

Electronic Supplementary Information

Hydrothermal formation of bismuth-titanate nanoplatelets and nanowires: the role of metastable polymorphs

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Materials

Bismuth(III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, Alfa Aesar), tetra-n-butyl orthotitanate (Sigma-Aldrich), sodium hydroxide (NaOH, Sigma-Aldrich), potassium hydroxide (KOH, Sigma-Aldrich), nitric acid (HNO_3 , Alfa Aesar), tert-butanol (EMSURE ACS).

Synthesis procedure

Bismuth titanate nanostructures were synthesized using a hydrothermal treatment of separately precipitated Ti^{4+} and Bi^{3+} ions. In a typical experiment, 1.1 g of titanium butoxide was dissolved in 20 mL of tert-butanol. The Ti^{4+} ions were precipitated with the addition of 40 mL of water under vigorous stirring. The white precipitate was separated with a centrifuge and washed two times with water and finally with the mineralizer hydroxide (NaOH or KOH) at the same concentration as used for the subsequent hydrothermal treatment. In parallel, the stoichiometric amount of $\text{Bi}(\text{NO}_3)_3$ ($\text{Bi}/\text{Ti} = 4/3$) was dissolved in diluted HNO_3 (17.5 wt.%). The Bi^{3+} ions were precipitated with the addition of aqueous ammonia (2.5 wt.%) under vigorous stirring to set the final pH to 7. The white precipitate was separated with a centrifuge and washed two times with water and finally with the mineralizer hydroxide. After washing with the mineralizer, the colour of the precipitate turned yellow. Finally, the both precipitates were quantitatively transferred to a 70 mL Teflon-lined autoclave and filled with the mineralizer aqueous solution to a final volume of 45 mL. The autoclave was closed and heated for different times at different temperatures ranging from 160 to 220 °C. The product was thoroughly washed with distilled water and dried at 60 °C.

Characterization

For the transmission (TEM) and scanning-transmission (STEM) electron microscopy studies, the nanoplatelets were suspended in ethanol and deposited on a copper-grid-supported lacy carbon foil.

The TEM analyses were performed using a field-emission electron-source TEM Jeol 2010F operated at 200 kV. Quantitative analyses were performed using an energy-dispersive x-ray spectroscopy (EDXS) microanalysis system (LINK ISIS EDS 300) and Oxford ISIS software containing a library of virtual standards. Because the bismuth evaporated/migrated from the nanoparticles under the intensive electron beam, the spectra for quantification were collected with the beam spread over an area of specimen containing several nanoparticles.

For the STEM analyses a probe-Cs-corrected Jeol ARM 200CF STEM was operated at 80 kV. During positioning and tilting of the nanoparticles in TEM mode the minimal intensity of beam was used to limit the degradation of the specimen in the beam. During the STEM imaging, HAADF and ABF detectors were used simultaneously at 68–180 and 10–16 mrad collection semi angles, respectively. To minimize the specimen drift,

images were taken several hours after the insertion of the sample into the microscope and at least 20 minutes after the last sample positioning to minimize the goniometer drift. The chemical composition was analyzed using a Jeol Centurio EDXS system with 100 mm² SDD detector and a Gatan GIF Quantum ER Dual EELS system. The background of the EELS spectrum was subtracted using an inverse power-law function and multiple-scattering and tailing effects of the zero-loss peak were deconvoluted using the Fourier ratio technique with the corresponding low-loss and zero-loss spectra, acquired simultaneously as core-loss spectra from the same specimen region. XRD patterns were recorded with a PANalytical X'Pert PRO diffractometer.

TEM of samples hydrothermally treated in NaOH of different concentrations

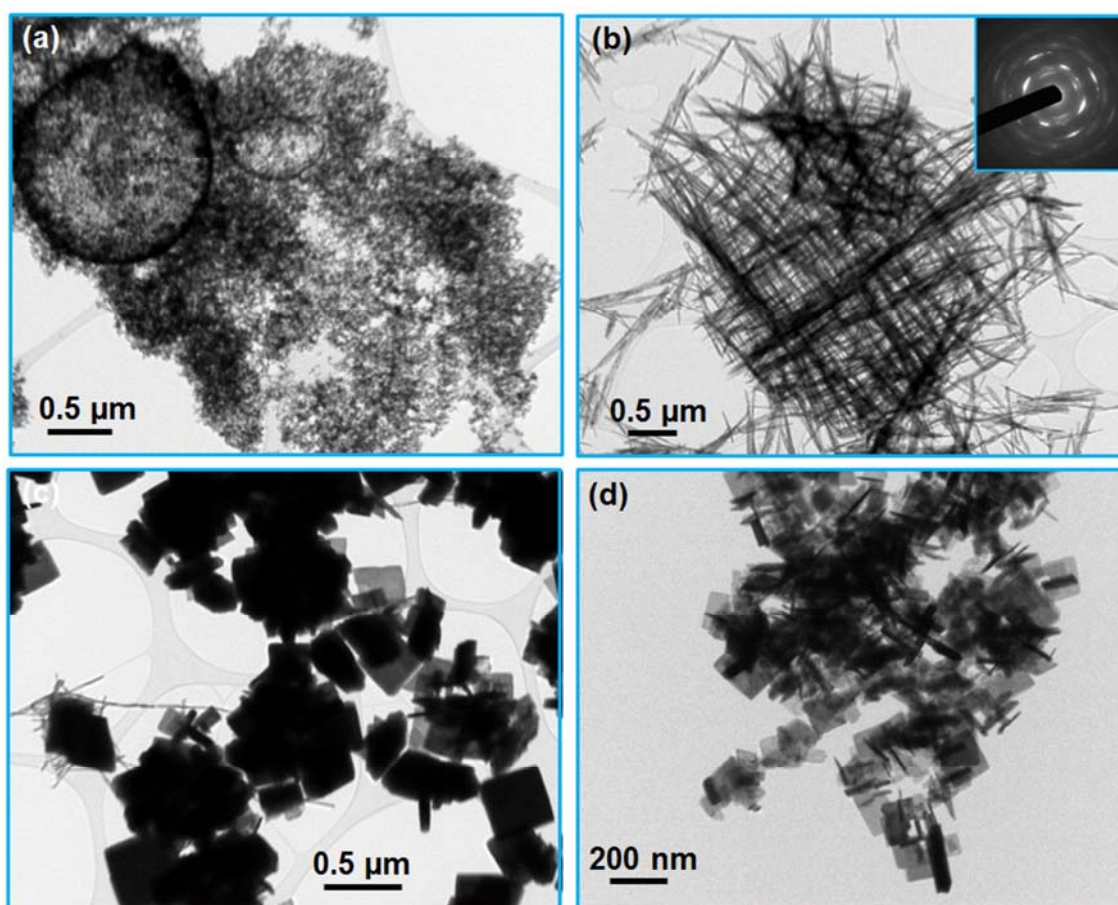


Fig. S11. TEM images of product synthesized by hydrothermal treatment of precipitated Ti^{4+} and Bi^{3+} ions for 38 hours at 200 °C in NaOH of different concentrations: (a) 0.002 mol/L, (b) 0.01 mol/L, (c) 0.75 mol/L, and (d) 4 mol/L.

TEM of samples hydrothermally treated in 12 mol/L NaOH

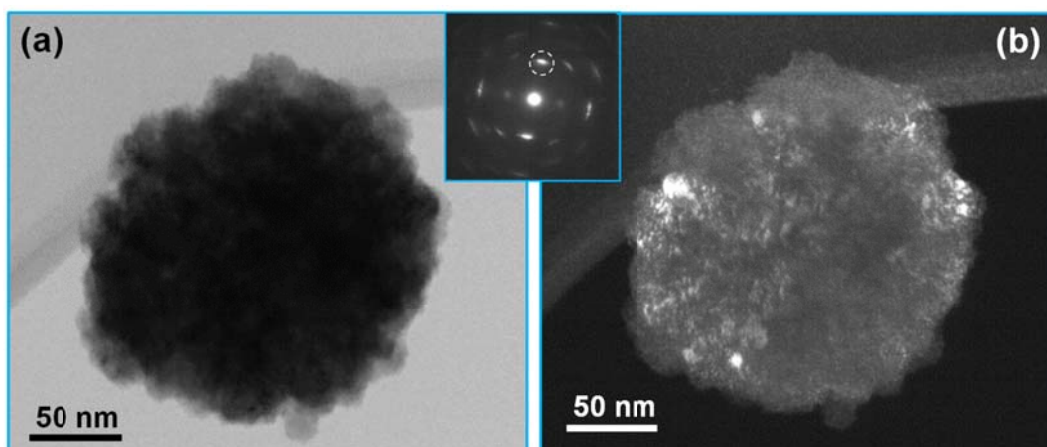


Fig. S12. BF (a) and DF (b) TEM images of a globular nanoparticles' aggregate in a sample synthesized with hydrothermal treatment in 12 mol/L NaOH for 38 hours at 200 °C. The DF was formed with the reflection marked with a circle on the corresponding electron diffraction pattern (inset).

TEM of precipitated Ti^{4+} and Bi^{3+} ions

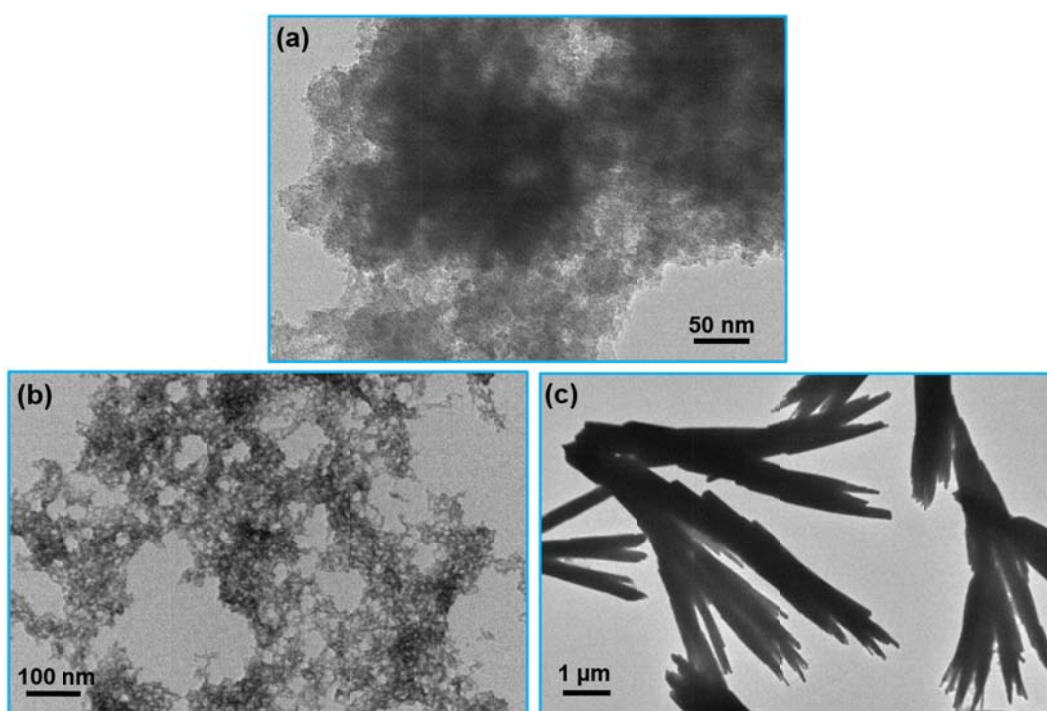


Fig. S13. TEM images of Ti^{4+} and Bi^{3+} ions at room temperature: Hydrolysis of Ti-butoxide with addition of water to its solution in t-butanol (a), Bi hydroxide precipitated with addition of ammonia to aqueous solution of $\text{Bi}(\text{NO}_3)_3$ to set pH to ~ 7 , before (b) and after (c) the precipitate was admixed into solution of NaOH (2 mol/L).

TEM of samples treated in 2 mol/L NaOH for 3 days at 80 °C

The sample treated for 3 days at 80 °C contained loose agglomerates composed of short, poorly defined nanowires mixed with globular nanoparticle and globular aggregates (100–200 nm in size) of small nanocrystallites with the quasi-cubic structure (Fig. SI4).

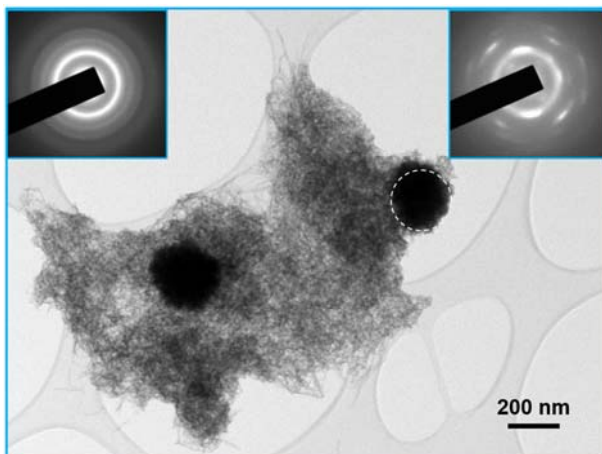


Fig. SI4. TEM image of sample treated for 3 days at 80 °C in 2 mol/L NaOH. Inset in upper left corner of the Fig. is SAED pattern recorded from agglomerated small nanoparticles and nanowires. Positions of the rings are consistent with the orthorhombic structure of nanowires with one additional diffuse ring, which can be ascribed to the (111) planes of quasi-cubic structure. Inset in upper-right corner of the Fig. is a SAED pattern recorded from globular aggregate marked with a circle. The reflections are consistent with the quasi-cubic structure.

TEM of samples treated in 2 mol/L NaOH at 100 °C

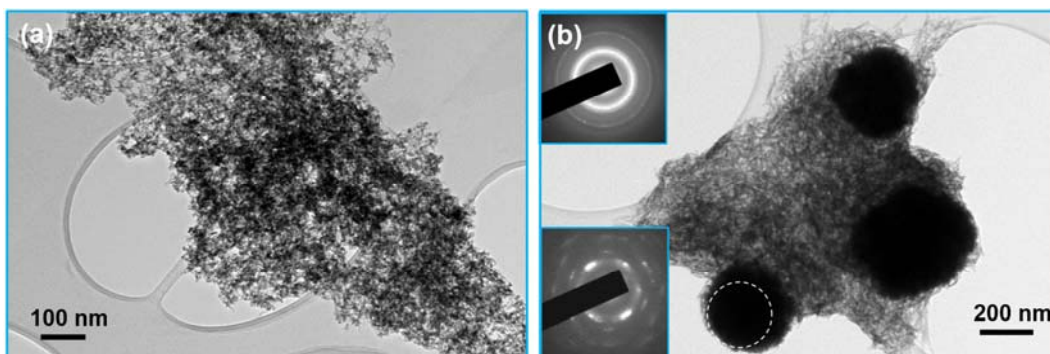


Fig. SI5. TEM images of sample treated in 2 mol/L NaOH at 100 °C for 2 hours (a) and 38 hours (b). Inset in upper-left corner of the Fig. (b) is a SAED pattern recorded from agglomerated nanoparticles nanowires and inset in lower-left corner is a SAED pattern recorded from globular aggregate marked with circle.

TEM of samples treated in 2 mol/L NaOH at 140 °C

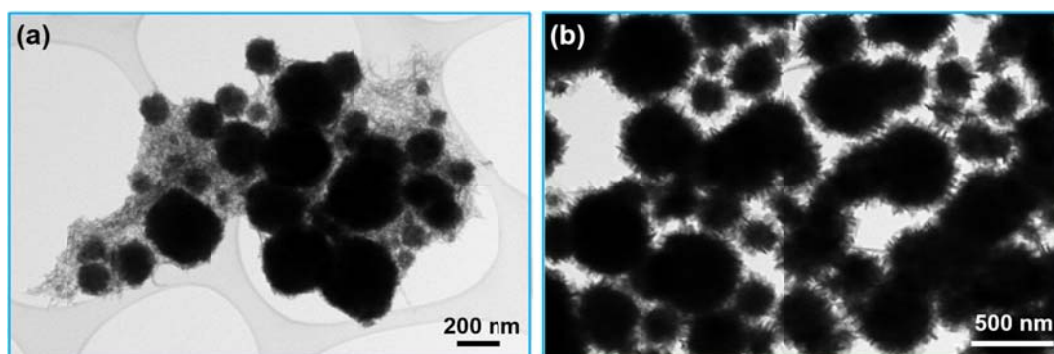


Fig. SI6. TEM images of sample treated for 2 hours (a) and 38 hours (b) at 140 °C in 2 mol/L NaOH.

TEM of samples treated in 2 mol/L NaOH at 160 °C

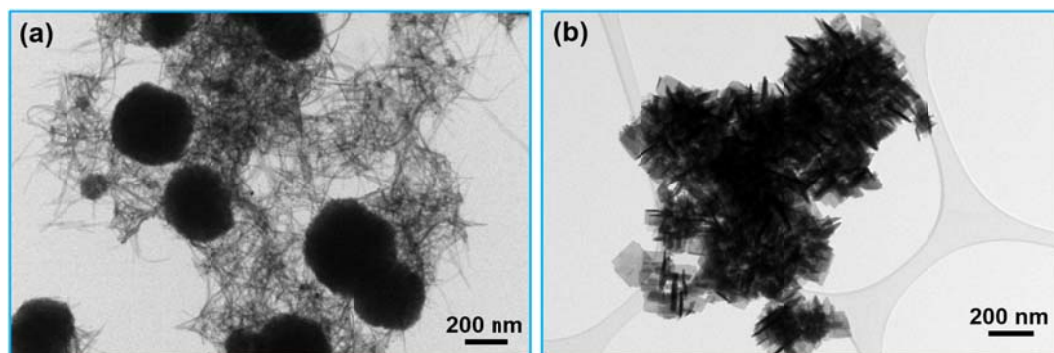


Fig. SI7. TEM images of sample treated for 2 hours (a) and 38 hours (b) at 160 °C in 2 mol/L NaOH.

TEM of samples treated in 2 mol/L NaOH at 180 °C

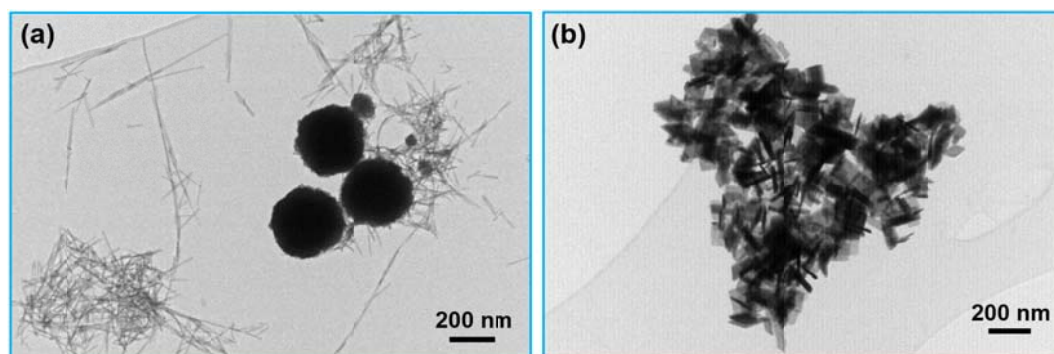


Fig. SI8. TEM images of sample treated for 2 hours (a) and 38 hours (b) at 180 °C in 2 mol/L NaOH.

STEM analysis of globular aggregates

When the nanoplatelets were synthesized in 2 mol/L NaOH with a hydrothermal treatment for 12 hours at 200 °C, while the reaction mixture was intensively stirred, the sample consisted of nanoplatelets, dense globular aggregates and loosely agglomerated nanoparticles with the quasi-cubic structure (Fig. SI9(a) and (b)). High-angle annular dark-field (HAADF) STEM imaging (Fig. SI9(c)–(f)) of the loosely agglomerated nanoparticles showed poor structural order. The atomic structure matched with the perovskite structure (Fig. SI9(f)).

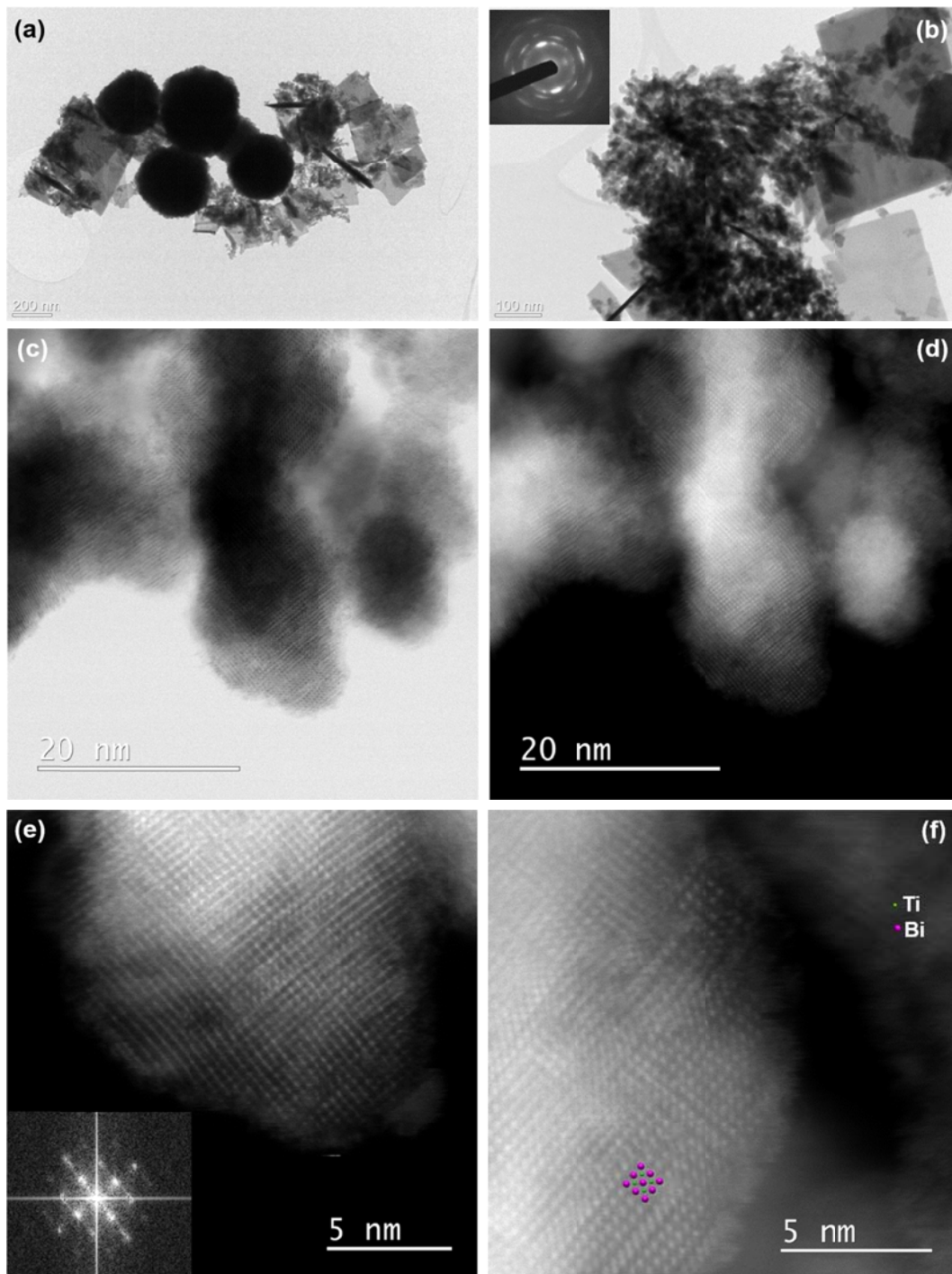


Fig. S19. Sample synthesized with hydrothermal treatment for 12 hours at 200 °C in 2 mol/L NaOH under intensive stirring: (a) and (b): TEM images (inset of (b): SAED pattern of agglomerate composed of small nanoparticles), (c) BF and (d)–(f) HAADF STEM images of the agglomerated nanoparticles (inset of (d): a corresponding FFT image). A projected model of perovskite structure is superimposed over the image (f) to illustrate the positions of the Bi^{2+} and Ti^{4+} ions.

ELNES of Ti-L_{2,3} edge in different bismuth-titanate phases

Special care was taken to minimize the radiation damage during the collection of the EELS spectra. In general, the fine structure near the L_{2,3} edge (ELNES) depends on the valence state, coordination, and site symmetry of the 3d transition metals, such as Ti. For the atoms incorporated at similar lattice sites in different phases, e.g., at the octahedrally coordinated sites in the perovskite, Aurivillius phases, or ilmenite (FeTiO₃), the Ti-L_{2,3} ELNES can be therefore used for the determination of the valence. For the Ti⁴⁺ both L₂ and L₃ the peaks are split into two peaks, resulting in the characteristic four-peak ELNES, whereas for the Ti³⁺ the two pairs of peaks are merged into two peaks, when the energy resolution is limited^{S1,S2}.

Ti-L_{2,3} ELNES was similar for the three different bismuth titanate phases: perovskite nanocrystallites, nanoplatelets with an Aurivillius layered perovskite structure and nanowires with an orthorhombic structure. Moreover, the Ti-L_{2,3} ELNES showed clear four-peak feature, which is regarded as the fingerprint of Ti⁴⁺. Moreover, the Ti-L_{2,3} ELNES for different bismuth-titanate phases matched to the Ti-L_{2,3} ELNES for ilmenite, which was used as the standard for Ti⁴⁺ incorporated at the octahedral sites.

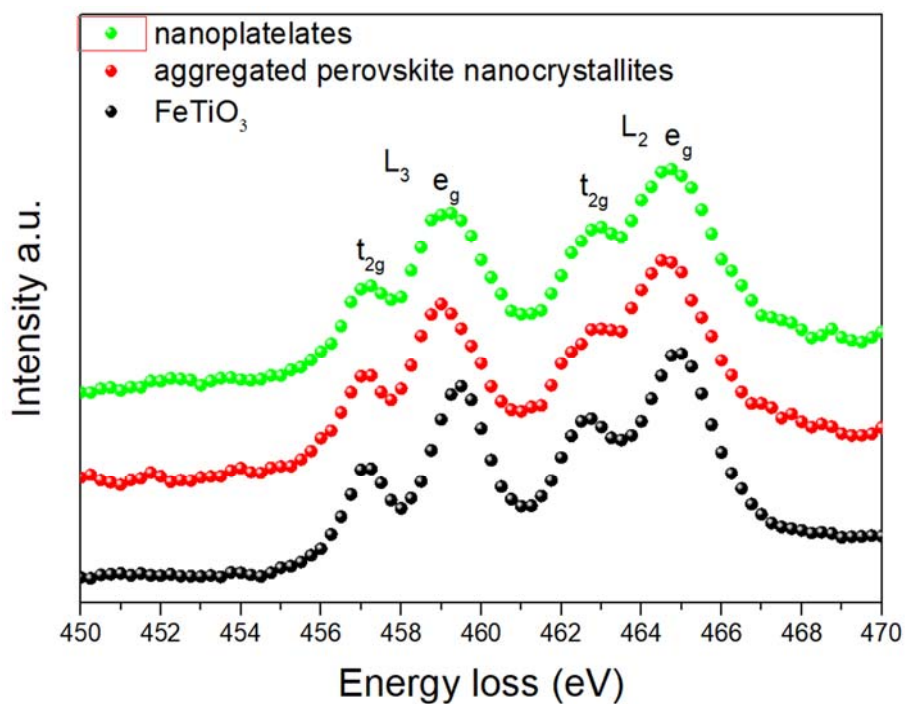


Fig. SI10. ELNES of Ti-L_{2,3} edge in three different bismuth-titanate phases and ilmenite (FeTiO₃) as a standard for Ti⁴⁺ incorporated at the octahedral lattice sites.

References

- S1. Y. Shao, C. Maunders, D. Rossouw, T. Kolodiaznyy and G. A. Botton, *Ultramicroscopy*, 2010, 110, 1014–1019.
- S2. L. Lin, Y. Ma, J. Wu, F. Pang, J. Ge, S. Sui, Y. Yao, R. Qi, Y. Cheng, C-g Duan, J. Chu and R. Huang, *J. Phys. Chem. C*, 2019, 123, 20949–20959.

EDXS elemental mapping of sample treated in 0.5 mol/L NaOH for 30 minutes at 200 °C

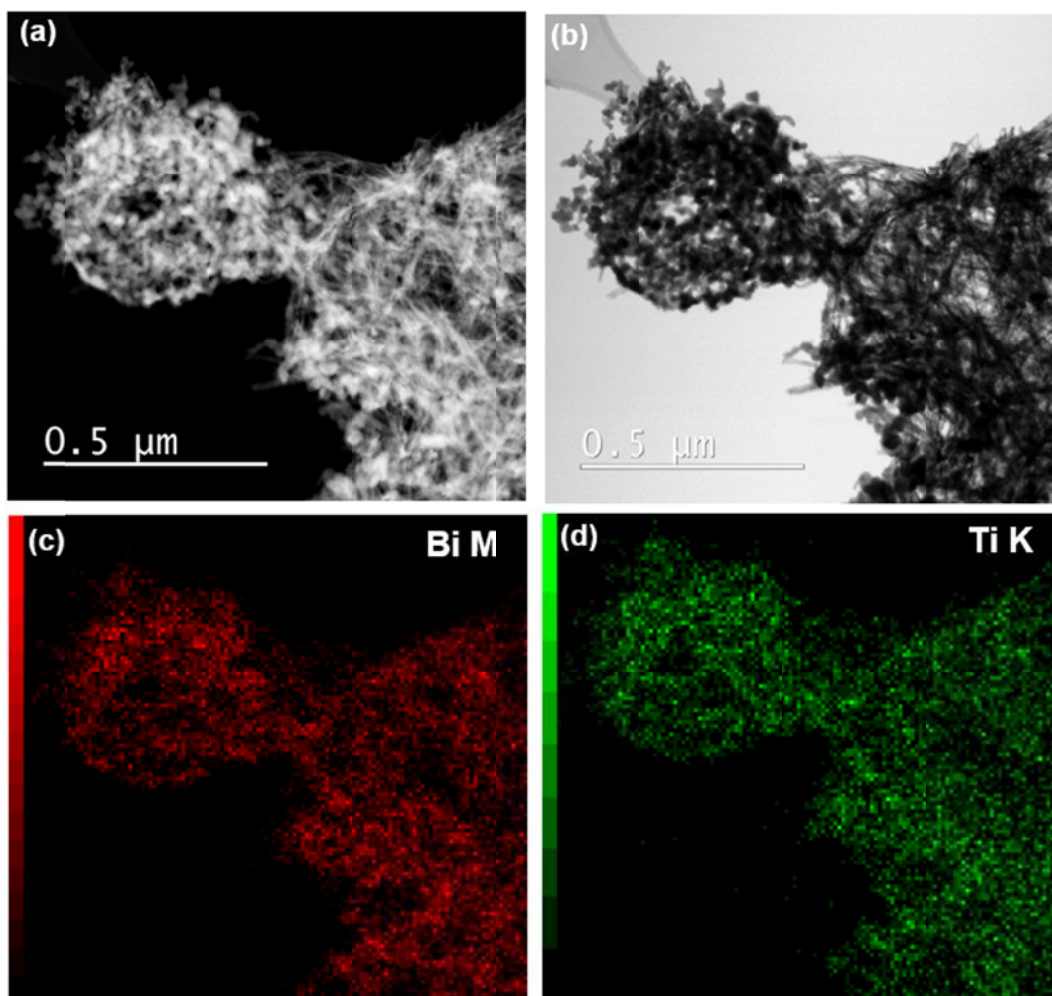


Fig. S111. HAADF (a) and BF (b) of nanowires and globular nanoparticles with the corresponding EDXS elemental maps for Bi (c) and Ti (d). The sample was hydrothermally treated in 0.5 mol/L NaOH for 0.5 hour at 200 °C.

XRD of sample treated in 0.5 mol/L NaOH at 200 °C

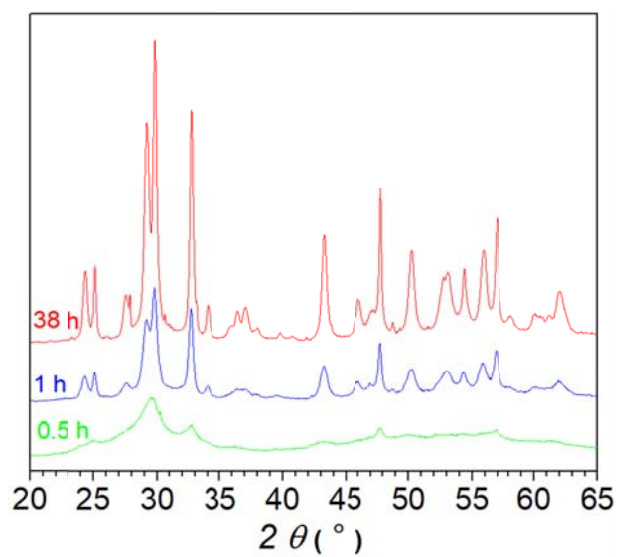


Fig. SI12. XRD patterns of samples hydrothermally treated in 0.5 mol/L NaOH for different times at 200 °C.

TEM of samples treated in 0.5 mol/L NaOH for 3 days at 80 °C

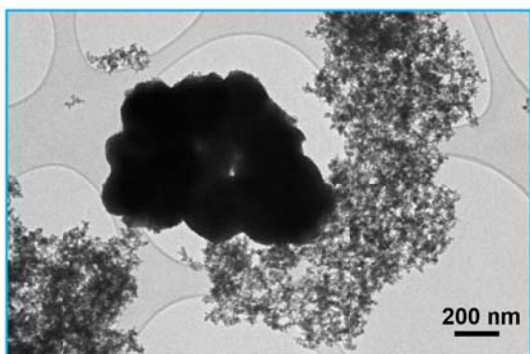


Fig. SI13. TEM image of sample treated for 3 days at 80 °C in 0.5 mol/L NaOH.

TEM of samples treated in 2 mol/L NaOH at 100 °C

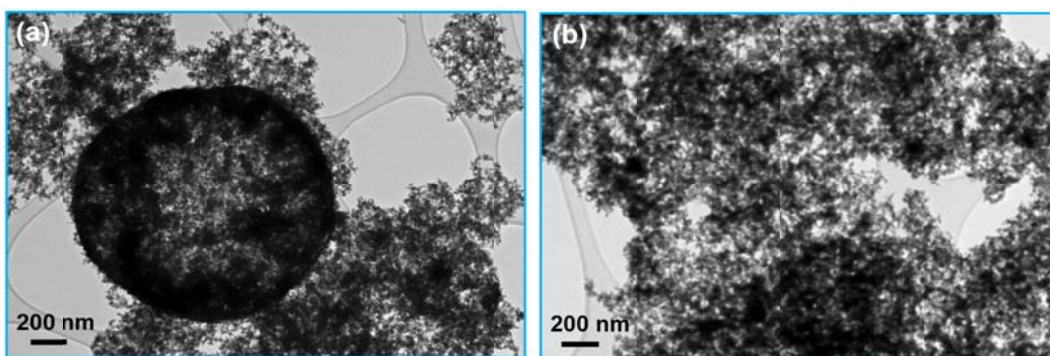


Fig. SI14. TEM images of sample treated for 2 hours (a) and 38 hours (b) at 100 °C in 0.5 mol/L NaOH.

TEM of samples treated in 2 mol/L NaOH at 140 °C

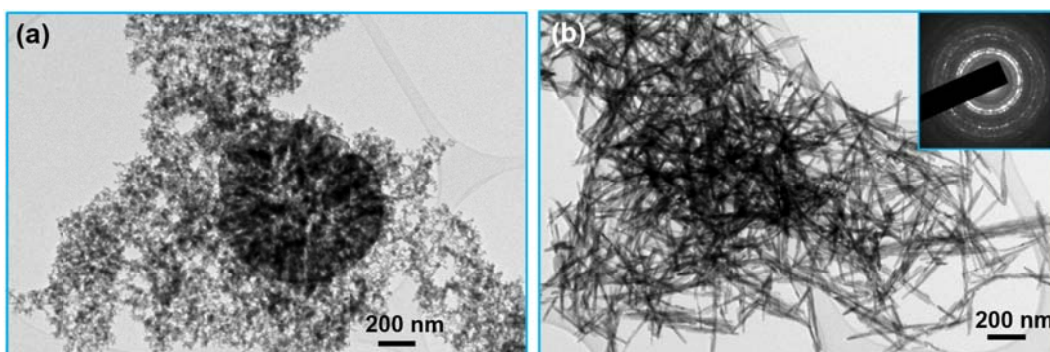


Fig. SI15. TEM images of sample treated for 2 hours (a) and 38 hours (b) at 140 °C in 0.5 mol/L NaOH.

Transformation of the perovskite phase during annealing at 550 °C

Fig. SI16 shows TEM images of the sample synthesized with hydrothermal treatment for 1 hour at 200 °C in 2 mol/L NaOH, before and after annealing for 2 hours at 550 °C. Before the annealing the sample was composed of nanowires and globular aggregates of perovskite nanocrystallites. With annealing, both the phases transformed into the Aurivillius nanoplatelets, which were present in the form of small aggregates. A globular shape of those aggregates suggests that they formed with the transformation of the globular perovskite aggregates.

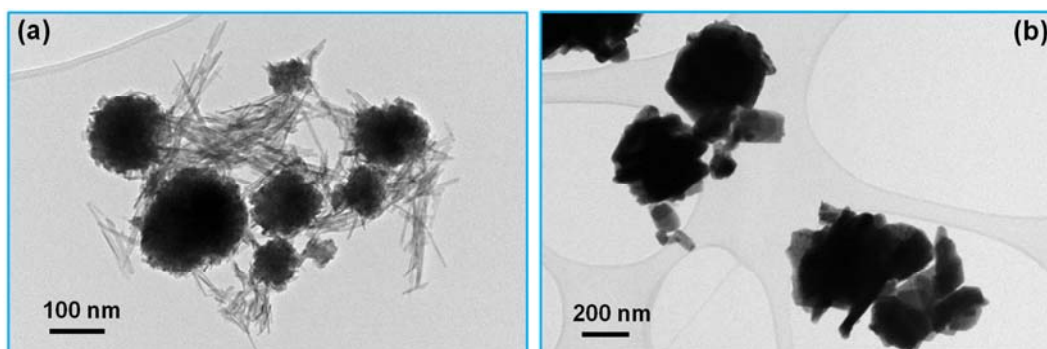


Fig. SI16. TEM images of sample treated for 1 hour at 200 °C in 2 mol/L NaOH before (a) and after (b) annealing for 2 hours at 550 °C.