ion-exchange reactions on nanocomposites do enable shape preservation, as the supporting silica matrix provides mechanical support during the conversion reaction, while the nanocrystals’ size improves the chemical reactivity.29,30 We rationalize that these shape-preserving properties of the nanocomposites can also be utilized for the conversion toward SnO2.

To perform the conversion, we position the Sn3(OH)2O2/SiO2 nanocomposites in a tube oven that is open to air. The oven is heated to 200 °C for 3 h to induce thermal dehydration (V) and subsequently heated for 3 h at 600 °C to form SnO2 (Figure 3A, reaction VI). XRD and EDS analyses confirm complete conversion of the nanocrystals in the nanocomposite to tetragonal SnO2 with a grain size of 10 nm (Figure 3C,D, see Supporting Information), while electron microscopy shows excellent preservation of the microscopic features of the nanocomposite (Figure 3B). Thus, the nanocomposites retain their coral-like shape, while the nanocrystalline interior is completely converted to SnO2.

To demonstrate the versatility and tunability of Sn3(OH)2O2/SiO2 nanocomposites as a precursor for functional compositions, we develop a second conversion route toward shape-controlled methylammonium tin halide perovskites (CH3NH3SnX3, with X = Br− or I−). These semiconductors have a tunable band gap in the visible and near infrared spectrum, which makes them attractive for photovoltaic applications. Moreover, tin perovskites have gained attention as an environmentally friendly alternative to the currently used tin oxide.44−46,54 Control of the halide moiety during the conversion offers tunability of the band gap of the perovskite semiconductor. We characterize this band gap using photoluminescence (PL) spectroscopy. The CH3NH3SnBr3/SiO2 and CH3NH3SnI3/SiO2 nanocomposites show PL with a peak at 610 nm and 880 nm, respectively (Figure 4G), which is slightly blue-shifted compared to previously reported values, likely because of the quantum confinement of the perovskite nanocrystals in the silica matrix.54−55 This confinement is consistent with the relatively broad PL peak, presumably from the size dispersion of the crystals. PL mapping furthermore shows light emission from the entire architecture, thus offering corroborative evidence of complete conversion (Figure 4D). These tin perovskites nanocomposites thus have the same photoluminescent properties as 2D tin perovskites, while offering the ability to straightforwardly program the 3D shape.

We show the proof of principle for the conversion toward methylammonium bromide tin perovskite (CH3NH3SnBr3). The Sn3(OH)2O2/SiO2 nanocomposites are placed in a tube oven, and an alumina boat containing CH3NH3Br is placed directly besides them. The pressure in the oven is reduced to 50 mbar, followed by a temperature increase to 120 °C for 30 min and subsequently passively cooling down the oven back to room temperature. SEM analysis shows that the initial macroscopic geometry is well preserved (Figure 4B). XRD and EDS analyses confirm that the nanocrystals in the resulting nanocomposites are completely converted to orthorhombic CH3NH3SnBr3 with a grain size of 90 nm (see Supporting Information), as shown in Figure 4E,F. A slight roughening of the surface is observed, which may be contributed to the insertion of methyl ammonium halide and the increase in the crystal lattice from 48 to 204 Å3 per tin atom. VII suggests that selecting the methylammonium halide precursor enables control over the halide moiety in the perovskite. Indeed, reaction of Sn3(OH)2O2 nanocomposites with CH3NH3SnI3 results in conversion to the methylammonium iodide tin perovskite with a grain size of 81 nm (CH3NH3SnI3, Figure 4C,E,F and Supporting Information).

Control of the halide moiety during the conversion offers tunability of the band gap of the perovskite semiconductor. We characterize this band gap using photoluminescence (PL) spectroscopy. The CH3NH3SnBr3/SiO2 and CH3NH3SnI3/SiO2 nanocomposites show PL with a peak at 610 nm and 880 nm, respectively (Figure 4G), which is slightly blue-shifted compared to previously reported values, likely because of the quantum confinement of the perovskite nanocrystals in the silica matrix.46,47,49 This confinement is consistent with the relatively broad PL peak, presumably from the size dispersion of the crystals. PL mapping furthermore shows light emission from the entire architecture, thus offering corroborative evidence of complete conversion (Figure 4D). These tin perovskites nanocomposites thus have the same photoluminescent properties as 2D tin perovskites, while offering the ability to straightforwardly program the 3D shape.

Figure 4. Conversion of Sn3(OH)2O2 to CH3NH3SnX3/SiO2 nanocomposites with X = Br− and I−. (A) Schematic representation of the conversion from Sn3(OH)2O2/SiO2 to CH3NH3SnX3/SiO2 nanocomposites, which occurs at elevated temperatures when CH3NH3X is added. (B) SEM of a CH3NH3SnBr3/SiO2 nanocomposite. (C) SEM of a CH3NH3SnI3/SiO2 nanocomposite. (D) PL intensity map of a CH3NH3SnBr3/SiO2 nanocomposite at 610 nm showing emission from the nanocomposite exclusively. Lighter color indicates higher intensity. (E) EDS and (F) XRD analyses of coral-like nanocomposites containing CH3NH3SnBr3 (top) and CH3NH3SnI3 (bottom). (G) PL spectrum of CH3NH3SnBr3/SiO2 (at 610 nm) and CH3NH3SnI3/SiO2 nanocomposites (at 880 nm).
CONCLUSIONS

Here, we introduce a shape-preserving conversion from BaCO₃/SiO₂ to Sn₃(OH)₂O₂/SiO₂ nanocomposites. We propose a mechanism based on a cascade of reactions which, driven by the local pH in the reaction zone, allows this one-step cation/anion exchange. We show that the Sn₃(OH)₂O₂ forms can straightforwardly be converted to functional tin compositions: the semiconductor tin perovskite (CH₃NH₃SnX₃) and the conductor tin oxide (SnO₂), while maintaining the 3D geometry and fine features of the original BaCO₃/SiO₂ nanocomposite. We envisage that localized reaction zones in nanocomposites may be further exploited. Specifically, our results may enable shaping metals such as molybdenum, ruthenium, or palladium, none of which form stable carbonates, but all of which are of wide interest for their catalytic activity. Moreover, these conversion reactions could also be applied to other complex-shaped nanocomposites, such as the wide catalogue of biominerals, and create intricate patterns using lithography methods. Ultimately, these findings may enable shaping metals into advanced morphologies for next-generation catalysts and optoelectronic devices.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.1c00393.

AUTHOR INFORMATION

Corresponding Author
Willem L. Noorduin — AMOLF, 1098 XG Amsterdam, The Netherlands; Van ’t Hoff Institute for Molecular Sciences, University of Amsterdam, 1090 GD Amsterdam, The Netherlands; orcid.org/0000-0003-0028-2354; Email: noorduin@amolf.nl

Authors
Hans C. Hendriksen — AMOLF, 1098 XG Amsterdam, The Netherlands
Stivell Hémon-Charles — AMOLF, 1098 XG Amsterdam, The Netherlands; Ecole Polytechnique l’Université de Nantes, 44035 Nantes, France
Lukas Helmbrecht — AMOLF, 1098 XG Amsterdam, The Netherlands
Eliane P. van Dam — AMOLF, 1098 XG Amsterdam, The Netherlands; Present Address: Department of Physical Chemistry II, Ruhr University Bochum, 44780 Bochum, Germany
Erik C. Garnett — AMOLF, 1098 XG Amsterdam, The Netherlands; orcid.org/0000-0002-9158-8326

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.cgd.1c00393

Author Contributions
All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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ABBREVIATIONSPARA

X-ray diffraction
energy-dispersive X-ray spectroscopy
scanning electron microscopy
infrared spectroscopy
witherite
hydroromarchite
romarchite
cassiterite
methyliammonium tin halide perovskite
methyliammonium halide.

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